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Symmetry In The Dissociative Recombination Of Polyatomic Ions And In Ultra-cold Few Body Collisions

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SYMmetry in the Dissociative Recombination of Polyatomic Ions and in Ultra-Cold Few Body Collisions

by

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B.S. Université Paris-Sud 11, 2006

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ABSTRACT

We discuss the role of symmetries in the dissociative recombinations (DR) of three polyatomic ions, namely the linear HCO$^+$ (formyl) ion and the two highly symmetric H$_3^+$ and H$_3$O$^+$ (hydronium) molecular ions. Regarding the HCO$^+$ ion, we apply a quantum mechanical treatment using the Multi-channel Quantum Defect Theory (MQDT) formalism to describe the ion-electron scattering process. Our study takes into account the Renner-Teller effect in order to model the non Born-Oppenheimer vibronic coupling in linear polyatomic ions. The coupling has shown to represent the main mechanism responsible for electronic capturing in highly excited Rydberg states associated with excited vibrational levels of the ionic core. We consider all internal degrees of freedom of HCO$^+$ and obtain the dissociative cross section as a function of the incident electron kinetic energy. We have also improved the theoretical approach by including the large permanent dipole moment of HCO$^+$ using a generalization of the MQDT formalism. To our knowledge, this is the first time the permanent dipole moment of an ion is included in a DR study. The obtained results are in good agreement with experimental data. We also study the DR of H$_3^+$ and H$_3$O$^+$ symmetric ions using a simplified theoretical treatment, which focuses on the key ingredient of the DR process, the electron capture in the first excited degenerate vibrational normal mode of the ions through non Born-Oppenheimer Jahn-Teller coupling. For both ions the obtained cross sec-
tions are in very good agreement with the available experimental data. Moreover, in the case of $\text{H}_3^+$, the results reproduce previous calculations from two independent theoretical studies. Finally, we investigate the role of symmetries in few body ultra-cold collisions by considering both three and four identical atoms systems. We derive allowed rearrangements of different fragments of the system, satisfying the complete symmetry of the molecular Hamiltonian. For that purpose we establish a correspondence between constants of motion of the system in different large-distance configurations and irreducible representations of the total symmetry group. Selection rules (forbidden transitions) and allowed states, which depend on the fermionic or bosonic nature of the atoms, can be derived from these results.
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CHAPTER 1
INTRODUCTION

1.1 Dissociative recombination at a first glance

1.1.1 What is dissociative recombination?

Dissociative recombination (DR) of a molecular ion $\text{ABC}^+$ with a low energetic electron is a reactive scattering process in which a polyatomic ion recombines with an electron to form an excited neutral state, which can eventually lead to the dissociation of the compounds into different final products. Considering a triatomic ion, the reaction is simply expressed as:

$$\text{ABC}^+ + e^- \rightarrow \text{AB} + \text{C} \quad \text{or} \quad \text{A}^* + \text{B} + \text{C}. \quad (1.1)$$

The different possible ways the neutral system can dissociate into, we name branches or channels. We stress that the final products of the dissociation in (1.1) can usually be observed in rotational, vibrational and even electronic excited states. Before treating in details the theoretical and experimental approaches to DR, we start by giving an introductory overview
of the wide range of areas in which DR processes are involved. Specifically, we discuss three main domains: astrophysics, airglows in the Earth’s atmosphere and medical science.

1.1.2 Fields of interest involving dissociative recombination

1.1.2.1 Astrophysics:

The conditions in the interstellar medium permit numerous different reactions to take place: radiative attachment, dissociative attachment, associative ionization (inverse process of DR) and dissociative recombination are only few examples of the list of present reactions. More than a hundred\textsuperscript{1} of known molecular species coexist in clouds [130]. Still, a very large number of observed spectral transitions remain unidentified, mainly because of overlapping spectral features, as well as an inadequate database of experimental transition frequencies.

The molecular species in the interstellar medium constantly participate in reactions of destruction and formation. Intense radiation from outer stars continuously bombard the atoms and molecules, which in turn emit photons or dissociate. Eventually, a pseudo-equilibrium can be reached sometime after millions of years, for which the density of the species is such that their rate of destruction balances their rate of creation. Strictly speaking, the interstellar medium is in constant evolution, presenting large disparities in densities and temperatures at the origin of star and planet formation. Commonly the temperature can vary from few

\textsuperscript{1}Wang \textit{et al.} [130] actually assess than exactly 135 interstellar species have been reported prior to 2008.
to thousands of Kelvins, thus letting different types of reactions alternatively predominate. The knowledge of the rates of the different reactions and densities of species at a given temperature $T$ enables one to determine, to a certain extent, the pseudo-equilibrium density of the various substances. Evidently, modeling the interstellar dust is not a trivial matter and a tremendous amount of computational calculations involving hundreds of different reactions have to be performed [120]. We stress two main reasons why the knowledge of the density of the elements in the clouds is needed by the astrophysical community.

First, as already stated, these clouds represent the origin of star formation. Understanding their evolution and composition is a key factor when studying the mechanisms of creation for different types of stars and planets. Since the interstellar dust is also permanently regenerated by the explosion of red giant stars, it represents the central point in the cycle of matter (see Fig. 1.1), as well as the place of production of most of the molecules that will later be found on planets.

For instance, it is believed [90] that water on earth, and anywhere else in the universe, is originally produced from the DR of H$_2$O$^+$ molecular ion (see Chapter 5). Recently, observations reported the unexpected presence of negative molecular ions in the interstellar medium [99, 124]. The process of formation of these ions is still rather unknown and theoretical work is being conducted to understand the mechanism underlying their existence. For instance, controversies exist on the possible presence of H$^-$ in the interstellar dust. The ion can not be spectroscopically detected since only a single bound level exists. An interesting study [9] proposed an indirect way to prove the existence of this ion through the possible presence of
H$_3^-$ ion formed from the radiative association: H$_2$+H$^-$ → H$_3^-$ + hν. Several bound states exist for H$_3^-$ ion, so that the detection of its spectrum from the interstellar medium would undoubtedly prove at once the existence of both H$^-$ and H$_3^-$ ions. Unfortunately, the calculated rate of radiative association of dihydrogen with H$^-$ is slow [9]. On that account, spectral detection of H$_3^-$ could be extremely difficult, even for the high resolution far infrared and sub-millimeter spectrum satellite *Herschel*\(^2\).

---

\(^2\)The satellite *Herschel* was launched by the European Space Agency (ESA) in May 2009. It represents the largest space telescope of its kind with its large mirror of 3.5 meters.
Second, the size of interstellar clouds remains uncertain. If one knows the spectrum of a star, it is possible to estimate the size of an interstellar cloud by analyzing the absorbency spectrum of the interstellar dust. The absorbency is roughly proportional to the thickness of the cloud. If a particular ray corresponding to one of the present species in the medium is studied and information on the density of the species are known, it is possible to get a quantitative idea of the thickness of the cloud via light extinction. Moreover, the blue component\(^3\) of the light is generally more scattered than the red. Hence, light passing through the interstellar dust is generally reddened (see Fig. 1.1) and this phenomenon enables an estimation of the thickness of an interstellar cloud. Of course, the latter description only intends to give a flavor of the interstellar medium data analysis treatments. Realistic studies require a high level of complexity, since many external factors often hinder a definite interpretation of the data. An example of interstellar cloud around a nebula is presented in Fig. 1.2.

Interestingly, dissociative recombination is also involved in processes concerning the reentry of spacecrafts into planet’s atmospheres. For instance, the molecular ion HCO\(^+\), which can undergo DR, is present in the cold atmosphere of Mars [82]. During landing on Mars, the shield of the spacecraft should resist sudden changes in temperature, which are directly related to the composition of the atmosphere. Furthermore, materials that compose the shield have to be adequately chosen in a way to minimize high temperature reactions between the shield of the spacecraft and the formed plasma just below it. For this purpose, it is

\(^3\)This well known phenomenon is responsible for the blue color of our sky.
desirable to know the various rates of reactions that take place at very high temperatures (thousands of Kelvins) to understand the composition of the plasma below the shield.

Figure 1.2: The left photograph, taken from [123], shows the oxygen green-line emission from our sky (577.7nm). On the right side, an image of the interstellar medium around the blue nebula NGC1999 (NASA, Hubble).

1.1.2.2 Airglows in Earth’s upper atmosphere:

We discussed DR reactions taking place in outer space, as well as in external planets. In fact, DR reactions also occur in the Earth’s atmosphere and are responsible for the well known phenomena of aurorae and airglows. The former is an irregular outbursts of light, which is a consequence of energetic solar particles guided to the polar regions by the Earth’s magnetic field. On the other hand, the airglows are a continuous and uniform glow, that illuminates our entire planet as a corona of light. Airglows are driven by solar and galactic
radiations, and the physics behind this impressive display of light incorporates a wide range of reactions, principally dissociative recombination.

Airglows generally takes place at high altitude, when the low pressure enables excited molecules to radiate instead of reacting with other species. Airglows originate from a combination of gravitational separation of the atmospheric constituents, as well as excitation and ionization due to solar radiation. The energy brought by the solar and galactic radiation in the Earth’s upper atmosphere is dissipated by radiative decay, mainly from the abundant diatomics $O_2$ and NO. Actually, the energy dissipation of these species is quite slow\(^4\) since they radiate in the infrared. Of course, the airglow emission is strongest during the day, but the scattering from our sunlight hinders any ground observations. However, during the night airglows can be observed and could be seen by the naked eye if not for its major contribution in the infrared.

Airglows also mostly originate from decay of excited atomic species like atomic oxygen. These species are not generally produced from direct excitation of the ground electronic state atom\(^5\), but rather by photodissociation or collisional process such as dissociative recombination. In fact, two main atomic line transitions are related to DR, namely the green and red line emissions of atomic oxygen. The auroral green-line emission at 577.7 nm arises from the $O(^1S)\rightarrow O(^1D)$ transition (see Fig. 1.2) and is often accompanied by the red-line emission of the $O(^1D)\rightarrow O(^3P)$ transition. As stated, the excitation process of atomic oxygen comes from photodissociation of $O_2$ and dissociative recombination. At night, DR is the dominant

\(^4\)The radiative lifetime of a state being proportional to $\lambda^3$, where $\lambda$ is the radiation wavelength.
\(^5\)Actually, excitation of the H atom does occur, which leads to the Lyman-$\alpha$ line emission.
airglow source, even though galactic radiation is still present. It has indeed been shown [6] that the DR of O$_2^+$ can produce both O($^1S$) and O($^1D$) excited atoms, making O$_2^+$ the main source of the green-line airglow.

The theoretical study on DR of O$_2^+$ started as early as 1931, when Kaplan proposed that this DR process was involved in the auroral green-line emission. This proposition was quite unexpected at that time, since the Earth’s upper atmosphere was believed to be very cold and mainly formed by hydrogen atoms. In 1935, Martyn and Pulley [94] predicted a hot and oxygen containing atmosphere, and in 1947, Bates and Massey [16] thereby suggested DR as the process of recombination in the atmosphere. Since then, several theoretical studies have modeled the DR process of O$_2^+$. The first attempt was made by Bates in 1950 [12], who gave an estimation of the direct DR cross section of about $10^{-7}$ cm$^3$/s$^{-1}$. In 1954, Nicolet [110] predicted that the O($^1S$) excited atoms are energetically allowed to be formed in the DR of O$_2^+$. From this point, it took more than three decades before a quantified production of O($^1S$) atoms could be found from DR of O$_2^+$. Indeed, Bates [13] made a step further in 1990, by suggesting that the indirect DR mechanism could be important. Guberman [51] confirmed the latter affirmation by including the spin-orbit coupling in a model of indirect DR of O$_2^+$ and found a finite O($^1S$) production, thereby showing that DR is the dominant green-line airglow source.

\footnote{More precisely, Nicolet argued using solely energetic reasons, that even two O($^1S$) atoms could be formed from the DR of O$_2^+$.}
1.1.2.3 Medical science:

A growing interest has recently emerged towards the study of the processes of destruction of chemical bonds of large biological molecules in reaction with electrons. Such processes are mostly dissociative recombination and dissociative electron attachment (DEA), which only differs from DR by the fact that in DEA the electron collides with a neutral molecule instead of an ion. Still, one should be aware that the theoretical treatments for both processes could be rather different. Usually, the secondary electrons entering in collision with the biological molecule are produced after absorption of X-rays by body tissues. The produced cascade of electrons can hit part of a large molecule, perturbing one of its specific bond and leading to its partial break. For instance, such processes have been observed on small peptides and proteins by Nielsen and coworkers using a Cyclotron Resonance instrument at the university of Aarhus. They observed dominant fragmentation channels after electron capture, as loss of ammonia and hydrogen, and mostly breakage of $N-C_\alpha$ bonds. Examples of DEA for formic acid [23], glycine [1] or uracil molecules [54] have been experimentally observed and theoretically studied.

For obvious reasons, the most interesting application of DR reactions for biological molecules concerns the most important among them, namely the DNA. Since its internal structure is a carrier of information, the break of one of its bonds by DR of secondary electrons could have dramatic impacts. Experiments by Sanche [118] have proved that low energetic electron can break double strand in DNA and damage isolated base pairs. There-
fore, it is understood that dissociative electronic attachment (directly to the DNA or to water molecules around the DNA, producing radicals that attack the DNA) is a major factor of DNA damage by ionization radiation. It is known that when cells divide, such errors in the DNA can usually be corrected, but mostly if only one break has occurred. If more than one break is made, the duplication of the DNA, via the RNA messenger, is rarely perfect.\footnote{In reality attack of the DNA by the telomerase protein is another factor of systematic deterioration.}

We know that damage of DNA is one cause of aging and cancer. Indeed, understanding the possible importance of the degradation of DNA by collisions with electrons is a source of attention. Theories on the DEA of biological molecules emerged only very recently and a tremendous amount of work still has to be pursued to understand the mechanisms underlying the destruction of these molecules.

1.1.3 General approach in the theoretical study of dissociative recombination

If we consider a low energy electron colliding with an heavy molecule, it appears at first glance rather unnatural to expect such a collision to lead to the dissociation of the molecule; the direct transfer of electronic energy into molecular motion is quite improbable. In 1950, Bates\cite{12} proposed a mechanism (direct mechanism), in a paper less than a full page in length, to describe the process of dissociative recombination. His approach remains nowadays the basic one to explain the DR of most molecular ions, neglecting higher order role of capture
in Rydberg states (indirect mechanism). Bates’s idea is that the electron does not transfer directly its energy to the kinetic motion of the nuclei, but rather to the electronic ionic cloud, thus forming a dissociative doubly excited resonant state:

\[ AB^+ + e^- \rightleftharpoons AB_{dd}^{**} \rightarrow A^* + B. \]  

(1.2)

In this model, the electron temporarily attaches to the molecule and changes the force exerted on the atoms for a time equivalent to the order of a vibrational period, inducing a distortion from equilibrium and a possible break down of the neutral system. In fact, the formed resonant state can only survive during a certain time, the autoionizing lifetime of the state. Henceforth, the electron is irretrievably ejected from the ion. Thus, if the dissociative process happens fast enough so that the products of dissociation are already at a large distance from each other after a time equivalent to the order of the autoionizing lifetime, most of the electronic energy is already converted into nuclei kinetic energy and autionization becomes impossible. In such a case, the system will irreversibly breakdown in one of the dissociative channels. The direct DR process is represented schematically in Fig. 1.3.

It may happen that the resonant state is situated way above the ionic ground state. In particular, this is often the case for closed shell ions, for which an electron needs a significant energy contribution to occupy an excited orbital. In that case, the direct capture of a low energetic electron into the resonant state is improbable. As mentioned previously, an indirect mechanism of dissociative recombination can still take place. For any ion, an infinite
set (quasi continuum) of Rydberg states (Section 2.3) exists below the ionization threshold. In a high Rydberg state, the external electron is loosely bound to the ion, with most of its probability of presence situated at large distance from the ionic core. In this outer region, the electron basically moves in a Coulomb potential as a hydrogenic electron. The Quantum Defect Theory (QDT) (see Section 2.3) introduces a quantum defect coefficient $\mu$, independent of energy near threshold, which describes the defect of the asymptotic wave functions and energies from the ones for a pure Coulomb field. Moreover, since the Rydberg energies can actually be close to each other, their separation become ultimately much smaller than the separation of vibrational energies of the ion. Indeed, this is a case of breakdown of the Born-Oppenheimer approximation (see Subsection 2.2.1), where vibration-electronic interactions can be non negligible. Therefore, an electron in the continuum is able to exchange

Figure 1.3: Direct mechanism: First, the electron approaches the ion in a hyperbolic (comet-like) trajectory due to the Coulomb potential. Then, the electron is captured in a doubly excited repulsive state. Two possible outcomes are sketched on the right hand side; either the electron is ejected from the ion, letting possibly the latter in an excited rovibrational state, or the system dissociate, with possible electronically excited fragments, which can radiatively decay.
its energy with the vibrational motion of the ion and, as a consequence, be captured in one of the Rydberg state. Then, the electron can be represented as descending in cascade from orbitals to orbitals, exchanging energy with the ionic core (see Fig. 1.4) until it either reionizes or reaches a path for dissociation:

\[ AB^+ + e^- \rightleftharpoons AB_{n,v} \rightarrow AB_d \rightarrow A^* + B. \]  

The two basic mechanisms for dissociative recombination are described in more details in Section 2.5.

Figure 1.4: Indirect mechanism: The Rydberg electron descends in cascade from orbitals to orbitals, transferring its energy to the rovibrational motion of the ionic core, until the system eventually finds a path for dissociation. Reionization of the electron from the Rydberg orbitals is still a possibility.

Generally, the theoretical work on DR focuses on the calculation of the DR cross section as a function of the entrance kinetic energy of the electron. The theoretical results should, in principle, reproduce available experimental data, mostly obtained in storage ring
and afterglow plasma experiments (see Subsection 1.1.4). In such experiments, a realistic
distribution of electronic energy is extracted in order to allow direct comparison between ex-
perimental data and theoretical calculations. By applying a convolution on the cross section
over the appropriate experimental distribution, one obtains results which can be compared
with the experimental data. For instance, in storage ring experiments, an undesired gaussian
uncertainty width $\Delta E_{\perp}$ and $\Delta E_{\parallel}$ of the transverse and longitudinal kinetic energy of the
electronic jet in the electron cooler is always present. The energy spread is due to several
factors, mainly to the electron-electron repulsion directly related to the electronic density.
Commonly, toroidal corrections due to the actual shape of the ring \[6, 36\] have also to be
taken into consideration. In afterglow plasma experiment, one can adopt a simple Maxwell-
Boltzmann distribution to describe the electronic gas in a plasma at a temperature $T$. We
will give a brief description of the convolution procedure in Subsection 3.3.2. Determination
of the thermal rate is explained in Subsection 3.3.3.

At present, we wish to point out the numerous difficulties inherent to the theoretical
treatment of DR. The study of polyatomic ions has the implication of treating systems with
several degrees of freedom. Specifically, one has to consider many different interactions,
purely electronic, vibronic and even rovibronic. It requires heavy computational codes and
the diagonalization of large matrices, as well as the use of \textit{ab initio} software\textsuperscript{8} to evaluate
electronic potential surfaces, structures and interactions. Furthermore, we saw that two
different types of DR mechanisms can be sorted out. If one establishes qualitatively, via

\textsuperscript{8}MOLPRO, MESA and GAMES are examples of \textit{ab initio} softwares commonly used.
electronic potential surfaces calculations, that a mechanism is highly predominant over the other (which is fortunately usually the case), it becomes possible to discard the negligible process and concentrate only on a single route for the reaction to happen. On the other hand, if the cross section for the two mechanisms happen to be of same order, interferences between two routes can occur, and one has to treat both mechanisms simultaneously. As we already mentioned, when an neutral excited state is formed, autoionization of the system is a possible outcome. Thus, the competition between autoionization and dissociation has to be also accounted for in order to obtain the DR cross section [115]. Studies of the most important and simplest molecular ions, namely H$_2^+$ and H$_3^+$, include at present all these different aspects. These studies are the product of years of research and collaborations by different groups. The most recent theoretical result on H$_3^+$ [36] shows extremely good agreement with experimentally measured data. The triatomic H$_3^+$ ion seems to be well understood at present, since it has been possible to reproduce numerous rotational and vibrational resonances in the DR cross section, which are in relative good agreement with experimental data. Another recent work focuses on reaching almost spectroscopic agreement between theory and experiment for this ion. As a conclusion, we point out the fact that in the present treatment of H$_3^+$, as well as in all treatments concerning DR in this thesis, no parameters were fit to experimental data and all results come from purely theoretical work and precise $ab$ $initio$ calculations.
1.1.4 Storage ring and afterglow plasma experiments

1.1.4.1 Storage ring experiment:

Storage ring experiments work on the same basic principles as the collision rings for particle in nuclei physics. There used to be four storage ring experiments\(^9\), namely ASTRID\(^5\), CRYRING\(^72\), TSR\(^85, 83\) and TARN II\(^121\). Storage rings are tools in which one confines charged particles jets, ions in our case, using magnetic fields. In the electron cooler, a beam of electrons produced at a cathode at a high temperature (about 1200K) is injected at a desired speed via adiabatic expansion and further acceleration. Therefore, an ionic and an electronic beam will collide at a relative desired speed over a region of about one meter. In the merging region, the DR reaction can take place. The electrons that are still present at the exit of this region are focused back on a collector via a magnetic field. The ions, which are way more massive, are only negligibly affected by the magnetic field. The product of the original ionic beam after the merging region is a mixture of ions and neutral molecules. Hence, the high magnetic field placed at a later turning spot only affects the trajectory of the ions, and the neutral elements will simply continue their straight trajectories to end up in a neutral beam detector. By measuring the amount of neutral molecules at the exit detector as a function of the energy of the ionic and electronic initial distribution energy, the DR cross section of the reaction can be obtained via deconvolution procedures. A schematic description of the CRYRING experiment in Stockholm is presented in Fig. 1.5.

\(^9\)In the present time, only TSR experiment is still working on DR reactions.
1.1.4.2 Afterglow plasma experiment:

The afterglow plasma experiment is another interesting type of experimental set up to study the DR of molecular ions at higher temperature [45, 46, 65, 4]. Unfortunately, the obtained data usually shows quite large discrepancies with theoretical results and storage ring experiments. We shall see that it is indeed the case for HCO⁺, for which experimental data can differ by a few orders of magnitude [89, 4]. The aim of this experiment is to study a post-discharge plasma. One stores a gas in a chamber and ionizes it using an electrical discharge. We will consider the gas as molecular hydrogen to make the underlying ideas more concrete. When ionizing molecular hydrogen, part of the molecules still remain neutral and the reaction H₂⁺ + H₂ → H₃⁺ + H can start. In the next step, it becomes indeed possible to study the DR of H₃⁺ in the plasma. An applied tension in between two electrodes accelerate the electrons, thus forming a current. Using a Langmuir probe, one can measure the electronic
density in the plasma. As the electrons collide with $\text{H}_3^+$ and cause its dissociation, one naturally observes a diminution of the electronic density with time. Assuming there is just one type of ion in the plasma, one can easily find the DR cross section rate $\alpha$. If $n_{\text{ions}}$ and $n_e$ are respectively the ionic and electronic densities, we know that $\frac{dn_e}{dt} = -\alpha n_e n_{\text{ions}}$. Finally, we should mention that there exist two different types of post-luminescence experiments. The first one is stationary, the plasma being stored in a chamber and the second one is dynamic since the plasma flows along a tube. For this reason it is named 'flowing plasma'.

1.2 Focus on the dissociative recombination of HCO$^+$

1.2.1 Why studying HCO$^+$?

The formyl cation HCO$^+$ is an important ion for radioastronomical probes of interstellar media. It is also present in the atmosphere of Mars [82] and is also involved in combustion processes [105]. It is considered as one of the primary molecular ions and is involved in essential chemical reactions. HCO$^+$ is believed to be mainly formed by a proton transfer from $\text{H}_3^+$ to CO. Since $\text{H}_3^+$ and CO are known to be abundant in interstellar gas, the formyl cations are accordingly widely present in the interstellar dust. The formyl cations can also be produced by various other associations, as for example $\text{H}_2 + \text{CO}^+$ or CH + O. On the other hand, HCO$^+$ ion is depleted by DR, almost solely through the channel $\text{H} + \text{CO}$, where the diatomic CO can be produced in an excited rovibronic state. Unfortunately, there is at
present no consensus among the various experimental measurements of the actual thermal DR rate coefficient of HCO\(^+\). As we already mentioned, results can differ by up to a factor of ten \[89, 4\] as can be seen in Fig. 1.6. In addition, a past theoretical work \[88\] on the DR cross section of HCO\(^+\) calculated DR rates one order of magnitude smaller than the lowest known experimental data. For this reason, efforts were pursued to improve the theoretical model, and a decisive step was made \[102\] with the introduction of the non Born-Oppenheimer \textit{Renner-Teller} effect in linear molecules (Section 3.2.2), formulated first by Landau. In fact, the introduction of this effect in HCO\(^+\) logically followed the former implementation of the so called \textit{Jahn-Teller} effect (Section 5.2) in the theoretical study of the symmetrical \(\text{H}_3^+\) molecular ion \[77\]. The results showed a large enhancement of the total cross section in both studies \[77, 102\], demonstrating that even small non Born-Oppenheimer couplings represent a decisive factor in the indirect DR mechanism of highly symmetric and linear molecular ions.

Despite the latter improvement, the general DR cross section for HCO\(^+\) remained overall smaller, by a factor of four to five, in comparison with the lowest experimental data \[89\]. In contrast, as we will see in Chapter 5, the results obtained for \(\text{H}_3^+\) \[77, 74, 49, 36\] are in good agreement with experiments. In fact, the model used to study the DR of HCO\(^+\) employed some approximations, which were applied to either decrease the complexity of the configuration space of HCO\(^+\) or because of the inherent limitations in the regular MQDT formalism. Furthermore, we stress that the latter treatment, as well as the present treatment, is less general than the two-step model introduced by Giusti \[42\], in the sense that dissociative
Figure 1.6: Experimental results in storage rings and afterglow plasma for the thermal rate of HCO$^+$ molecular ion, demonstrating large discrepancies between different experimental data.

Channels are not directly treated. Hence, we consider that once the electron is captured into an excited vibrational Rydberg state of the ion, the system dissociates. Therefore, autoionization is not taken into account, but a qualitative discussion on the competition between dissociation and autoionization is given in Subsection 3.4.2. Taking the last points into consideration, a deeper study was desired to find the key missing ingredients. As will be described in details in Chapters 3 and 4, we improved the treatment in two different aspects.
1.2.2 Theoretical study considering all internal degrees of freedom

First, we allowed the previously frozen CO bond to vibrate, since considering more vibrational degrees of freedom for the ion should, in principle, allow more routes of energy interactions between the molecular ion and the electronic motion. Although the CO bond is not directly responsible for the dissociation of HCO$^+$ via the channel$^{10}$ H+CO, its motion is always coupled to the vibration of the hydrogen around CO, either by vibronic couplings (vibration-electronic interactions that induce transition between states belonging to different vibrational channels) or simply because the channels themselves are already a mixture of different vibrational modes (anharmonicities in the electronic potential). Since the CO bond is more rigid (stiff electronic potential) than the relative hydrogen motion around CO, the vibrational excitations of CO occurs at relatively large electronic energy in comparison with excitation of the doubly degenerate mode of hydrogen vibration around the axis of symmetry of HCO$^+$. Consequently, the cross section should only start to be affected by CO vibration at electronic energies of the order of the first excited energy of the CO bond vibration. The theoretical treatment of the dissociative recombination of HCO$^+$, including all internal degrees of freedom, is fully described in Chapter 3.

$^{10}$The fact that HCO$^+$ mainly dissociates into the channel H+CO was the main reason why CO was treated as frozen at its equilibrium value in [102].
1.2.3 Theoretical study including the permanent dipole of HCO$^+$

Second, the HCO$^+$ linear ion has a large permanent dipole moment around 4 Debyes at its equilibrium geometry. The presence of a dipole moment is one of the usual features of a linear molecule, which is not symmetric with respect to a plane perpendicular to its axis of symmetry. On the other hand, a highly symmetric molecular ion like H$^+_3$ has no dipole moment at its equilibrium position. Still, H$^+_3$ has a quadrupole moment, but its effect should be rather insignificant on the electronic capture process. Including the dipole moment of a molecular ion in the theoretical treatment of DR has, to our knowledge, never been done before. On that account, we include the dipole moment of HCO$^+$ in our study since it could (1) explain why the last theoretical cross section is still below the experimental data, (2) be a benchmark study for general treatment of DR (or DEA) accounting for dipole moments of ions (or molecules). As we already pointed out, regular MQDT has some limitations, in the sense that a pure Coulomb potential is assumed at large distances. Therefore, any dipolar, quadrupolar, and higher order terms are set to zero in the outer region at large distance from the ionic core. A Generalized Multi-channel Quantum Defect Theory (GMQDT) was developed by Greene, Fano and Strinati in 1979 [47], which accounts for dipolar terms with only slight modifications in the regular MQDT formalism. The generalization of the theory will be introduced in Section 4.1.3. Another work by Gao et al. [39] also generalized MQDT to include quadrupolar, octopolar and even higher order terms in the theory.
Explaining why the introduction of the permanent dipole of HCO$^+$ in our treatment should in principle change significantly the DR cross section is not a trivial matter and perhaps no simple explanation can be given. We discuss this point in details in Section 4.2.2. For the moment, we can at least provide qualitative general ideas, expressing why it was reasonable to expect the dipole to affect the electronic capture probability. First, adding any non-diagonal couplings in an electron-molecule scattering process could potentially increase the cross section for electron capturing, since we basically add more paths for the electron to excite vibrations of the ion. Moreover, as will be described in Chapter 4, different forms of the electronic asymptotic phase shifts are obtained from the GMQDT in comparison with the regular MQDT formalism. As the cross section of a single partial wave can be expressed via its asymptotic phase shift, a change in the cross section can be expected when we add the strong permanent dipole moment of HCO$^+$ in the formalism.

1.3 Focus on the dissociative recombination of H$_3^+$ and H$_3$O$^+$

1.3.1 Why studying H$_3^+$ and H$_3$O$^+$?

Since hydrogen represents the most abundant element in the universe, its derived molecular ionic species, H$_2^+$ and H$_3^+$, have been extensively studied over the years, specifically because the chemistry is dominated by the reactions of ionized species in the low temperature interstellar medium. The H$_3^+$ molecular ion was discovered almost one century ago, in 1911,
by Thompson in his studies of plasma discharge [125]. By using an early form of a mass spectrometer, he found an abundant species in the plasma with a ratio mass-charge of three. Observing an increase of the signal in pure hydrogen gas, he logically assigned the species as $H_3^+$. Actually, $H_3^+$ is the most abundant species in molecular hydrogen plasma, indicating its stability and easy formation. Its mechanism of production was discovered in 1925 in plasma discharge cells experiment [64]. It is based on the following two-step process:

$$H_2 + \text{discharge} \rightarrow H_2^+ + e^-$$  
$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$  

The ionization of $H_2$, accomplished by cosmic radiations in the interstellar medium, is a slow reaction and depends strongly on the initial density of molecular hydrogen. On the other hand, the recombination of $H_2^+$ and $H_2$ is a very efficient reaction. Hence, the rate of formation of $H_3^+$ mainly depends on the rate of ionization of $H_2$. Differently from its formation, destruction of $H_3^+$ can occur through different pathways. In dense medium, its destruction happens principally via proton donation to a neutral molecule, and probably to the second most abundant species in interstellar clouds, carbon monoxide CO [62, 63]:

$$H_3^+ + CO \rightarrow HCO^+ + H_2.$$  

(1.4)

In fact, the proton donor behavior of $H_3^+$ triggers a chain of reactions leading to the formation of the vital water molecule (via DR of $H_3O^+$), as well as to the formation of several hydro-
carbons, as depicted in Fig. 1.7. These interesting chemical properties make $\text{H}_3^+$, one of the

Figure 1.7: Branches of reactions engendered by the $\text{H}_3^+$ ion. For clarity, we have not drawn the numerous reactions originating from the $\text{CH}_3^+$ ions, mostly producing hydrocarbons which can further attach nitrogen or oxygen atoms.

most important ions in interstellar media [96]. In 1996, observations revealed the presence of $\text{H}_3^+$ in two interstellar clouds [40], and the suggestion by Herbst and Klemperer, that $\text{H}_3^+$ initiates a large network of ions and molecules formation, was indeed confirmed. Moreover, spectroscopic analysis of an interstellar cloud enables one to determine the ortho-para ratio of $\text{H}_3^+$ and thus to obtain a qualitative idea of the temperature of the cloud.

In diffuse interstellar medium, the most common pathway for destruction of $\text{H}_3^+$ is dissociative recombination with slow electrons [62], which proceeds into two different dissociative
The DR rate of $\text{H}_3^+$ has been experimentally investigated since the late 40’s, with large discrepancies (up to four orders in magnitude) between different data as shown in Fig. 1.8. The big uncertainty translated into a large error in the estimation of density, leading to absurd conclusions that the size of clouds were larger than the distance between stars. Storage rings and afterglow plasma experiments started in the 80’s and the DR rate coefficients only recently converge to similar values in agreement with theoretical calculations.

The most recent theoretical work by Fonseca dos Santos et al. [36] is in good agreement with the last storage ring data obtained from TSR and CRYRING experiments [98, 97]. As will be qualitatively explained in Subsection 1.3.2, the latter study requires high order of complexity and heavy computational work. In Chapter 5, we introduced a simpler model, which only demands the determination of a few parameters given by ab initio calculations, to obtain the DR cross section within correct order of magnitude.

Finally, we want to stress the fact that the molecular ion $\text{H}_3^+$ is not only important in the interstellar medium, but also relevant in planetary science. It was first detected in 1989 in Jupiter’s aurora, and presently the information of its emissions is used as a remote probe for the description of Jupiter’s atmosphere [127, 112]. Also, emission lines of $\text{H}_3^+$ were detected in the ionosphere of Saturn [41] and Uranus [84].
Figure 1.8: Figure taken from [117], showing the DR rate coefficients of H$_3^+$ (300K) measured over the years from different experimental setups. Convergence in the measurements was reached only very recently, and the results are in good agreement with the last theoretical study by Fonseca dos Santos et al. [36].

The molecular hydronium ion H$_3$O$^+$ is another important species in the interstellar medium. It is formed (see Fig. 1.7) by a chain of chemical reactions, starting with the reaction of H$_3^+$ with an oxygen atom [58]:

\[
\begin{align*}
O + H_3^+ &\rightarrow OH^+ + H_2 \\
OH^+ + H_2 &\rightarrow H_2O^+ + H \\
H_2O^+ + H_2 &\rightarrow H_3O^+ + H.
\end{align*}
\]
+
The formed closed shell of the H3 O molecular ion does not react with atomic or molecular
hydrogen, but can be depleted by DR with electrons, which are also abundant in diuse
interstellar clouds. For instance, in the inner coma of Comet Halley, DR is predicted to be

+
the major mechanism of destruction of H3 O , and observations by the spacecraft Giotto [53]
reported the hydronium ions as the most abundant ionic species in this comet. Since water
is one of the most important molecules in interstellar dust and in the tail of comets, its

+
synthesis has been considered to come mostly from the dissociative recombination of H3 O
[128, 90]. Knowledge of the abundance of water is critical, since it plays a signicant role in
the evolution of the interstellar medium, and possibly in star formation. In 1996, Andersen

et al.[58] demonstrated experimentally that H2 O is indeed a product of the recombination of
+
H3 O , with an eciency for this reaction of about 33%, as shown in (1.7). This result is in
good agreement with observations of the ratio

[H2 O]/[H3 O+ ]

in the interstellar medium. In

fact, four dierent dissociative channels have been measured in the heavy-ion storage ring
ASTRID in Denmark [59] with the following eciency:

H3 O+ + e− −→





H2 O + H







 OH + H2



OH + H + H







 O + H2 + H

33%
18%
(1.7)

48%
1%

The branching ratios in (1.7) are important parameters for the chemistry of interstellar
clouds, in the sense that they determine which species in between

28

H2 O or O2

is the dominant


oxygen-containing in clouds. A complete quantum-mechanical treatment for this dissociative process is extremely complex due to the large number of neutral potential surfaces on which the process can occur. Contradictions in theoretical results have been obtained [61, 14].

1.3.2 Theoretical study using a simplified treatment

A theoretical description of dissociative recombination in H$_3$O$^+$ (and other polyatomic ions, in general) is complicated due to the large number of vibrational degrees of freedom and many electronic states of the neutral molecule H$_3$O that have to be included into the complete theoretical model. Theoretical methods for DR in triatomic molecular ions, H$_3^+$ [77, 75, 36], HCO$^+$ [102, 29], and LiH$_2^+$ [55] have been developed during the last decade, showing relatively good agreement with the experimental data. The structure of the H$_3^+$, HCO$^+$, and LiH$_2^+$ ions are similar in the way they recombine with electrons. They all have a closed electronic shell, which makes their dissociative resonant states lie above their ground electronic potentials, such that the potential energy surfaces of the resonant electronic states do not cross the ionic potential surface in the Franck-Condon region. For this reason, direct DR with low energy incident electrons is improbable for such molecular ions. The dominant DR mechanism for these ions proceeds through the capture of an electron into a Rydberg state associated with a vibrationally excited ionic core.

A completely quantum-mechanical treatment that has been employed previously for DR in H$_3^+$ [75, 74, 36] requires the knowledge of the full electronic potential surfaces in a large
configuration space, for both the ion and the neutral state. If used for \( \text{H}_3\text{O}^+ \), the treatment would require accurate \textit{ab initio} calculations performed for the ground electronic state of the ion and for several excited electronic states of the neutral molecule \( \text{H}_3\text{O} \) for all six vibrational degrees of freedom. Once the potential energy surfaces are available, one would have to do the vibrational dynamics in several dimensions, ideally along all six vibrational coordinates. Thus, the full completely quantum-mechanical treatment for indirect DR of polyatomic ions require heavy computational codes in order to compute the DR cross section.

It is desirable to produce a simpler model, which only takes into account the key factors in the DR mechanism with the goal to give a correct estimate for the DR cross section. An important step forward\(^{11} \) for such simple DR theory for polyatomic ions was made in the previous and present studies of DR in \( \text{HCO}^+ \) [102, 29], presented in Chapter 3. In this study, the dissociative channels are not taken into account explicitly, and reionization is neglected. Competition between reionization and dissociation are discussed qualitatively in Subsection 3.4.2, where it is shown that reionization should only slightly decrease the probability for dissociation after the electron is captured into a predissociated Rydberg state. On the other hand, the treatment uses \textit{ab initio} calculations on the full configuration space, including different electronic couplings. Moreover, adiabatic vibrational states depending parametrically on the dissociative coordinates are computed. The procedure of channel elimination (see Subsection 2.3.3) is performed and positions and widths of resonances are

\(^{11}\)Both studies were based on the ideas suggested in [77].
obtained. Finally an averaged cross section for electronic capture in any ionic vibrational state is computed. Thus, this treatment is still rather complicated.

Jungen and Pratt \[70, 71\] made another step further in simplifying the treatments for both \( \text{H}_3^+ \) \[71\] and \( \text{HCO}^+ \) \[70\], by considering solely the capture in the first excited doubly degenerate vibrational normal mode (harmonic approximation). This later approximation simplifies greatly the model and the obtained results are in very good agreement with the more detailed approaches. Our study of DR of \( \text{H}_3\text{O}^+ \) will rely on the same basic principles discussed in \[77, 102, 29, 70, 71\] with the exception that the \( \text{H}_3\text{O}^+ \) ion has two Jahn-Teller active normal modes. Before introducing the approach in details, we start with a brief description of the \( \text{H}_3\text{O}^+ \) vibrational modes around the equilibrium position. The presentation of this theoretical model and its application to the DR of \( \text{H}_3^+ \) and \( \text{H}_3\text{O}^+ \) are presented in Chapter 5.

### 1.4 Symmetries in collisions of identical particles

The role of symmetries in theoretical physics has been considerably raised during the last century. Although symmetries have already been long-studied, for instance in analytical mechanics via the Hamiltonian or Lagrangian formulations, they were mostly considered secondary consequences of the theory and were generally used as a convenient tool to treat complex classical systems. The principle of Relativity and the concepts of Quantum Mechanics have placed symmetries as intrinsic parts of modern physics and motivate deeper
studies on group theory. As early as in 1927, theoreticians like Wigner and von Neumann used widely the theory of representations of permutation and rotation groups to study the properties of symmetry inherent to the Schrödinger equation. In this sense, group theory took place at the foundation of quantum mechanics and is widely used today in different domains of physics, such as: atomic physics, spectroscopy, crystal and molecular vibrations, chemical bonds and elementary particles physics.

There are numerous routes one can follow while introducing the vast concept of symmetry in physics. Symmetry seems to be an intrinsic part of nature and it is therefore not surprising that any theory to describe the world should reveal somehow a certain symmetry. For this reason, we can say that symmetries play a role in almost any theory in physics. This is perhaps even more true in modern theories, where symmetry happens to be an inherent requirement. For instance, any relativistic theory should be Lorentz invariant, which means it should transform in a specific way under the operations of symmetry of a group when changing frames of reference. It is a well known fact, that Dirac actually found his famous equation by trying to fulfill this requirement. The standard model, which is without any doubt, the most complete present theory to describe the world of physics, is also based on group theory. From symmetry considerations, high energy physicists even predicted the existence of particles, and this is still a present matter today with the research of the Higgs boson at CERN in Switzerland. Coming back to lower energies, symmetry are already fully present in classical and non-relativistic quantum theories. Let us consider a classical Hamiltonian $H$ expressed via coordinates and momenta $q$ and $p$. Let us consider an infinitesimal
canonical transformation, generated by the dynamical variable \( g(q,p) \), transforming to new variables \( \bar{q} \) and \( \bar{p} \) in the following way:

\[
\begin{align*}
q_i \to \bar{q}_i &= q_i + \epsilon \frac{\partial g}{\partial p_i}, \\
p_i \to \bar{p}_i &= p_i - \epsilon \frac{\partial g}{\partial q_i}.
\end{align*}
\] (1.8)

If \( H \) is invariant under this transformation, which means it owns a specific symmetry related to the dynamical variable \( g \), we then get

\[
\delta H = \sum_i \frac{\partial H}{\partial q_i} \left( \epsilon \frac{\partial g}{\partial p_i} \right) + \frac{\partial H}{\partial p_i} \left( -\epsilon \frac{\partial g}{\partial q_i} \right) = \epsilon \{ H, g \} = 0.
\] (1.9)

It is well known that \( \dot{g} = \{ g, H \} \), we thus conclude that \( g \) is a conserved quantity. This is probably the most important result of symmetry in classical dynamics, and it holds in quantum mechanics as well, for the simple reason that the formula for the time evolution of an operator in the Heisenberg picture is the same as in (1.9) if we replace Poisson brackets by commutators. Since Poisson brackets and commutators obey the same transformation properties, any classical constant of motion will ultimately be a constant of motion in quantum mechanics.

The consequences of symmetries in quantum mechanics are broader than in classical mechanics. Indeed, symmetries are used to classify the fundamental particles and discuss the selection rules that govern the allowed spectroscopic transition. They also inform whether integrals are zero or not, which is extremely helpful since integrals are involved in expectation
energies and in the calculation of the dipole moment matrix. Furthermore, group theory anticipate the occurrence of degree of degeneracy. Finally, symmetries are very powerful tools to construct and classify the molecular orbitals.

In the thesis, symmetries are constantly used either to find the form of vibronic couplings in Chapter 3 and Chapter 5 or to set up selection rules and allowed states in rearrangements of systems of identical atoms in Chapter 6 and Chapter 7. The basics of group theory are reviewed in Chapter 2.

1.5 Organization of the thesis

We now present the organization of the thesis by describing succinctly the content of each different chapter.

Chapter 2: We present the building blocks of the general theory used in the present thesis. Therefore, this chapter is devoted as a reference for the following concepts and first principles needed in our theoretical development. First, we discuss the general aspects of group theory and its applications in molecular quantum chemistry. We review the non Born-Oppenheimer couplings from the symmetry point of view. We also discuss the basic ingredients needed for our study of DR by reviewing the MQDT theory, the vibrational frame transformation and finally the direct and indirect DR mechanisms.
Chapter 3: Motivations, history and backgrounds on the DR of HCO$^+$ are discussed. Then, we present our theoretical treatment of the process of dissociative recombination of HCO$^+$. We start by introducing the Hamiltonian of the problem. The adiabatic Schrödinger equation for the ionic Hamiltonian is solved in a system of Jacobi coordinates and we show the obtained adiabatic potential curves. The Renner-Teller effect and the electron-ion interaction Hamiltonian are discussed, as well as the construction of the short- and long-range reactance matrix describing the electron-ion collision. Autoionizing Rydberg resonant curves and related avoided crossings are presented. We also describe the calculation of the cross section, as well as the convolution procedure and the thermal rate coefficient calculation. Finally, we show the DR cross section and the thermal rate coefficient for both HCO$^+$ and DCO$^+$ ions and compare them with experimental data and previous theoretical calculations. Finally, we discuss the results.

Chapter 4: We discuss an improvement of the previous treatment by including the strong permanent dipole moment of HCO$^+$. The basic steps of the approach remain the same as in Chapter 3 and we focus on the changes brought to the theory when considering the effect of the Coulomb plus dipolar field on the electron. For this purpose, we discuss an extension of the regular MQDT, named Generalized Multi-channel Quantum Defect Theory, which apply to more general potentials than the pure Coulomb potential. New eigenchannels and form of the reactance matrix are found. The procedure of channel elimination also has to be slightly modified. As a conclusion, we discuss the resulting cross section and give an interpretation.
of the reason why the permanent dipole moment of HCO\(^+\) increases the cross section over the whole range of energy.

**Chapter 5:** We present a simplified theoretical model to treat the dissociative recombination of the H\(_3\)O\(^+\) and the H\(_3^+\) ions. In analogy with recent studies, we consider the non Born-Oppenheimer Jahn-Teller effect as the key factor for electronic capture in Rydberg states associated with excited vibrational levels of the ions. We use the simplified Jahn-Teller model for highly symmetric ions and adopt the normal mode approximation for the vibrational states of H\(_3\)O\(^+\) and H\(_3^+\). Using the MQDT formalism and *ab initio* calculations, we derive the cross sections for electronic capture from the initial ground vibrational state of the ion to the first excited state of a doubly degenerate vibrational normal modes of H\(_3\)O\(^+\) or H\(_3^+\). To conclude, we compare our theoretical calculations of the cross section for both ions with available experimental data and with previous accurate theoretical results in the case of H\(_3^+\).

**Chapter 6:** In this chapter, we consider the collision of three identical atoms and derive scattering selection rules from initial to final states of the system. We use either hyperspherical or Jacobi coordinates depending on which one is best suited to describe three different configurations of the atoms: (1) three free atoms, (2) a quasi-bound triatomic, or (3) a dimer and a free atom. We summarize quantum numbers conserved during the collision as well as quantum numbers that are appropriate for a given configuration but may change during the scattering process. The total symmetry of the system depends on these quantum numbers.
and is found by projecting an unsymmetrized wave function of the system on the different irreducible representations of the symmetry group. Based on the obtained selection rules, we construct correlation diagrams between different configurations before and after a collision. In particular, we describe a possible fragmentation of the system into one free atom and a dimer, which can be used to identify possible decay products of quasi-stationary three-body states or three-body recombination.

**Chapter 7:** We discuss in detail the symmetries of a system of four identical atoms with different separated fragments at large distances from each other. Namely we consider respectively the system as: (1) two dimers, (2) a trimer and a free atom, (3) one dimer and two free atoms. The general approach to treat this problem relies on introducing the eigenfunctions of the Hamiltonian for each large distance configuration and to label these spaces with constants of motion of the system. The study of the symmetry of the system can then be performed by decomposition of these subspaces in irreducible representations of the total symmetry group $G_{48}$ of four identical atoms. We adopt a different approach than the one in Chapter 6 since the use of projectors would be quite cumbersome in this case. Instead, we consider appropriate subgroups related to the symmetry of the system in the different large distance configurations. Moreover, we treat the spin symmetry in the different configurations. The obtained results could be used to study the different possible rearrangements of four identical atoms in collisions, since it is well known that the symmetry of the wave function of the system is conserved in such processes. Correlation diagrams between dif-
different configurations can be obtained. The selection rules imposed by these considerations of symmetry and the allowed quantum states satisfying the symmetrization postulate for fermions or bosons can also be explicitly determined from these results.

Chapter 8: We conclude the thesis by harvesting and interpreting the different results of our research. We discuss the interest of the results and possible improvements of the models. Finally, we exhibit the perspectives and propose future studies following the present work.
CHAPTER 2
THEORETICAL BACKGROUND

2.1 Group theory in the theoretical study of molecular systems

2.1.1 Groups of molecular physics

Symmetry properties of the physical systems under consideration in our study represent one of the central point in this thesis. In order to clarify the ideas, we review main ideas of group theory relevant to the present thesis by introducing the different groups of symmetry. We shall not give mathematical details on the exact formulation of the approximations and the corresponding form of the equations and their solutions, but rather focus on the insights of the role of symmetry in quantum chemistry. More details on symmetries will be brought through the development of our studies, when we consider the Jahn-Teller and Renner-Teller effects (Chapters 3 and 5), and when we study ultra-cold collisions of systems composed with three or four identical atoms (Chapters 6 and 7).

Groups of molecular physics are related to invariance of the molecular Hamiltonian with respect to symmetry transformations. Thus, operations belonging to a symmetry group commute with the molecular Hamiltonian. Basically, the Hamiltonian of an isolated system
is invariant under four types of operations, namely the permutations of identical particles, the inversion, the rotations, and the translations of the molecular system. Inversion and permutations of identical particles are connected to the complete nuclear permutation inversion group (CNPI) and the rotations to the rotation group. These groups are introduced in the present subsection. However, since we consider collisions in the center of mass coordinates system, we do not discuss the translation group related to conservation of total momentum.

For certain types of molecules, as CH$_3^+$ or H$_3$O$^+$, there exist several symmetric equilibrium configurations referred as versions of the molecule. If tunneling from an equilibrium configuration to another is negligible\(^1\), some elements of the CNPI group are called unfeasible. This is the case for so called rigid molecules and one only needs to consider a subgroup of feasible elements of the CNPI group, named the molecular symmetry (MS) group. The MS group is defined in the following development.

The Schrödinger equation can almost never be solved exactly for realistic systems. For this reason, one usually seeks for approximate solutions by introducing a molecular frame bound to the molecule at its equilibrium. This procedure allows to consider the whole motion of the molecule as independent motions of rotation of the frame attached to the rigid molecule and of vibronic motions of the particles relative to the molecular frame. The role of the point groups is to describe the symmetry of this vibronic motion and determine easily

\(^1\)Tunneling is negligible when there exists a high potential barrier to overcome to go from one version of the molecule to another. For instance, this is the case for the methane molecule, for which the experimental resolution is not high enough to detect any splitting in energy.
non vanishing couplings. We explain the relation between the CNPI group, the rotation group, and the point group in the following development.

2.1.1.1 The Complete Nuclear Permutation and Inversion (CNPI) group:

Let us consider a system composed of three identical particles labeled 1, 2 and 3, whose positions are represented respectively by the coordinates \( \{X_i, Y_i, Z_i\} \) for \( i = 1, 2 \) or 3. A permutation of particles transforms any function \( f \) of these coordinates into a new function, which is defined by permutation of the coordinates. For instance, the operation \((12)\) exchanges the coordinates of the particles 1 and 2. Therefore, \((12)\) simply acts on \( f \) to give the new function \( f^{(12)} \) defined by

\[
f^{(12)}(X_1, Y_1, Z_1, X_2, Y_2, Z_2, X_3, Y_3, Z_3) = f(X_2, Y_2, Z_2, X_1, Y_1, Z_1, X_3, Y_3, Z_3).
\] (2.1)

Another type of permutation involving more than two particles exchanges for instance the coordinates of particles 1 \( \leftrightarrow \) 2, 2 \( \leftrightarrow \) 3, and 3 \( \leftrightarrow \) 1. This type of permutation is called a *cycle* and is denoted \((123)\). We can define the product law of any two operations as their successive action, where the operation on the right acts first. Let us mention that the order in products of permutations is important. For this reason, the product law is said to be *non-commutative*.

It is also important to realize that all permutations are not only transpositions or cycles. On the other hand, it is always possible to write any permutation as a product of sequences...
of transpositions. This decomposition is not always unique, but the even or odd number of transpositions in the product remains the same whatever decomposition is used.

An extremely important operation in quantum mechanics is the parity or inversion operation $E^*$, which changes the sign of the coordinates related to all particles of the system. If we denote compactly the coordinates of all the particles of the system by $X$, the inversion\(^2\) operation acts on $f$ to give a new function $f^{E^*}$ defined by

$$f^{E^*}(X) = f(-X). \quad (2.2)$$

If we consider the set of all permutations, including the identity operation denoted $E$, it can easily be shown that this set forms a group generally called $S(3)$ (permutation group). Usually, the latter group is named complete nuclear permutation group ($G_{CNP}$) when permutations are applied to identical nuclei and simply denoted $S^{(e)}$ when permutations apply on electrons. We obtain the complete nuclear permutation inversion group $G_{CNP\text{I}}$ by adding the inversion to $G_{CNP}$. The latter group is used throughout this thesis to define the symmetry of the wave function of the molecular systems under consideration. The important properties of this group resides in the fact that its elements commute with the Hamiltonian of a molecular system. Thus the elements of $G_{CNP\text{I}}$ reflect part of the symmetry\(^3\) of the Schrödinger equation of an isolated system.

\(^2\)We stress that the inversion operation changes the sign of the coordinates of the nuclei and electrons.\(^3\)In fact, the weak interaction is not parity invariant, so that $E^*$ commutes with the Hamiltonian only if the weak interaction is negligible. This condition is always fulfilled in this work.
Let us for instance show that the elements of $G_{CNPI}$ commute with the Hamiltonian of the water molecule ($\text{H}_2\text{O}$). We label the hydrogen atoms 1 and 2, the oxygen atom 3 and the electrons from 4 to 13. If we denote by $R_{ij}$ the distance between particle $i$ and $j$, the Hamiltonian of the water molecule takes the following form\(^4\)

\[
\hat{H} = \frac{1}{2m_H}(\hat{P}_1^2 + \hat{P}_2^2) + \frac{1}{2m_O}\hat{P}_3^2 + \frac{1}{2}\sum_{r=4}^{13} \hat{P}_r^2 + \frac{1}{R_{12}} + 8(\frac{1}{R_{13}} + \frac{1}{R_{23}}) - \sum_{r=4}^{13} \frac{1}{R_{1r}} - \frac{1}{R_{2r}} - \sum_{r=4}^{13} \frac{1}{R_{3r}} + \sum_{r<s=4}^{13} \frac{1}{R_{rs}}.
\]

(2.3) (2.4) (2.5) (2.6) (2.7)

The effect of applying the operation (12) to this Hamiltonian interchanges $\hat{P}_1^2$ and $\hat{P}_2^2$ in (2.3), leaves (2.4) unchanged, leaves $R_{12}$ unchanged, interchanges $R_{13}$ and $R_{23}$ in (2.5), interchanges $R_{1r}$ and $R_{2r}$ in (2.6) and finally leaves (2.7) unchanged. Therefore the Hamiltonian is globally invariant under the operation (12). We could show in the same way that this is also true under permutations of electrons. Let us now consider the effect of applying the parity operation $E^*$ to this Hamiltonian. Obviously all the distances are unchanged and all kinetic operators, which involve second derivatives of these coordinates are also unchanged.

We conclude that the Hamiltonian of a molecular system is invariant under all elements of $G_{CNPI}$, as well as under the elements of $S^{(e)}$, so that any operator $\hat{R}$ of these groups com-

\(^4\)We use atomic units in the thesis.
mute with the Hamiltonian of the system: \([\hat{R}, \hat{H}] = 0\). The Hamiltonian considered in (2.3) is somehow simplified as we omit a few terms\(^5\) in our expression, but its invariance under operations of \(G_{\text{CNPI}}\) and \(S^{(e)}\) remains.

2.1.1.2 The Molecular Symmetry (MS) group:

As demonstrated, the CNPI group commutes with the molecular Hamiltonian of the system. It happens that for molecules with more than one equilibrium configuration, *structural degeneracies* arise. For example, the methane molecule has two equilibrium positions corresponding to the motion of the carbon atom through the plane formed by the hydrogen atoms. These two versions of the molecule have equivalent symmetrical potentials around each position, but the potential barrier between these two configurations is too high to allow any penetration. Hence, some elements of \(G_{\text{CNPI}}\) transform an equilibrium configuration into another. Due to the symmetry induced by this or these element(s), structural degeneracies arise. Considering again methane, the rotation-vibration energies are labeled \(A_1^+ \oplus A_1^-\), \(A_2^+ \oplus A_2^-\), \(E^+ \oplus E^-\), \(F_1^+ \oplus F_1^-\) and \(F_2^+ \oplus F_2^-\), where we introduced the irreducible representations of the point group \(T_d(M)\) for methane. The signs '+' and '-' refer to the even or odd characters of the irreducible representation by inversion. These *accidental* degeneracies are not required by the symmetry of the CNPI group and appear due to the special form of the potential. We shall encounter several of these accidental degeneracies in Chapters 6 and 7.

\(^5\)For instance spin-spin interactions, spin-orbit interactions or nuclear quadrupole interaction energy with the electric field gradients.
due to the assumed asymptotically vanishing potentials. A way to avoid such extra degeneracies is to omit unfeasible elements from $G_{CNPI}$ and use the molecular symmetry (MS) group, which is simply a sub-group of $G_{CNPI}$. The MS group approximates the molecule as an entity in a given version, that can vibrate around its equilibrium position but can not tunnel to another version.

2.1.1.3 The rotation groups:

Let us start with an equilateral triangular prism and seek for the rotations that let it unchanged. If we choose an axis $a$ passing vertically through the center of the triangular face and apply a rotation around this axis by an angle $\frac{2\pi}{3}$ or $\frac{4\pi}{3}$, the geometrical figure will come back to its initial position. These two rotations are respectively denoted $C_{3a}$ and $C_{3a}^2$. Three other rotations by angle $\pi$ have also this characteristic of symmetry, with their different axes $b$, $c$, and $d$ belonging to the plane of symmetry of the prism, passing through each summit of the triangle and crossing the other side perpendicularly. The latter rotations are denoted $C_{2b}$, $C_{2c}$, and $C_{2d}$. If we include the identity $E$ among the rotations previously introduced, we form the rotational symmetry group $D_3$:

$$D_3 = \{ E, C_{3a}, C_{3a}^2, C_{2b}, C_{2c}, C_{2d} \}$$  \hspace{1cm} (2.8)

\footnote{An axis like $a$ is called a 3-fold rotational axis. Axes like $b$, $c$, and $d$ are 2-fold rotational axis and we can define $n$-fold and $\infty$-fold rotational axes.}
It has to be verified that this is indeed a group. We can check it by setting up a so-called *multiplication table*, which gives the result of the multiplication of any two rotations. For instance, we obtain \( C_2^3 \cdot C_2^b = C_2^c \) or \( C_3^a \cdot C_3^a = C_2^a \).

If we consider the rotational group of a sphere, it can be seen that any rotation of any axis passing through the center of the sphere with any angle of rotation will let the sphere unchanged. This infinite group is called *three dimensional rotation group* and denoted \( K \). Other infinite rotational groups are \( C_{\infty} \) (cone) or \( D_{\infty} \) (cylinder). Since we do not explicitly need rotational groups, but merely operators of rotation as elements of the point group, we do not describe in more details their properties. We stress that when considering rotation groups of molecules only the groups \( K, D_2 \) and \( D_{\infty} \) are needed. The group \( K \) is used in two different ways, either as the group \( K(spatial) \) of the rotations around all axes passing through the center of mass of the molecule and fixed with respect to the laboratory, or as the group \( K(mol) \) of the rotations of all axis passing through the center of mass of the molecule and fixed to the molecule. The group \( K(spatial) \) is related to the invariance of the Hamiltonian by rotations around fixed axes. The groups \( K(mol), D_{\infty} \) and \( D_2 \) are respectively used to classify the rotational states of spherical top molecules (methane), symmetric top molecules (methyl fluoride) and asymmetric top molecules.
2.1.1.4 The point group:

Let us consider any three dimensional geometrical figure and find all operations of symmetry that let this figure unchanged. To the rotations, previously introduced, we need to add possible reflexions through a plane. The composition of two rotations is always a rotation (if the two axes of rotation cross), the composition of two reflexions is a rotation (if the planes are not parallel), but the composition of a reflexion and a rotation is in general neither a rotation nor a reflexion and for this reason has its own name \textit{rotation-reflexion}. If we consider all these symmetry operations: rotations, reflexions and rotation-reflexions, we form the so-called \textit{point-group}, named in this way because all planes of reflexion or axes of rotation pass through the center of symmetry of the three dimensional object (if it was not the case, the product of two rotations could induce a translation of the object and therefore would not let this object unchanged). With these considerations, it is easy to find the symmetry group of most geometrical figures and therefore of molecules at their equilibrium configurations. In general, the point group symmetry of an object is determined from the following:

- $C_n$ one n-fold rotation axis.
- $C_{nv}$ one n-fold rotation axis and n reflexions planes containing this axis.
- $C_{nh}$ one n-fold rotation axis and one reflection plane perpendicular to this axis.
- $D_n$ one n-fold rotation axis and a n twofold rotation axes perpendicular to it.
• $D_{nd}$ those of $D_n$ plus $n$ reflections planes containing the $n$-fold rotations axis and bisecting the angles between the $n$ twofold rotation axes.

• $D_{nb}$ those of $D_n$ plus a reflection plane perpendicular to the $n$-fold rotation axis.

• $T_d$ all rotations, reflections and rotation-reflections of a regular tetrahedron.

In our later developments, we will need point groups to study the symmetry of the vibronic wave function or simply the symmetry of the electronic wave function (in the Born-Oppenheimer approximation) of rigid molecules. It could appear unnatural at first sight to treat vibrating atoms and orbiting electrons using a group referring to a static picture of a vibrating object in space. We discuss how the point group is introduced in the theory in Subsection 2.1.3.2.

2.1.2 Representations of groups

2.1.2.1 Definition of a representation:

Let us consider a group $G$ of linear quantum operators with elements denoted $\hat{R}$. We introduce a vector space $E_n$ of finite dimension $n$. If each element $\hat{R}$ of the group $G$ acts on a vector $\psi$ to give a transformed vector $\psi'$ belonging to the same space $E_n$, then the group $G$ is said to form a representation, generally denoted $\Gamma$. The space $E_n$ is the space of representation of the group $G$. The action of these operators on the vectors of $E_n$ can be
represented by a matrix $M(\hat{R})$ and the set of all these matrices form a *matricial representation* of the group $G$. The trace of each matrix (which is invariant by change of basis) is called the character of the element $\hat{R}$ and denoted $\chi(\hat{R})$.

### 2.1.2.2 Decomposition of representations in irreducible representations:

We consider again the vector space $E_n$. If it is possible to write this space as the direct sum $E_n = F_1 \oplus F_2$, where both $F_1$ and $F_2$ spaces are stable under any operators of the group $G$, then the representation $\Gamma$ is said to be reducible and we denote $\Gamma = \Gamma_1 \oplus \Gamma_2$, where $\Gamma_1$ and $\Gamma_2$ are representations with respective subspaces $F_1$ and $F_2$. If on the other hand, no subspace of $E_n$ is actually stable under all the elements of $G$, then $\Gamma$ can not be decomposed as a sum of representations and is said to be an *irreducible representation*. The irreducible representations are fundamental signatures of a group and have been listed for all important point groups of molecular physics. Therefore, whatever space of representation is considered, it can always be decomposed into spaces of irreducible representations. This fundamental aspect is used through the thesis.

### 2.1.2.3 Projection formula and representations of subgroups:

The basic concepts of representations of groups introduced previously is a starting point in our treatments on symmetries of molecular systems composed with identical atoms. Basically
we consider a space of representation $E_n$, composed of vectors $\psi$, and look for irreducible representations this space can be decomposed into. Two different methods to treat either three or four identical atoms are used in our developments. First, we study the system of three identical atoms using the projection formula. This equation is quite easy to handle in this case since the group of symmetry does not have too many elements and the irreducible representations are at most doubly degenerate.

Let us consider a vector $\psi$ which transforms according to a reducible representation $\Gamma$ by action of the elements of the group $G$. If we denote by $D^{\Gamma_i}(\hat{R})$ the matrix of the operator $\hat{R}$ in the irreducible representation $\Gamma_i$, it can be derived that the following operator is a projector on the representation space of the irreducible representation $\Gamma_i$:

$$\hat{P}^{\Gamma_i}_{mm} = \frac{l_i}{h} \sum_{\hat{R} \in G} D^{\Gamma_i}_{mm}(\hat{R}) \hat{R}. \quad (2.9)$$

In this expression $l_i$ is the dimension of the representation $\Gamma_i$, $h$ is the order of the group $G$ and $D^{\Gamma_i}_{mm}$ is one of the diagonal element of the matrix $D^{\Gamma_i}(\hat{R})$. Therefore, we see that there are as many projectors as the dimension of the irreducible representation. We notice that if the irreducible representation is one dimensional, then the formula simply becomes:

$$\hat{P}^{\Gamma_i}_{mm} = \frac{l_i}{h} \sum_{\hat{R} \in G} \chi^{\Gamma_i}(\hat{R}) \hat{R}, \quad (2.10)$$

where $\chi^{\Gamma_i}(\hat{R})$ is the character of the operator $\hat{R}$ in the irreducible representation $\Gamma_i$. Applying the projector on a vector $\psi$, we can check (using properties of orthogonality of matrix
elements) that the obtained function $\hat{P}_{mm} \psi$ transforms as the irreducible representation $\Gamma_i$. If the results of this projection is actually null, we conclude that our function is orthogonal to this irreducible representation space. This is the way we proceed while considering the case of three identical atoms to find allowed symmetries.

On the other hand, when treating systems of four identical atoms, projectors become long sums and hard to deal with. For this reason, we treat our system of four identical atoms with a second method based on the use of appropriate subgroups of the group of symmetry of the system and establish a correspondence between the irreducible representations of these subgroups to the ones of the total symmetry group.

Let us consider again the space $E_n$ stable under the elements of the group $G$, as well as a subgroup $H$ of the group $G$. These two groups have different irreducible representations, but any irreducible representation of the group $G$ could formally be decomposed as irreducible representation of $H$. The formula to find the correct decomposition in irreducible representations of $H$ uses the characters of each irreducible representation and applies for any dimension of the irreducible representation (contrary to equation (2.10), which applies only for one-dimensional irreducible representation). If we denote by $\Gamma$ an irreducible representation of $G$, the decomposition can be written as $\Gamma = \oplus_i a_i \Gamma_i$, where $\Gamma_i$ are the irreducible representations of $H$. The coefficients $a_i$ are given by

$$a_i = \frac{1}{\hbar} \sum_{\hat{R} \in H} \chi^\Gamma(\hat{R}) \chi^{\Gamma_i}(\hat{R}). \tag{2.11}$$
In the above expression, \( h \) is the order of the group, \( \chi^\Gamma(\hat{R}) \) and \( \chi^{\Gamma_i}(\hat{R}) \) are respectively the characters of the element \( \hat{R} \) in the \( \Gamma \) and \( \Gamma_i \) irreducible representations. We will discuss these points in practical situations in Chapters 6 and 7.

### 2.1.3 Application in quantum mechanics

#### 2.1.3.1 Wave functions as elements of a representation space:

We consider a molecular Hamiltonian \( \hat{H} \) and a group \( G \) of operators whose elements commute with \( \hat{H} \). We introduce an eigenfunction of this Hamiltonian \( \psi \) with energy \( E \) so that \( \hat{H}\psi = E\psi \). Applying any element \( \hat{R} \in G \) on the left and right sides of this equation leads to

\[
\hat{R}\hat{H}\psi = \hat{H}\hat{R}\psi = E[\hat{R}\psi].
\]

We deduce the important result that \( \hat{R}\psi \) is also an eigenfunction of \( \hat{H} \) with energy \( E \). This fact is known as the Wigner theorem. It means that the space of energy \( E \) is stable under any element of the group \( G \) and therefore is a representation space of the group \( G \). Therefore, this space transforms as an irreducible representations of \( G \). Accidental degeneracies arise when the subspace is decomposed as the sum of several irreducible representations of \( G \). Accidental degeneracies are rare and occurs when the interaction potential in consideration has a specific behavior and is not treated within the MS group. The irreducible representations are used
for labeling eigenenergy spaces of a molecular system. They give crucial informations on symmetries and degeneracies. Furthermore, since the elements of $G$ commute with the Hamiltonian, irreducible representations are conserved. Starting with a state of specific symmetry, it will remain in the same symmetry. This fact is extensively used to set up selections rules.

2.1.3.2 Relating rotation groups, point groups and CNPI groups:

The full group of symmetry of a molecular system in its system of mass coordinates is

$$G_{\text{Full}} = G_{\text{CNPI}} \otimes K(\text{spatial}) \otimes S^{(e)}.$$  \hfill (2.13)

If we consider a rigid molecule without possible tunneling to another version, we replace the $G_{\text{CNPI}}$ group in (2.13) by the MS group (Subsection 2.1.1). If the Schrödinger equation was exactly solvable, none other group would be needed to study the symmetry of the system. The representations of the MS group, of $S^{(e)}$ and $K(\text{spatial})$ are sufficient to define exactly the symmetry of the quantum states of the system. In Subsection 2.2.1, we review the main approximations introduced in order to find the so-called zeroth order approximate solution. This procedure involves separation of the system coordinates as a global rotation of a fixed-body frame attached to the molecule and vibronic motion relative to the fixed-body frame.
If we consider a given operation \( \hat{R} \) of the MS group, it can be shown that

\[
\hat{R} = \hat{R}_{\text{rot}} \hat{R}_{\text{ve}} \hat{R}_{\text{spin}},
\]

(2.14)

where \( \hat{R}_{\text{rot}} \) transforms the rotational coordinates (Euler angles), \( \hat{R}_{\text{ve}} \) transforms the vibronic coordinates without change in the rotational coordinates and finally \( \hat{R}_{\text{ns}} \) exchanges the nuclei spin coordinates. The set of all operators \( \hat{R}_{\text{rot}} \) defined in this way forms the group \( K(mol) \) introduced in Subsection 2.1.1. It so happens that the set of operators \( \hat{R}_{\text{ve}} \) forms the point group of the rigid geometric figure representing the molecule at its equilibrium configuration. Moreover, the MS group and point group are isomorphic\(^7\). Therefore, one can use the point group when considering vibronic motions in the fixed body reference frame. This group is easier to apprehend and represent the different transformations of the MS group on the vibronic coordinates in a clear way. Finally, we stress that the point group is a group of symmetry of the vibronic Hamiltonian only, but not of the total Hamiltonian. On the other hand, the MS group is a symmetry group of the total Hamiltonian but is also the symmetry group of the vibronic Hamiltonian. Therefore one can use either group to study vibronic motion.

\(^7\)This is only true for non linear rigid molecules.
2.2 The general approach in molecular physics

2.2.1 Approximating the Schrödinger equation

Obtaining an exact solution of the multi-dimensional Schrödinger equation is impossible. A naive method to computationally solve this equation consists on spanning the space with a grid of close neighboring points $X_i$ and center a physical function $\phi_i(X)$ (generally a Gaussian) at each of these points. One can evaluate the coupling elements $\langle \phi_i | \hat{H} | \phi_j \rangle$ of the Hamiltonian $\hat{H}$ of the system for any set $\{i, j\}$ and diagonalize this matrix to find the eigenenergies and eigenfunctions of the problem. If this method works for low-dimensional problems, it is unfortunately not applicable in general since the matrices one deals with are too large to be handled by the most powerful computers. For this reason, one tries to approximate the exact solution as much as possible by separating the Hamiltonian in independent terms, which are expressed by different sets of coordinates and neglecting at first the qualitatively small interactions between the different motions.

2.2.1.1 The Born-Oppenheimer approximation:

The starting approximations in studying any molecular system is the Born-Oppenheimer (BO) approximation, which consists in neglecting at first the slow motion of the nuclei on the time scale of the motion of the electrons.
In order to uncouple the nuclei and electronic motions, one solves the following Schrödinger equation at clamped nuclei in the nuclei center of mass reference frame

\[ [\hat{T}_e + V(R_N, r_{elec}) - V_{nn}(R_N)] \phi_{elec}(R_N; r_{elec}) = V_{elec}(R_N) \phi_{elec}(R_N; r_{elec}). \] (2.15)

In the above expression, \( R_N \) and \( r_{elec} \) are the sets of coordinates related respectively to the nuclei and the electrons, \( V(R_N, r_{elec}) \) is the total electrostatic potential and we neglect the nuclei-nuclei repulsive electrostatic term \( V_{nn}(R_N) \) given by

\[ V_{nn}(R_N) = \sum_{i,j=1}^{N} \frac{C_i C_j}{R_{ij}}. \] (2.16)

In this expression, \( C_i \) represent the charge of the nuclei and \( R_{ij} \) the different internuclear distances. By solving this equation, one obtains electronic eigenfunctions \( \phi^a_{elec}(R_N; r_{elec}) \) parametrically dependent on the nuclei positions denoted \( R_N \). The index \( a \) refers to the different electronic states solutions of the Born-Oppenheimer equation with energy \( V^a_{elec}(R_N) \).

Then, one seeks for solutions of the form \( \phi_{rv}(R_N) \phi^a_{elec}(R_N; r_{elec}) \), where \( \phi_{rv} \) is a rotation-vibration wave function of the nuclei.

The approximation consists on neglecting the effect of the motion of the nuclei on the electronic wave function and is mathematically equivalent of assuming that

\[ \hat{T}_N[\phi_{rv}(R_N) \phi^a_{elec}(R_N; r_{elec})] = \phi^a_{elec}(R_N; r_{elec})[\hat{T}_N \phi_{rv}]. \] (2.17)
Here, the operator $\hat{T}_N$ is the nuclei kinetic operator in the nuclei center of mass

$$\hat{T}_N = -\frac{1}{2} \sum_{i=2}^{N} \frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_N} \sum_{i,j=2}^{N} \nabla_i \cdot \nabla_j.$$  \hspace{1cm} (2.18)

In this expression, $N$ is the number of nuclei, $m_i$ the mass of each nucleus and $M_N$ is the total mass of the nuclei. Finally, incorporating the Born-Oppenheimer solution in the Schrödinger equation, leads to the rotation-vibration equation

$$[\hat{T}_N + V_{\text{elec}}(R_N) + V_{nn}(R_N)]\phi_{rv}(R_N) = E_{rv}\phi_{rv}(R_N)$$  \hspace{1cm} (2.19)

It can be shown, as it is for instance nicely exposed in [27], that the BO approximation is a good approximation if the separation between adjacent electronic energies is large compared to the separation between rovibronic energies related to the same electronic state. This requirement is generally always fulfilled, since the energy splitting of adjacent electronic energies is usually around hundred times bigger than the energy splitting of adjacent rovibronic energies. There exist cases for which the BO approximation breaks down severely. We explain these cases in Subsection 2.2.2 and will study them in more detail in Chapters 3,4 and 5.

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2.2.1.2 The rigid-rotor and harmonic approximations:

Considering the complex form of the kinetic operator in (2.18), one usually applies a rigid rotor approximation to treat rigid-molecules. The latter approximation consists on separating the global motion of rotation of the molecule from the vibrations of the nuclei around their equilibrium positions.

We start by introducing the nuclei center of mass reference frame defined by a set of three axes ($xyz$) and construct a new reference frame that describes the general rotation of the system. It is still centered at the nuclei center of mass but has a new set of molecular fixed axes ($XYZ$). The transformation from the ($xyz$) to the ($XYZ$) system of axes is performed by the three Euler angles $\alpha$, $\beta$ and $\gamma$ (see [27, 21]). There are three degrees of freedom in choosing the orientation of the axes ($XYZ$) when spatial coordinates of the nuclei are given. Therefore, three equations are needed to find the values of the three Euler angles, as well as the displacements of the nuclei from their equilibrium positions in the rotating frame ($XYZ$). The choice of these equations has to be made in a way that the vibrating motion of the nuclei in the reference frame ($XYZ$) system is uncoupled as much as possible from the global rotational motion of the system. Roughly speaking, the best choice of reference frame axes ($XYZ$) is the one for which no rotation is induced by the vibration of the nuclei around their equilibrium position so that the vibrational angular momentum in the ($XYZ$) reference frame is zero (or at least made as small as possible). This requirement is fulfilled by the Eckart equations, obtained from the former assumption, and whose derivations and
forms are given in [21]. Finally the rigid-rotor approximation leads to a kinetic separation between a global rotation of the molecule considered at its equilibrium geometry, and the vibration\footnote{The displacements coordinates in the (XYZ) frame should not only fulfilled the nuclei center of mass condition, but the Eckart equations as well.} of the nuclei around their equilibrium position in the (XYZ) frame.

The obtained vibrational equation in the (XYZ) frame in the BO approximation is still rather difficult to treat due to the complexity of the electronic potential. Thus, one generally uses the familiar harmonic approximation to obtain the lowest vibrational energies and wave functions. In this approximation, one constructs $3N - 6$ normal coordinates $Q_i$, superpositions of the nuclei displacements, which separate simultaneously the kinetic operator of displacements $\hat{T}_{vib}$ and the electronic potential $\hat{V}_{elec}$ in independent terms in a way that

$$\hat{T}_{vib} = \frac{1}{2} \sum_{i=1}^{3N-6} \left( \frac{d\hat{Q}_i}{dt} \right)^2; \quad \hat{V}_{elec} = \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i \hat{Q}_i^2.$$ (2.20)

As a result of this approximation, the vibrational equation can actually be analytically solved and one can find approximate vibrational energies and corresponding wave functions.

The final form of the Hamiltonian of the system in the framework of the BO approximation is expressed by decomposing the full kinetic operator $\hat{T}_N$ of the system in terms of the rovibronic angular momentum operators along the molecule fixed axes, the vibrational angular momenta and the normal coordinates and momenta $\hat{P}_i$ and $\hat{Q}_i$. The final expression was derived by Watson (1968) and its form is given in [21]. The full rotation-vibration Hamiltonian of the system can be separated as
\[ \hat{H}_{\text{re}} = \frac{1}{2} \sum_{\alpha=x,y,z} \mu_{\alpha} \hat{J}_{\alpha}^2 + \frac{1}{2} \sum_{i=1}^{3N-6} (\hat{P}_i^2 + \lambda_i \hat{Q}_i^2) + \hat{T}_{\text{cent}} + \hat{T}_{\text{Cor}} + \hat{V}_{\text{anh}}, \tag{2.21} \]

where the operator \( \hat{T}_{\text{cent}} \) is responsible for centrifugal couplings, \( \hat{T}_{\text{Cor}} \) for Coriolis couplings and finally \( \hat{V}_{\text{anh}} \) for anharmonic couplings. In the framework of the approximations discusses above, the coupling operators \( \hat{T}_{\text{cent}}, \hat{T}_{\text{Cor}} \) and \( \hat{V}_{\text{anh}} \) are discarded at first and treated as perturbation\(^9\) to obtain more accurate solutions. We will not need them in the later development since the main factor of coupling in the indirect DR mechanism comes from break down of the BO approximation.

### 2.2.2 Non Born-Oppenheimer interactions and symmetries

The Born-Oppenheimer approximation is valid if the splitting between vibrational levels of the molecule is significantly smaller than the splitting between electronic energies. This approximation is accurate in most cases since electronic energy splittings are typically about hundred times bigger than vibrational splittings. Nevertheless, it may happen that the approximation can break down severely. In the thesis, there are two main causes for the breakdown of the BO approximation.

First, Rydberg electron energies are extremely close to each other (the energy splitting is proportional to \( 1/n^3 \)) below the ionization threshold, so that the spacing between electronic energy becomes indeed smaller than the spacing between vibrational energies. The

\(^9\)The exact expression of these coupling operators is given in [21].
latter break down of the BO approximation is responsible for the exchange energy between
the electron an the ion, which results in electron capturing in Rydberg states associated
with vibrationally excited ionic states. The latter point is made clear when we present the
vibrational frame transformation in Section 2.4.

Second, the symmetry properties of the molecular ions HCO$^+$, H$_3^+$ and H$_3$O$^+$ allows de-
genenerate electronic states to exist at their their equilibrium geometry. Thus, the electron
energies lie close to each other, even at asymmetric displaced geometry, so that the BO
approximation is not valid. For these particular cases, the breakdown of the BO approxi-
mation are named Renner-Teller for linear ions and Jahn-Teller effect for highly symmetric
non linear ions. We will describe the model to treat such a case in Chapters 3 and 5.

Let us no describe briefly the different forms of the non Born-Oppenheimer couplings
one can sort out from the vibronic Hamiltonian and their vanishing or non-vanishing nature
using symmetry consideration.

The couplings can be classify as follow:

\[ \hat{T}_{vib} = \frac{1}{2} \sum_r \hat{p}_r^2, \]  \hspace{1cm} (2.22)

\[ \hat{T}_{ev} = \frac{1}{2} \sum_{\alpha,\beta} \mu_{\alpha,\beta} (\hat{p}_\alpha \hat{L}_\beta + \hat{L}_\alpha \hat{p}_\beta), \]  \hspace{1cm} (2.23)

\[ \hat{T}_{er} = -\frac{1}{2} \sum_{\alpha,\beta} \mu_{\alpha,\beta} (\hat{J}_\alpha \hat{L}_\beta + \hat{L}_\alpha \hat{J}_\beta), \]  \hspace{1cm} (2.24)

\[ \hat{T}_{ee} = \frac{1}{2} \sum_{\alpha,\beta} \mu_{\alpha,\beta} (\hat{L}_\alpha \hat{L}_\beta). \]  \hspace{1cm} (2.25)
In the expressions above, the index $r$ refers to the different normal coordinates, $\hat{J}$ is the rovibronic angular momentum and $\hat{L}$ is the molecule fixed electronic angular momentum. The indexes $\alpha$ and $\beta$ refer to the different axis of the molecular frame. The operator $\hat{p}$ is the vibrational angular momentum operator and the matrix $\mu$ is almost the inverse of the instantaneous inertia matrix.

Symmetry considerations help us to find the non vanishing couplings. We will use such considerations when we treat the Renner-Teller and Jahn-Teller effects. From now, let us for instance consider the operator $^{10}\hat{T}_{\text{vib}}$ in (2.22). It can be shown that the coupling of two vibronic states $\phi_e\phi_{\text{vib}}$ and $\phi_{e'}\phi_{\text{vib}}'$ through $\hat{T}_{\text{vib}}$ is approximately proportional to the term

$$Y_{rr}^{ee'} = \left\langle \phi_{e'} \left| \frac{1}{2} \sum_r \hat{P}_r^2 \right| \phi_e \right\rangle. \quad (2.26)$$

The term above is non vanishing only if the symmetry of the normal coordinate $Q_r$ connects the symmetry of the electronic functions in the MS group. In the case of $\text{H}_3^+$, two electronic states of $E$ irreducible representations in the $D_{3h}(M)$ point group can be connected by the degenerate vibrational coordinate of $E$ symmetry. Therefore, the Jahn-teller effect can occur through vibronic couplings between the degenerate electronic states and the degenerate normal coordinates. This point will be discussed in detail in Chapter 5.

$^{10}$This operator is responsible for the non Born-Oppenheimer Jahn-Teller coupling in the DR of $\text{H}_3^+$ and $\text{H}_3\text{O}^+$.
2.3 Overview of Multi-channel Quantum Defect Theory (MQDT)

2.3.1 Rydberg electron

Let us consider a given molecular ion $M^+$ and an external electron in a highly excited state. At large separation distances from the ionic core, the long range attractive Coulomb potential of the ion shields any other residual interactions, which only survive at small distances (chemical region) where the exact internal structure of the ion becomes effective. Beyond a radius $r_0$, the electron merely moves in a pure Coulomb potential of the form

$$V_C(r) = I - \frac{Z}{r} + \frac{l(l+1)}{2r^2},$$  \hspace{1cm} (2.27)

where $I$ is the continuum threshold, $r$ is the electron radius and $l$ its angular momentum. The well known energy eigenvalues for a pure Coulomb field are

$$E_n = I - \frac{1}{2n^2}, \hspace{0.5cm} n = l + 1, l + 2, ...$$  \hspace{1cm} (2.28)

If the potential $V(r)$ differs from the pure Coulomb form only through a short-range\textsuperscript{11} potential $V_s(r)$

$$V(r) = V_C(r) + V_s(r),$$  \hspace{1cm} (2.29)

\textsuperscript{11}The potential $V_s(r)$ should fall off faster than $1/r^2$ as $r \to \infty$ for the general results of QDT to be valid.
One can show, for example using the quantization condition (WKB) or as shown in the next subsection, that the eigenvalues energy take the following form

\[ E_n = I - \frac{1}{2\nu^2} = I - \frac{1}{2(n - \mu_{n,l})^2}, \]  

(2.30)

where the quantum defect \( \mu_{n,l} \) depends only weakly on the principal quantum number \( n \) for large values of \( n \). The number \( \nu = n - \mu_{n,l} \) is called the effective quantum number and the energies (2.30) form a Rydberg series. This series becomes extremely dense\(^{12}\) below the ionization threshold, where the density of electronic states is proportional to \( n^3 \).

Rydberg states are involved in a wide range of areas and play an important role in the indirect recombination mechanism (Section 2.5) of molecular ions with low energy electrons. One of the main features of Rydberg electrons undergoing a scattering process with a molecular ion resides in the so-called Seaton theorem. If we consider a low energy incident electron, the asymptotic phase shift \( \delta(E) \) of its radial wave function is related to the quantum defect \( \mu_n \) by

\[ \lim_{n \to \infty} \mu_n = \mu(E = I) = \frac{1}{\pi} \lim_{E \to I} \delta(E). \]  

(2.31)

Therefore, one can actually extract the scattering phase shift beyond threshold from the quantum defect. This important result is systematically used throughout our study of DR. Indeed, we use \textit{ab initio} calculations of highly excited\(^{13}\) Rydberg states and sort out the

\(^{12}\)The technology of high resolution laser spectroscopy has made possible to observe very highly excited states, with lines up to \( n = 300 \). At such high effective quantum numbers, the spacing between energy levels is less than \( 10^{-8} \) a.u and the size of the Rydberg molecule about \( 10^5 \) Bohr radii.

\(^{13}\)Usually one calculates the energy of Rydberg state up to principal quantum number \( n = 4 \) or \( n = 5 \).
quantum defect. From the results of quantum defect theory (QDT), we can use the parameter \( \mu \) to represent the electronic state of any highly excited Rydberg states, as well as low energy electron continuum states. We now describe in more detail the multi-channel quantum defect theory (MQDT) and start by considering the one channel case.

2.3.2 The one channel approach

A Rydberg electron in the field of an ionic core with unit charge can be assumed to be moving in a purely Coulomb potential (2.27) with \( Z = 1 \), over a region of configuration space \( r > r_0 \). Above the radius \( r_0 \), its wave function can always be written as a superposition of two independent linear functions \( (f_l, g_l) \) (rescaled by \( r \)) of the second-order radial Schrödinger equation. These functions are usually chosen by convenience such that:

(1) \( f_l \rightarrow 0 \) as \( r \rightarrow 0 \)

(2) \( f_l \rightarrow \sqrt{\frac{2}{\pi k}} \sin(kr + \frac{1}{k} \ln r + \eta) \) as \( r \rightarrow \infty \), \( \epsilon = \frac{1}{2} k^2 \)

(3) \( g_l \rightarrow \sqrt{\frac{2}{\pi k}} \cos(kr + \frac{1}{k} \ln r + \eta) \) as \( r \rightarrow \infty \), \( \epsilon = \frac{1}{2} k^2 \)

(4) \( (f_l, g_l) \) for \( \epsilon < 0 \) join smoothly the positive energy solutions.

Condition (1) defines the regular solution, which is the physical solution in a purely Coulomb field (without short range interactions). This requirement ensures that the wave function for large \( l \) will tend to \( f_l \) without any superposition of \( g_l \). Conditions (3) and (4) ensure that
both functions are energy normalized and that $g_l$ lags $90^\circ$ in phase with $f_l$. One notices the logarithm phase accumulation characteristic of Coulomb field and the long-range phase shift $\eta$ given by

$$\eta = \frac{1}{k} \ln(2k) + \arg \left( l + 1 - \frac{i}{k} \right) - \frac{1}{2} l \pi. \quad (2.32)$$

Finally, condition (4) ensures that any rapid energy variation comes from the actual structure of the scattering process and not from the choice of the reference function.

At energies $\epsilon < 0$, we define $\kappa = (-2\epsilon)^{\frac{1}{2}} = \frac{1}{\nu}$, where $\nu$ is the effective quantum number.

The asymptotic form of the wave functions beyond the classical turning point is

$$f_{\epsilon,l}(r) \rightarrow \sqrt{\frac{1}{\pi k}} \left( \sin \beta D^{-1} r^{-\nu} e^{\kappa r} - \cos \beta D r^\nu e^{-\kappa r} \right), \quad (2.33)$$

$$g_{\epsilon,l}(r) \rightarrow \sqrt{\frac{1}{\pi k}} \left( \cos \beta D^{-1} r^{-\nu} e^{\kappa r} + \sin \beta D r^\nu e^{-\kappa r} \right). \quad (2.34)$$

In (2.33) and (2.34), the coefficients $\beta$ and $D$ are constants depending on $l$ and $\epsilon$. The constant $\beta = \pi (\nu - l)$ measures the number of half wavelengths in the radial solution between $r = 0$ and $r \rightarrow \infty$. The general solution $F_\epsilon(r)$ of the Schrödinger equation in the region $r > r_0$ is a superposition of (2.33) and (2.34) such that

$$F_\epsilon(r) = N_l [f_{\epsilon,l}(r) \cos \pi \mu_l - g_{\epsilon,l}(r) \sin \pi \mu_l], \quad (2.35)$$

where $N_l$ is a coefficient and $\pi \mu_l$ a phase. The fact that $F_\epsilon(r)$, $f_{\epsilon,l}(r)$ and $g_{\epsilon,l}(r)$ are slowing varying function of the energy near threshold implies that $\mu_l$ is also slowly varying. If we
report the expressions (2.33) and (2.34) in (2.35), we finally obtain

\[ F_i(r) = N_i \sqrt{\frac{1}{\pi k}} \left( \sin(\beta + \pi \mu_l) D^{-1} r^{-\nu} e^{\kappa r} - \cos(\beta + \pi \mu_l) D r^{\nu} e^{-\kappa r} \right) \quad (2.36) \]

The bound state solutions forces (2.36) to be exponentially decreasing as \( r \to \infty \) so that it reads simply

\[ \sin(\beta + \pi \mu_l) = 0, \quad (2.37) \]

or \( \nu - l + \mu_l = n_r \), with \( n_r \) an integer. If we define the principal quantum number \( n = n_r + l \),
the bound states energies are

\[ \epsilon_{n,l} = -\frac{1}{2(n - \mu_l)^2}. \quad (2.38) \]

The factor \( \pi \mu_l \) represent the defect from the pure coulomb potential due to the addition of the short-range potential \( V_s(r) \). For large \( l \), the quantum defects tends to zero since the centrifugal barrier is too high for the radial wave function to penetrate the region where \( V_s(r) \) is effective. Of course \( \mu_l = 0 \) for a pure Coulomb potential and we find the energies of the hydrogen atom. Let us now apply the same procedure in a multi-channel representation.

2.3.3 The multichannel approach

The previous approach assumed that the system was confined to a single channel, so that just one possible two body breakup mode was possible. Let us now consider the general
case, where the ionic core states are described by a discrete set of functions $\Phi_i(\omega)$, where $\omega$ include all ionic coordinates as well as the angular part of the external electron. The index $i$ characterizes different vibrational states of the ion with the external electron in different angular momentum states. We now consider a given molecular Hamiltonian $\hat{H}$ and seek for solutions of the Schrödinger equation of the form

$$\Psi_\beta = \frac{1}{r} \sum_i \Phi_i(\omega) F_{i\beta}(r). \quad (2.39)$$

Equation (2.39) is not antisymmetrized since exchanges at $r > r_0$ can be neglected. The index $\beta$ refers to the number of independent solutions of the equation. If we have $N$ channels, the second-order Schrödinger will have $N$ independent solutions since the condition $F_{i,\beta}(0) = 0$ for any $i$ is required. The Schrödinger equation is written

$$F''_{i\beta} + 2 \sum_i [\epsilon_i - V_{ij}(r)] F_{i\beta} = 0, \quad (2.40)$$

where $\epsilon_i = E - E_i$ is the asymptotic electron energy in channel $i$ and the operator $V_{ij} = \langle \Phi_i | \hat{H} | \Phi_j \rangle$, where the integration is performed over all coordinates $\omega$. Until this point, the procedure does not differ from the usual close-coupling treatment. The main difference occurs in the next step, where MQDT only takes account of the asymptotic form of the potentials $V_{ij}(r)$ and discard any non diagonal contribution falling off faster than $1/r^2$ at infinite electronic radii. Taking this point into consideration and using a Legendre expansion

\[14\]This procedure describes the regular MQDT approach. In Chapter 4 we use a generalization of the MQDT formalism, which takes into account non diagonal potential falling off as $1/r^2$ as $r \to \infty$.  

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of the different distances between the external electron and the particles composing the ion, one can show that

\[ V_{ij}(r) \rightarrow \left( \frac{l_i(l_i + 1)}{r^2} - \frac{1}{r} \right) \delta_{ij} \]  

(2.41)

The solutions of the Schrödinger in (2.40) can thus be expressed using the regular (2.33) and irregular (2.34) functions for the one-channel equation at the appropriate asymptotic energy. The \( i \) component of the \( \beta \) solution is then simply written as

\[ F_{i\beta}(r) = f_i(r)I_{i\beta} - g_i(r)J_{i\beta}, \]

(2.42)

where \( I_{i\beta} \) and \( J_{i\beta} \) are matrices. It is possible to show that one can construct new independent functions superpositions of \( F_{i\beta}(r) \) with the following convenient form

\[ M_{ii'}(r) = f_i(r)\delta_{ii'} - g_i(r)K_{ii'}. \]

(2.43)

The latter form defined the reactance matrix \( \hat{K} \) used in Chapters 3 and 4 to study DR of HCO\(^+\). The form in (2.43) has the advantage to allow working with real quantities. On the other hand, the reactance matrix also has a few disadvantages and its relation to physical quantities is not always clear. Therefore, one can prefer to work with the familiar scattering matrix \( \hat{S} \). The scattering matrix relates incoming and outgoing radial wave functions with
asymptotic behavior

\[
f^\pm(r) \rightarrow \begin{cases} 
(\pi k)^{-\frac{1}{2}}r^{\pm i/kc^{\pm ikr^\pm i\eta}}, & \epsilon = k^2/2 > 0; \\
(2\pi k)^{-\frac{1}{2}}e^{\pm i\beta}(D^{-1}r^{-\nu}e^{\kappa r} \mp Dr^\nu e^{-\kappa r}), & \epsilon = -\kappa^2/2 < 0.
\end{cases}
\]

The general form of the solutions expressed using the \( \hat{S} \) matrix is

\[
M_{ii'}(r) = \frac{1}{i\sqrt{2}}f_i^+(r)\delta_{ii'} - \frac{1}{i\sqrt{2}}f_i^-(r)S^+_{ii'}.
\]

The scattering matrix \( \hat{S} \) is related to the reactance matrix \( \hat{K} \) by the following relation

\[
\hat{S} = \frac{1 + i\hat{K}}{1 - i\hat{K}}.
\]

Until now, we have not discussed the physical significance of the solutions. It is clear that if the total energy of the system \( E > E_0 \), where \( E_0 \) is the smallest channel ionic energy, there will exist solutions for any given energy \( E \) since at least one channel is always open for the electron. On the other hand, if \( E < E_0 \), the system is bound and only a set of discrete energies \( E_n \) will be allowed. To extract the physical solutions, one needs to separate three cases.

**All channels are open:** In such a case, the system has \( N \) independent solutions given either by (2.43) or by (2.45). All these solutions are physically acceptable.
Some channels are closed: We assume that we have $N_o$ open channels and $N_c$ closed channels ($N = N_o + N_c$). The solutions corresponding to closed channels have to vanish asymptotically to be physically acceptable. Thus, the Schrödinger equation has only $N_o$ independent solutions. In order to express the physical solutions, one partitions the scattering matrix in blocks:

$$\hat{S}^+ = \begin{pmatrix} S^{+}_{oo} & S^{+}_{oc} \\ S^{+}_{co} & S^{+}_{cc} \end{pmatrix} \quad (2.47)$$

The different blocks refer to the open or closed nature of the incoming and outgoing channels. $S^{+}_{oo}$ is a $N_o \times N_o$ matrix, $S^{+}_{oc}$ is $N_o \times N_c$, $S^{+}_{co}$ is $N_c \times N_o$ and finally $S^{+}_{cc}$ is $N_c \times N_c$. Using superpositions of the different independent functions in (2.45) (different $i'$), one constructs $N_o$ independent solutions for which the total coefficient in front of the exponentially increasing functions (see equation (2.44)) vanishes for each closed channel. The final asymptotic form of the physical solution in the open channels is

$$M^{(-)}_{i'i}(r) \rightarrow (2\pi k_i)^{-\frac{1}{2}}(e^{ik_ir}\delta_{ii'} - e^{-ik_ir}S^{+\text{phys}}_{ii'}), \quad (2.48)$$

with the form of the physical scattering matrix given by

$$\tilde{S}^{+\text{phys}} = e^{-i\eta} [S^{+}_{oo} - S^{+}_{oc}(S^{+}_{cc} - e^{2i\beta})^{-1}S^{+}_{co}] e^{-i\eta}. \quad (2.49)$$

In (2.49), $e^{-i\eta}$ and $e^{2i\beta}$ are diagonal matrices with corresponding value of $\eta$ and $\beta$ for each channel. The solutions in the closed channels can be expressed via the physical scattering
matrix $S^{\text{phys}}$ and with the aid of Whittacker functions (decreasing exponential function). The different resonances can be obtained form studying the behavior of the asymptotic phase shift in the open channels.

**All channels are closed:** If all channels are closed, the system of equations will have physical solutions only at certain energies verifying

$$\det|S^+_{cc} - e^{2i\beta}| = 0. \quad (2.50)$$

This is the usual way one relates the form of the scattering matrix to *ab initio* calculations. Finally, we stress that results using the reactance matrix are similar in form than the results above.

### 2.4 The concept of vibrational frame transformation in DR

We discuss at present the important concept of frame transformation, introduced by Fano in 1970 [35, 24] and which is extensively used to study electron-molecule collisions at low energies. This approach is suited for studying ion-electron collisions as we outline in the following development. In order to simplify the discussion, we present the concept of frame transformation on a diatomic system using the MQDT formalism and consider solely electronic capture by vibrational excitation. In other word, we disregard any capture by rotational excitation. Implementation of rotational excitation in the MQDT formalism is actually not as
straightforward as it was initially thought and its effect could be quite important, especially when the indirect DR process is the dominant one. Let us consider at first the electron in the region $r < r_o$, where other interactions than Coulomb are present (chemical zone). Due to the strong long range Coulomb attraction, the electron has been considerably accelerated before entering in this region and its motion is thus faster than the vibrational motion of the nuclei. For this reason, the usual Born-Oppenheimer approximation is well suited to describe the physics at this short distance. The determination of the relative velocity of the electron in the external region usually shows that the BO approximation is valid beyond the boundary $r_o$ in a region typically referred as the inner part of the external region and named Region A. Beyond the electronic radius $r_o$, the electronic radial functions can be expressed using the regular and irregular Coulomb functions, with a phase shift $\pi \mu(R)$ introduced by the short range interactions and parametrically dependent on the vibrational coordinate $R$. Finally, the exchange interactions can be disregarded when $r > r_o$ and we can omit anti-symmetrization of the wave function. Using the latter considerations, the total ionization channel wave function in the inner part of the external zone is

$$\Psi^A_v = \chi_v(R) \Phi_{\text{core}}(q^+, \Omega, R)[f_l(\nu, r) - \tan(\pi \mu(R)) g_l(\nu, r)]$$

(2.51)

In this expression, $\Phi_{\text{core}}(q^+, \Omega, R)$ is the ionic core wave function, where $q^+$ denote all the core electronic coordinates and $\Omega$ the angular part of the external electron, $\chi_v(R)$ is a bound molecular vibrational function in a state $v$ (we do not consider dissociative states
here), $f_l(\nu, r)$ and $g_l(\nu, r)$ are respectively the regular and irregular solutions of the radial Schrödinger equation in a Coulomb potential for a partial wave $l$. We do not consider $l$ mixing for now but we treat such a case when we include the dipole moment of HCO$^+$ in Chapter 5. Furthermore, non-adiabatic couplings between different electronic states are not considered at all for now, so that equation (2.51) represents a one channel case and $\nu = (-2\epsilon)^{-1/2}$ is the effective quantum number. The quantum defect dependent term in (2.51) can be recognized as the standard short range reactance coefficient in the one channel case such that $K(R) = \tan(\pi\mu(R))$. The wave function (2.51) depends on the electronic energy $\epsilon$, assumed to be small in order for QDT to be valid. In the inner part of the external region $|\epsilon| \ll |V(r)|$ and therefore the Coulomb functions $f_l(\nu, r)$ and $g_l(\nu, r)$ are weakly dependent on energy and converge towards the threshold wave function as $\epsilon \to 0$ (if we apply an energy normalization in the pseudo-continuum below threshold). Thus, we can assume that $\Psi_i^A$ is actually independent on energy in Region A. Finally, as the low energetic electron is generally captured in a high Rydberg state, an adiabatic molecular potential energy curve looks very similar to its parent ionic potential, and we can consider with a good accuracy that $\chi(\nu)(R) = \chi_{\nu^+}(R)$.

Let us now focus on the outer part of the external region, named Region B, and defined for $r \to \infty$. In this region, vibronic couplings vanish so that the total energy of the system is well separated in an electronic and vibrational part. In region B, one of the independent total wave function, expressed in term of the $\hat{K}$ matrix and written as a superposition of the
different $N$ channels functions is

$$
\Psi_{v_0^+} = \sum_{v^+} \chi_{v^+}(R) \Phi_{\text{core}}(q^+, \Omega, R) [f_l(\nu_{v^+}, r) \delta_{\nu_{v^+}, v^+} - K_{\nu_{v^+}, v^+} g_l(\nu_{v^+}, r)].
$$

(2.52)

In the above expression, the effective quantum numbers are now dependent on the channel such that $\nu_{v^+} = 1/\sqrt{2(E - E_{v^+})}$, where $E_{v^+}$ is the ionic vibrational energy in state $v^+$ and $E$ is the total energy of the system. The form (2.52) is valid in the entire region where $r > r_\text{o}$, since it only requires the separation of the energy in an ionic and an electronic part. This means there is an overlap region where both expressions (2.52) and (2.51) are valid. Thus, there is a unitary transformation from one set of functions to another. For instance, we can expand the function (2.52) with the help of (2.51)

$$
\Psi_{v_0^+} = \sum_{v^+} a_{v^+} \Psi_{v^+}^{A}.
$$

(2.53)

Now, considering the expansion over the regular Coulomb functions on both sides of this equation using (2.52) and (2.51) and still assuming that these functions are nearly identical for different channels in this short distance region, it is straightforward to show that $a_{v^+} = \delta_{v_{v_0^+}, v^+}$. Considering this fact and treating the coefficient of the irregular Coulomb function on both sides, we obtain

$$
K_{v_{v_0^+}, v^+} \chi_{v^+}(R) = \tan(\pi \mu(R)) \chi_{v_{v_0^+}}(R).
$$

(2.54)
By multiplying both sides of the equation by $\chi^*_{v^+}(R)$ and integrating over $R$, we finally get the desired result that

$$K_{v_0^+,v^+} = \int \chi^*_{v^+}(R) \tan(\pi \mu(R)) \chi_{v_0^+}(R) dR. \quad (2.55)$$

Another straightforward way to obtain this result is to consider that the different assumptions are equivalent to state that $\langle R' | \tilde{K} | R \rangle = K(R) \delta(R' - R)$. In a configuration at clamped nuclei, the fast electron does not affect the positions of the nuclei (equivalent that BO). As we also assumed that the different Coulomb functions are nearly equivalent, we can apply a simple change of basis to the $\hat{K}$ matrix to find the exact same result

$$K_{v_0^+,v^+} = \langle v^+ | \tilde{K} | v_0^+ \rangle = \int \int \langle v^+ | R \rangle \langle R | \tilde{K} | R' \rangle \langle R' | v_0^+ \rangle dR dR'$$

$$K_{v_0^+,v^+} = \int \langle v^+ | R \rangle K(R) \langle R | v_0^+ \rangle dR. \quad (2.56)$$

To conclude this section, we point out that the frame transformation is suited in electron-ion collisions due to the pertinence of the applied approximations. In more general case, its usefulness comes most often from the quality of the obtained results.
2.5 Direct and indirect processes of dissociative recombination

2.5.1 Direct process

The direct DR mechanism occurs through the electron capturing into a doubly excited dissociative resonant state. The direct DR process for a diatomic ion \(\text{AB}^+\) is schematically presented in Fig 2.1, where the ground ionic potential curve and the modulus of the ground ionic wave function are plotted as a function of the inter-nuclear distance \(R\). The resonant curve \(\text{AB}^{**}\) has a dissociative character and crosses the ground ionic potential close to its minimum value. \(E_{\text{tot}}\) is the total energy of the system and \(E_c\) the entrance kinetic energy of the incident electron. It can be shown that the direct DR cross section is given approximately\(^{15}\) by

\[
\sigma_d \sim \frac{\pi}{k^2} \left| \int \chi_{v_o}(R)V_{el}(R)F(R)dR \right|^2
\]  

(2.57)

In the above expression, \(\chi_{v_o}(R)\) is the wave function of the initial\(^{16}\) vibrational level of the molecular ion, \(V_{el}(R)\) is the matrix element for the electron capture (autoionization), and \(F(R)\) is the regular solution of the Schrödinger equation in the final state potential \(V^*(R)\) (referred to \(\text{AB}^{**}\) state in Fig 2.1) at energy \(E_{\text{tot}} = k^2/2M\). Therefore, the direct dissociation is possible only if the overlapping\(^{17}\) between \(F(R)\) and \(\chi_{v_o}(R)\) is not too small. Usually, for a given total energy of the system \(E_{\text{tot}}\), the point \(R_o\) (Franck-Condon point) where \(V^*(R)\)

---

\(^{15}\)This expression is derived using the Fermi golden rule. Therefore, it is a first order approximation.

\(^{16}\)Usually the ground ionic vibrational state.

\(^{17}\)The overlapping factor is referred as the Franck-Condon factor, in a same way as defined for optical vibrational transitions.
crosses $E_{\text{tot}}$ should be situated in a region for which $\chi_{v_0}(R_0)$ is not negligible for the process to be possible at total energy $E_{\text{tot}}$. This means that direct DR of low incident electron energy is possible only if the excited resonant potential crosses the ionic ground potential close to the equilibrium position of the ion.

![Figure 2.1: Representation of a favorable situation for direct DR. The resonant state $AB^{**}$ crosses the ground ionic potential energy $AB^+$ close to its minimum, where the ground ionic function has significant values. The energies $E_{\text{tot}}$ and $E_c$ are the entrance electron kinetic energy and the total energy of the system, respectively.](image)

For closed shell ions like HCO$^+$, H$_3^+$ or H$_3$O$^+$, the doubly excited states generally cross the ionic ground potential far from its equilibrium, so that direct dissociation is indeed small. Fig 2.2 represents such a case, where the overlapping at low entrance kinetic energy of the electron is negligible.

---

\(^{18}\)This is understood as the excitation energy of an electron in a closed shell molecule is usually large.
Figure 2.2: Representation of an unfavorable situation for direct DR, where the overlapping region is negligible.

Another indirect process is still possible via capture in excited Rydberg state, as shown in Fig 2.3. In this figure, we draw the first excited vibrational ionic energy as well as the corresponding Rydberg series associated with this vibrational excited state. If the energy $E_{\text{tot}}$ matches the Rydberg resonance, the electron is captured. This resonant state lies in the electronic continuum such that the electron should be autoionized if no predissociation occurs. We discuss briefly the capture and predissociation paths in the next subsection.
Figure 2.3: Representation of the indirect process via electron capture in Rydberg states associated with excited ionic vibrational states.

2.5.2 Indirect process and predissociation

As explained, indirect process occurs via electron capture in Rydberg states. When captured, the electron can either autoionized or the system can dissociate through a path depicted in Fig 2.4. At the small arrow, a vibrationally excited resonant Rydberg state is formed. This Rydberg state can subsequently predissociate by a doubly excited valence state (lower $AB^{**}$ potential curve). Also, the elongation of the molecular bond $R$ in the vibrationally excited Rydberg state may open a predissociation pathway through a doubly excited state (upper $AB^{**}$ curve) that would otherwise be closed for direct dissociation.
We discussed example of indirect process for a diatomic molecule to simplify the ideas. In our DR study, we deal with the triatomic molecular ion HCO$^+$. In this case, we still choose a dissociative coordinate and quantize all other degrees of freedom of the ion. In this way, we can reproduce the method applied for diatomics, except that we have now several excited ionic curves corresponding to quanta of energy associated with the other degrees of freedom. The Rydberg curves associated with these excited quanta of vibration can actually
have a dissociative nature so that the electron can be captured directly\textsuperscript{19} in a dissociative Rydberg state. We can use the form of equation (2.57) to calculate such capture process.

\textsuperscript{19}Although this capture is direct in nature, one usually reserves the denomination direct DR process for capture in doubly excited electronic states of the molecules, so that direct capture in dissociative vibrationally excited Rydberg states are still referred as being part of the indirect process.
CHAPTER 3
DISSOCIATIVE RECOMBINATION OF LINEAR HCO$^+$
MOLECULAR ION

3.1 Past and present studies on the DR of HCO$^+$

3.1.1 Background and history

The HCO$^+$ ion was discovered more than a century ago and represents the first ion observed in interstellar space via microwave spectroscopy [20]. It was classified as unidentified element at the time of discovery. Later Klemperer [73] suggested the linear HCO$^+$ ion as a candidate, which was later confirmed by experiments [135]. Since then, HCO$^+$ molecular ion has been shown to be of considerable importance in astrochemistry [52], in combustion [57], as well as in planetary atmosphere science [82]. In space, the HCO$^+$ ion can be formed by several possible associations such as H$_2$ + CO$^+$ or CH + O and also H$_3^+$ + CO [44, 93] and depleted by DR. Dissociative recombination of molecular ions like HCO$^+$ plays an important role in the chemistry of interstellar clouds and therefore allows astronomers to probe remotely various characteristics of the interstellar dust.
These last two decades, HCO\(^+\) and other small polyatomic ions have been extensively studied theoretically: their electronic structure, potential energy surfaces and equilibrium geometry have been systematically investigated [136, 122]. The spectroscopy of neutral HCO in the energy range relevant to these DR studies has been extensively mapped out by Grant and coworkers [32]. Different types of laboratory experiments have been performed in order to study DR of HCO\(^+\): afterglow plasma, merged-beam and storage ring experiments [44, 43, 3, 89, 4, 114]. Unfortunately, there is at present no consensus among different experimental measurements of the actual DR rate coefficient, as they can differ by up to a factor of ten [89, 4], as shown in Fig. 1.6. Possible explanations for these discrepancies have already been proposed, we shall discuss them in Chapter 8.

Figure 3.1: Taken from [87]. Energies of the doubly excited resonant states \( ^2\Sigma^+ \) (left) and \( ^2\Pi \) (right) of HCO in function of the dissociative distance C-H. From these graphs, it can confidently be asserted, that direct dissociative recombination via one of these resonant states should be negligible, the resonant curves crossing the ground ionic potential far from its minimum.
In 1985, Kraemer and Hazi started the first study on the process of HCO\(^+\) recombination [81]. They found that the lowest dissociating neutral resonant state crosses the ionic ground state so far from its minimum, that it should not be accessible for direct DR with low energetic electrons. The states in consideration were the first excited \(2\Sigma\) state of HCO, with asymptotic character H\((^2S)\)+CO\((a^3\Sigma^+)\), and the first excited \(2\Pi\) state associated asymptotically to the channel H\((^2S)\)+CO\((a^3\Pi)\). Kraemer and Hazi found that these states intersected the ionic ground state about 1.5eV above the minimum of the HCO\(^+\) potential energy. From a laboratory experiment by Adams and coworkers in 1991 [108], it was demonstrated that DR in HCO\(^+\) proceeds mainly into the H+CO channel. This afterglow plasma study revealed that at 300K (1) the OH is not formed, although the channel is exothermic by 0.75eV, (2) the CO\((a^3\Pi)\) is a detected product\(^1\), leading to the conclusion that the \(2\Pi\) state dissociating to H\((^2S)\)+CO\((a^3\Pi)\) should play a role [2]. Another recent afterglow plasma experiment [116] confirmed the conclusions of Adams, as they observed the long lived electronically excited CO\((a^3\Pi)\) via band intensities. They also demonstrated that the formation of CO\((a^3\Sigma^+)\) was rather weak through DR of HCO\(^+\), but quite strong by DR of HOC\(^+\) ion.

The fact that the measured experimental value of the DR rate coefficient of HCO\(^+\) was rather large, and that CO\((a^3\Pi)\) was actually observed, seemed to be in conflict with the conclusions from Kraemer and Hazi. Bates [15] argued that the conclusions of Kramer and Hazi were indeed correct. If the direct process, as calculated using their curves, should be quite small (about 1.7\(\times\)10\(^{-11}\) cm\(^3\)/s\(^{-1}\)), a multi-step mechanism by capture in excited Ryd-\(^1\)On the other hand, this study was not able to determine if the CO\((a^3\Sigma^+)\) was also formed, as their spectroscopic technique was not capable of measuring emission from this state.
berg states, with subsequent cascade to lower \( n \) and higher molecular vibration, could lead to the dissociation of the molecule. In 1997, a merged-beam study by LePadellec et al. [89], supported by extensive quantum mechanical calculations by Talbi and coworkers, contradicted the results of Kraemer and Hazi. In their study, it was argued that Kraemer and Hazi only used excited valence states of HCO, and no Rydberg mixing in the corresponding wave function was observed. They proposed another approach to calculate the resonant states at linear geometry, using the configuration-interaction (CI) method with projected localized orbitals. Applying a diabatization procedure, they found a quasidiabatic potential that crosses the ionic ground potential near its minimum, and therefore arguing that for electronic energy higher than 0.3eV, a dissociative channel for direct dissociation opened. Their results revealed to be in contradiction with a later study by Larson et al. [88], who used a multi-reference configuration-interaction (MRCI) method, with a very large basis set and found no neutral potential crossing the ionic ground potential close to its minimum. Specifically, a very recent and accurate study by Larson and Orel [87], who calculated electronic resonant curves of HCO\(^2\), confirmed that the direct DR process should be negligible for low energetic incident electrons, as can be seen in Fig. 3.1, where the potential curves\(^3\) of excited \( ^2\Sigma \) and \( ^2\Pi \) are presented. Moreover, the asymptotic energy of the first excited \( ^2\Pi \) state of HCO, situated about 2eV above the minimum of the ionic ground potential, seems to confirm that CO\((\alpha^3\Pi)\) can be formed by DR of HCO\(^+\). Since the ground state ionic vibrational energy calculated by Puzzarini et al. [122] is about 0.4eV above the minimum of the ground ionic

\(^2\)Resonant curves adiabatic with respect to each other, but diabatized with respect to the Rydberg states just below the ionic ground potential.

\(^3\)These potential curves converge to excited states of HCO\(^+\).
electronic potential, we conclude that CO(a^3Π) can be formed by DR of HCO^+ for incoming electronic energies larger than about 1.5eV.

From the latter considerations, effort towards a study of indirect DR mechanism for HCO^+ were pursued. A theoretical study by Kokouline et al. [77] on the DR of H_3^+ molecular ion, demonstrated that the rate of dissociation of the ion is actually quite large, although the process is indirect in nature. They hereby confirmed previously measured DR rate of H_3^+ in storage ring experiments. They indeed showed that the non Born-Oppenheimer Jahn-Teller effect is crucial in the electronic capture. In 2005, Larson and coworkers [88] followed a similar idea and calculated the indirect DR cross section of HCO^+ via capture in Rydberg states. Fig. 3.2 shows their calculated Rydberg energies, at stretched dissociative r_{ch} coordinate and at bent geometry. From the figure, it can be seen that the electronic state corresponding to n=2 has a dissociative character, confirming that indirect DR via electronic capture in Rydberg states associated with excited vibrational levels of the ionic core was indeed possible without further capture in a doubly excited dissociative resonant state. On the right side of the figure, a strong Renner-Teller splitting is found for the states A′ and A″ at bent geometry, and the ground electronic state A′ even has a minimum at \( \theta = 125^\circ \). However, since only high Rydberg states are important for electronic capture, and considering that the Renner-Teller splitting decreases dramatically for n=3, it was concluded that the Renner-Teller effect should not play an effective role in the electronic capture. Thus, the Renner-Teller coupling was disregarded in [88] and the obtained DR cross section was
more than one order of magnitude smaller than the experimental results by Lepadellec et al. [89].

Figure 3.2: Lowest electronic Rydberg states of HCO as a function of the dissociative coordinates $r_{ch}$ (left) and as a function of the bending angle (right). The electronic state corresponding to $n=2$ depicts an avoided crossing with a neutral dissociative state below the ionization threshold, confirming the possibility of indirect DR for HCO$^+$ via capture into excited vibrational states.
3.1.2 Present study including Renner-Teller effect and all internal degrees of freedom of HCO⁺

In 2006, Mikhailov et al. [102] argued that even a small Renner-Teller coupling could induce crucial changes in the indirect DR process of HCO⁺. They made a step further by introducing the Renner-Teller coupling in the formalism and found an enhancement of the cross section by about a factor three compared with the previous study [88].

As depicted in Fig. 3.3, the Renner-Teller effect induces a coupling between the vibrational and the electronic motions, origin of an instability in the HCO molecule, which can lead to its dissociation. In fact, a few approximations were made in the latter study, and the obtained DR cross-section still remained about a factor 2.5 smaller than the lowest ex-
perimental cross-section. In the present chapter, we present one of the two improvements we applied to the treatment of Mikhailov et al. [102].

One of the possible reasons explaining why the theoretical cross-section was smaller in [102] compared with the experimental data, could come in part from the approximation of freezing CO coordinate at its equilibrium value. Although the main dissociation pathway does not involve this coordinate, it was already argued in [102], that the CO vibration could potentially increase the probability of electron capturing and indeed enhance the overall DR cross-section. In the foregoing chapter, we present our theoretical treatment of the DR study of HCO$^+$ and investigate the explicit role of the CO vibration.

## 3.2 The theoretical approach employed in the thesis

### 3.2.1 Modeling the internal vibrations of HCO$^+$ ion: adiabatic potentials

The theoretical treatment presented here resembles in many respects the approach applied previously to the H$_3^+$ [77] and HCO$^+$ [102] target ions. Below, we describe the new elements of the theoretical approach. We represent the Hamiltonian of the ion+electron system as

\[ \hat{H} = \hat{H}_{ion} + \hat{T}_e + \hat{H}_{int}, \]

where $\hat{H}_{ion}$ is the ionic Hamiltonian, $\hat{T}_e$ is the electronic kinetic operator and $\hat{H}_{int}$ describes the electron-ion interaction. We will denote the electronic Hamiltonian in a compact way as $\hat{H}_{elec} = \hat{T}_e + \hat{H}_{int}$. 
Figure 3.4: Jacobi system of coordinates used to describe HCO\(^+\) molecular ion, where the point \(G\) represents the center of mass of CO.

Let us first consider the ionic Hamiltonian \(\hat{H}_{\text{ion}}\) written in the center-of-mass reference frame. We use Jacobi coordinates to represent all vibrational degrees of freedom. Introducing \(G\) as the center of mass of C-O, the set of internuclear coordinates, depicted in Fig. 3.4, is represented by the quartet \(Q = \{R_{CO}, R_{GH}, \theta, \phi\}\). Here \(R_{CO}\) and \(R_{GH}\) represent respectively the distances C-O and G-H, \(\theta\) is the bending angle between \(\overrightarrow{OC}\) and \(\overrightarrow{GH}\), and \(\varphi\) is the azimuthal orientation of the bending. Here, we consider \(R_{GH}\) as the adiabatic coordinate representing the dissociation path. In the previous study [102], the inter-nuclear distance \(R_{CO}\) was fixed at its equilibrium value \((R_{CO} = 2.088\ \text{a.u})\) and the \(R_{GH}\) coordinate was treated as the dissociative coordinate. The vibrational Hamiltonian in the Jacobi coordinates is

\[
\hat{H}_{\text{ion}} = -\frac{\hbar^2}{2\mu_{CO}} \frac{\partial^2}{\partial R_{CO}^2} - \frac{\hbar^2}{2\mu_{H-CO}} \frac{\partial^2}{\partial R_{H-CO}^2} + \frac{L^2(\theta, \varphi)}{2\mu_{H-CO} R_{H-CO}^2} + \hat{V}^+(R_{CO}, R_{GH}, \theta), \quad (3.1)
\]
where \( \mu_{CO} \) and \( \mu_{H-CO} \) are respectively the reduced masses of the C–O and H–CO pairs; 
\( \hat{L}^2(\theta, \varphi) \) is the familiar operator of angular momentum corresponding to relative rotation of H around the CO axis. The ionic potential \( \hat{V}^+(R_{CO}, R_{GH}, \theta) \) is obtained from \textit{ab initio} calculations.

Figure 3.5: Adiabatic curves \( U_{m\varphi,l}(R_{GH}) \) versus the adiabatic coordinate \( R_{GH} \). The origin of energy corresponds to the electronic ground state at equilibrium position of HCO\(^+\). The curves are labeled with quantum numbers \( \{v_1 v_{m\varphi} v_3\} \) of normal modes of HCO\(^+\). The \( v_1 \) quantum in our model corresponds approximately to motion along \( R_{GH} \) and therefore is not defined for the adiabatic curves since \( R_{GH} \) is not quantized. The curves \( \{v_1 2^{\pm 2} 0\} \) and \( \{v_1 2^0 0\} \) are almost degenerate.

Representing the ion by the above Hamiltonian depending on \( \{R_{CO}, R_{GH}, \theta, \varphi\} \) only, we neglect the rotational motion of the CO bond in space, but included relative rotation of H and CO. This approximation is justified by a large CO/H mass ratio. As a result of the approximation, the projection \( m_\varphi \) of the angular momentum \( \hat{L} \) on the CO axis is conserved.
We solve the Schrödinger equation with the Hamiltonian (3.1) keeping the $R_{GH}$ coordinate fixed, so that the partial derivative on $R_{GH}$ in (3.1) is omitted. This determines vibrational wave functions $\Phi_{m, l}(R_{GH}; R_{CO}, \theta, \varphi)$ and corresponding adiabatic energies $U_{m, l}^+(R_{GH})$ that depend parametrically on $R_{GH}$. Several of these curves are shown in Fig. 3.5. The lowest adiabatic curves can approximately be characterized by quantum numbers $\{v_1, v_2, v_3\}$ of the three normal modes of the HCO$^+$ ion. The $v_1$ quantum number is not specified in the figure, because it corresponds approximately to the motion along the adiabatic coordinate, which is not quantized in the present treatment.

Table 3.1: Comparison of vibrational energies obtained in the adiabatic approximation with the exact calculation [122]. The result of the previous study [102], where a different adiabatic approximation was used is also shown. In that study CO was not quantized and thus, $00^01$ was not calculated. The overall error is about 12%, which translates into about 25% for vibrational wave functions. The energies are given in meV.

<table>
<thead>
<tr>
<th>${v_1v_2v_3}$</th>
<th>Present calculation</th>
<th>Previous calculation</th>
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</tr>
<tr>
<td>00^01</td>
<td>298</td>
<td>no value</td>
<td>270.6</td>
</tr>
</tbody>
</table>

A reasonable measure of accuracy of the adiabatic approximation is provided by comparing the energy splitting between our adiabatic potentials $U_{m, l}^+(R_{GH})$ with exact calculations of the corresponding vibrational splittings [122] (see Tab. 3.1). The obtained values are practically the same as in the previous study [102] also shown in the table, since a similar (but not identical) adiabatic approximation was used in that study.
3.2.2 Background on the Renner-Teller effect

Before developing how the electronic Hamiltonian is constructed in this study, we start by introducing few general aspects of the non-adiabatic Renner-Teller effect for linear molecules. If we consider a linear molecule, as HCO, at its linear equilibrium configuration, the symmetry of its electronic states is described by the point group $C_{\infty v}$, with doubly degenerate irreducible representations corresponding to electronic states $\Pi$, $\Delta$, $\Phi$, and so on. When the molecule is bent, the new point group describing the electronic states is simply $C_s$, with two one dimensional irreducible representations $A'$ and $A''$, which implies that the degeneracy is lifted, as represented schematically in Fig. 3.6 for the case of $p$ orbitals. It is rather clear, that we are in the case where strong non Born-Oppenheimer effects could take place, since the electronic energies are degenerate at equilibrium configuration and almost degenerate at small displacements. Hence, strong vibronic interactions are present between the ionic core of HCO$^{+}$ and the out-shell electron near the linear configuration. Usually the electronic angular momenta $\hat{L}_\alpha$ are smaller than the vibrational momenta $\hat{P}_r$, so that the breakdown of the Born-Oppenheimer approximation comes from a coupling induced by the operator $\hat{T}_{\text{vib}}$. In the case of chain molecules, like HCO, HCCH or HCN, there could be a strong interaction due to the coupling operator $\hat{T}_{\text{er}}$ and $\hat{T}_{\text{ee}}$ introduced in Subsection 2.2.2, between rotational motion of the electron and of the nuclei around the axis of symmetry. The coefficient $\mu_{zz}$, that appears in the later operator, is almost inversely proportional to the moment of inertia.

---

4Here we still use the term vibronic couplings, even though in the peculiar case of a linear triatomic molecule, the vibration of the nuclei around the axis of symmetry of the molecule can be considered in part to be a rotation of the nuclei around this axis.
matrix, and can therefore become extremely high close to linear configuration. Actually we do not need to evaluate such non Born-Oppenheimer coupling elements explicitly, as we can treat the incoming continuum electron at far distance from the ionic core in a diabatic basis, with corresponding non diagonal vibronic coupling elements. For that matter, we reintroduce the widely used simplified Renner-Teller model.

We start by writing the vibronic wave function as follow:

\[ \Psi(q, Q) = \psi_{elec}^{(a)}(q)\chi_n(Q) + \psi_{elec}^{(b)}(q)\chi_{n'}(Q). \]  

(3.2)

In the latter expression, \( q \) and \( Q \) represent respectively the sets of electronic and vibrational coordinates, \( \psi_{elec}^{(a)}(q) \) and \( \psi_{elec}^{(b)}(q) \) are the two degenerate orthonormal electronic wave functions at linear configuration and \( \chi_n(Q) \) and \( \chi_{n'}(Q) \) are corresponding vibrational wave functions. Here we note that the electronic wave functions do not depend on the vibrational coordinates \( Q \). This particular form of the electronic functions represents the central part of the approximation. On that account, the trial solution in equation (3.2) is restricted, but has the advantage of simplifying considerably the theory and remains a good starting point. This approximation will happen to be accurate if other electronic states are energetically not too close from the degenerate level, so that they only perturb negligibly the electronic states \( \psi_{elec}^{(a)} \) and \( \psi_{elec}^{(b)} \) at bent angle. In such case, the real adiabatic electronic eigenfunctions can be represented in the basis \( (\psi_{elec}^{(a)}, \psi_{elec}^{(b)}) \) to a good level of approximation.
Figure 3.6: Cartoon depicting the degeneracy breaking of $p$-orbital at bent geometry. On the left side, the HCO$^+$ ion is at its symmetric linear geometry and the orbitals $p_x$ and $p_y$, as well as any constructed orbital $p_{x'}$ and $p_{y'}$ by rotation of the $x$ and $y$ axis around the $z$ axis, belong to the doubly degenerate $E$ irreducible representation of the point group $C_\infty v$. On the right side, the molecule is bent in the $(xz)$ plane (we deliberately exaggerate the bending to clarify the idea). At this geometry, we have two orbitals with different expectation energies (energy splitting), as can be clearly seen from the asymmetric position of the hydrogen atom with respect to each of these orbitals. The system is now described by the $C_s$ point group, where the $p_x$ orbital, symmetric with respect to the $(xz)$ plane, belongs to the $A'$ irreducible representation. The $p_y$ orbital, antisymmetric with respect to that same plane, belongs to the $A''$ irreducible representation.

Each group which has at least one doubly degenerate irreducible representation, also has at least one symmetry element $C$ (rotation of an angle $\varphi$ through the symmetry axis in our case) for which there exist complex electronic forms $\psi_{elec}^{(+)}$ and $\psi_{elec}^{(-)}$ verifying:

$$C\psi_{elec}^{(+)} = \omega\psi_{elec}^{(+)}; \quad \psi_{elec}^{(-)} = \omega^*\psi_{elec}^{(-)},$$

(3.3)
where \( \omega \) is a complex number of modulus unity. Writing the vibronic function in this new electronic basis, we get

\[
\Psi(q, Q) = \psi_{elec}^{(+)}(q)\chi^{+}(Q) + \psi_{elec}^{(-)}(q)\chi^{-}(Q).
\]  

(3.4)

While solving the Schrödinger equation, one can expand the non diagonal electronic terms \( \int \psi_{elec}^{(\pm)^*} \hat{H}_{elec} \psi_{elec}^{(\pm)} dq \) as Taylor’s series until order two in the normal coordinates. In the case of a trimer, we have in general two non degenerate normal coordinates \( Q_1 \) and \( Q_2 \) and two doubly degenerate normal coordinates denoted \( (Q_+, Q_-) \) which transform as

\[
CQ_+ = \omega_1 Q_+ ; \quad CQ_- = \omega_1^* Q_-.
\]  

(3.5)

In (3.5), \( \omega_1 \) is a complex number of modulus unity, which does not need to be equal to \( \omega \). Thus we obtain the following expansion:

\[
\int \psi_{elec}^{(\pm)^*} \hat{H}_{elec} \psi_{elec}^{(\pm)} dq = W^{\pm} + \sum_i W_i Q_i + \frac{1}{2} \sum_i \sum_j W_{ij} Q_i Q_j
\]

(3.6)

\[
\int \psi_{elec}^{(-)^*} \hat{H}_{elec} \psi_{elec}^{(-)} dq = V^{\pm} + \sum_i V_i Q_i + \frac{1}{2} \sum_i \sum_j V_{ij} Q_i Q_j.
\]

(3.7)

Here the subscripts \( i \) and \( j \) run over 1, 2, + and -. Then, symmetry considerations can be used to find the non vanishing expansion coefficients in (3.6) and (3.7). The left hand side of equation (3.6) is unchanged when we apply the operation \( C \). This is easily seen in the view of equation (3.3) and considering the fact that \( \hat{H}_{elec} \) is completely symmetric. Therefore the
right hand side has to be also symmetric. If we apply the operation $C$ on the right hand side of (3.6) and use the transformations in (3.5), we deduce that $W_{++} = W_{--} = 0$. Furthermore, if we assume that the molecule is stable by changes in $Q_1$ and $Q_2$, we obtain $W_1 = W_2 = 0$. At present, if $Q_1$ and $Q_2$ are from different one dimensional irreducible representations, ultimately $W_{12} = 0$, on the other hand, if they are from the same irreducible representation, it is always possible to construct superposition of them to also obtain $W_{12} = 0$. Thus, the final expression is:

$$
\int \psi_{\text{elec}}^{(+)} \hat{H}_{\text{elec}} \psi_{\text{elec}}^{(+)} dq = W^{0} + \frac{1}{2} W_{11} Q_1^2 + \frac{1}{2} W_{22} Q_2^2 + W_{+-} Q_+ Q_-.
$$

(3.8)

Similar arguments can be used to deduce the expression of the non diagonal element in equation (3.7). Applying $C$ on the left hand side multiplies it by $\omega^2$. In our case where $C$ is the rotation by an angle $\theta$ through the symmetry axis, the transformation factor for $Q_+$ is $\omega_1 = e^{i\varphi}$ and the one for $\psi_{\text{elec}}^{(+)}$ is $\omega = e^{i|\Lambda|\varphi}$ where $\Lambda$ is the projection of the electronic angular momentum on the symmetry axis. Therefore if $|\Lambda| = 1$, the expression (3.7) reduces to

$$
\int \psi_{\text{elec}}^{(-)*} \hat{H}_{\text{elec}} \psi_{\text{elec}}^{(+)} dq = \frac{1}{2} V_{++} Q_{++}^2.
$$

(3.9)

For any other non-zero value of $\Lambda$, the only terms in the matrix elements which do not vanish are the fourth power or higher. For this reason, one often considers $\Pi$ states to be the only ones responsible for non-vanishing coupling elements in the Hamiltonian.
Figure 3.7: Potential energies of the ionic ground state of HCO$^+$ and of the different Rydberg states of the HCO molecule considered in our study. The origin of energies corresponds to the ionic electronic groundstate at equilibrium configuration of HCO$^+$. The potentials are plotted at the equilibrium bond distances $R_{GH} = 3.27 \text{ a.u}$ and $R_{CO} = 2.088 \text{ a.u}$ of the molecule, as a function of the bending angle $\theta$ defined in Section 3.2. The Rydberg potentials represented correspond to states with principal quantum number $n = 3$. One can observe the degeneracy at $\theta = 0^\circ$, as well as the Renner-Teller splitting between the symmetric and antisymmetric states $p\pi'$ and $p\pi''$.

From (3.8) and (3.9), we conclude that the normal coordinates $Q_1$ and $Q_2$ are totally uncoupled from other motions, so that the vibronic solution in equation (3.4) can be written

$$\Psi(q, Q) = \chi_1(Q_1)\chi_2(Q_2)(\psi_{\text{elec}}^{(+)}(q)\chi^+(Q_+, Q_-) + \psi_{\text{elec}}^{(-)}(q)\chi^-(Q_+, Q_-)).$$

One generally introduces coordinates $\rho$ and $\phi$ defined by $Q_\pm = \rho e^{\pm i\phi}$ and uses them rather than $Q_+$ and $Q_-$ to express the different terms in the Hamiltonian. Using the latter coordi-
nates, the form of $\hat{H}_{\text{elec}}$ in the $(\psi_{\text{elec}}^{(+)}, \psi_{\text{elec}}^{(-)})$ electronic basis is:

$$
\hat{H}_{\text{elec}}(Q) = \begin{pmatrix}
W_o + W_{+-} \rho^2 & \frac{1}{2} V_{++} \rho^2 e^{2i\varphi} \\
\frac{1}{2} V_{++} \rho^2 e^{-2i\varphi} & W_o + \frac{1}{2} W_{+-} \rho^2
\end{pmatrix}.
$$

(3.11)

Finally, these symmetry considerations help us to understand why the Renner-Teller effect is a quadratic effect, whereas we will discuss the linear Jahn-Teller effect in Chapter 5, for the case of highly symmetric $\text{H}_3^+$ and $\text{H}_3\text{O}^+$ molecular ions. If we diagonalize the matrix $\hat{H}_{\text{elec}}$ in the basis $(\psi_{\text{elec}}^{(+)}, \psi_{\text{elec}}^{(-)})$, we should obtain the adiabatic electronic energies to a good level of accuracy for small degenerate displacements. From the form of the non diagonal elements, we will obtain two electronic potentials splitted to second order in the $\rho$ coordinate. In Fig. 3.7, we show the different Rydberg electronic potentials, corresponding to principal quantum numbers $n=3$, as a function of the bending angle $\theta$. These low Rydberg states calculated by Larson et al. [88] are used in our present study of the process of DR of $\text{HCO}^+$. On Fig. 3.7, one can observe the degeneracy at the linear configuration, as well as the splitting at bent geometry. Even small, this splitting plays an important role in the electronic capture in vibrationally excited Rydberg states. Moreover, we also include couplings between $p\sigma$ and $p\pi$ states in the next section. They are also named Renner-Teller couplings in the present study and are crucial in the electronic capture, since they depend to first order on $\rho$. 
3.2.3 The electronic Hamiltonian in the present treatment

We apply at present these previous results to the case of HCO⁺ ion. The structure of our electronic Hamiltonian \( \hat{H}_{\text{elec}} \) includes \( ns\sigma, np\pi^{-1}, np\sigma, np\pi^{+1} \), and \( nd\sigma \) electronic states only.

Here, \( np\pi^{-1} \) and \( np\pi^{+1} \) denote respectively states with negative and positive projection of the angular momentum along the symmetry axis of the molecule. In the basis of the five electronic states, the Hamiltonian has the following block-diagonal form for each principal quantum number \( n \):

\[
\hat{H}_{\text{elec}}(Q) = \begin{pmatrix}
E_{s\sigma} & 0 & 0 & 0 & 0 \\
0 & E_{p\pi} & \delta e^{i\varphi} & \gamma e^{2i\varphi} & 0 \\
0 & \delta e^{-i\varphi} & E_{p\sigma} & \delta e^{i\varphi} & 0 \\
0 & \gamma e^{-2i\varphi} & \delta e^{-i\varphi} & E_{p\pi} & 0 \\
0 & 0 & 0 & 0 & E_{d\sigma}
\end{pmatrix}, \tag{3.12}
\]

where \( E_{s\sigma}, E_{p\sigma}, E_{p\pi}, \) and \( E_{d\sigma} \) are the diagonal elements of the electronic Hamiltonian.

The energies \( E_{s\sigma} \) and \( E_{d\sigma} \) are geometry varying parameters over the whole configuration space. On the other hand, in the present diabatic representation, \( E_{p\sigma} \) and \( E_{p\pi} \) only vary with the \( R_{GH} \) and \( R_{CO} \) coordinates, but actually represent diagonal diabatic energies at bending angle. Thus, they do not depend on \( \theta \) and \( \varphi \) and are kept at the adiabatic energies at linear configuration of the ion. The geometry dependent parameters \( \delta \) and \( \gamma \) represent the real non-Born-Oppenheimer diabatic coupling elements. The coefficient \( \gamma \) can be recognized
as containing the Renner-Teller effect discussed above, which couples $p\pi$ states. Since this is a second order effect, the coupling elements in (3.12) are directly proportional to $e^{\pm 2i\varphi}$. The other coefficient $\delta$ couples $p\sigma$ and $p\pi$ states and can not be strictly recognized as Renner-Teller couplings in the form introduced previously. The $p\sigma$ and $p\pi$ states are not degenerate at the equilibrium configuration. Furthermore, the present coupling is first order in $\rho$, considering that no symmetry reason imposes this term to vanish. Therefore, $\delta$ is the dominant coefficient for small displacement around equilibrium and has a crucial impact on the DR cross section. Both couplings $\delta$ and $\gamma$ depend on $Q$ and are denoted as Renner-Teller interaction in the foregoing development in an aim of simplicity. They are zero at linear geometry of the ion.

The diagonalization of the Hamiltonian $\hat{H}_{elec}$ is accomplished by the unitary transformation matrix in (3.13),

$$
\hat{U} = \frac{1}{\sqrt{2}} \begin{pmatrix}
1 & 0 & 0 & 0 & 0 \\
0 & e^{i\varphi} & e^{i\varphi}w_- & e^{i\varphi}w_+ & 0 \\
0 & 0 & \sqrt{2}w_+ & -\sqrt{2}w_- & 0 \\
0 & -e^{-i\varphi} & e^{-i\varphi}w_- & e^{-i\varphi}w_+ & 0 \\
0 & 0 & 0 & 0 & 1
\end{pmatrix},
$$

(3.13)

with the following abbreviations,

$$
w_\pm = \sqrt{(1 \pm \Delta/w)/2}, \quad \Delta = (E_{\sigma} - E_{\pi} - \gamma)/2, \quad \Delta = (E_{\sigma} - E_{\pi} - \gamma)/2,
$$

(3.14)

$$
w = \sqrt{\Delta^2 + 2\delta^2}.
$$
When diagonalized, the Hamiltonian becomes

$$\hat{U}^+ \hat{H}_{\text{elec}} \hat{U} = \text{diag}\{E_{s\sigma}, V_{\pi''}, V_{\sigma}, V_{\pi'}, E_{d\sigma}\},$$  \hspace{1cm} (3.15)

with the following relations

$$V_{\pi''} = E_{\pi} - \gamma, \quad V_{\sigma} = (E_{\sigma} + E_{\pi} + \gamma)/2 + w,$$

$$V_{\pi'} = (E_{\sigma} + E_{\pi} + \gamma)/2 - w.$$  \hspace{1cm} (3.16)

We obtain adiabatic states and denote respectively by \(p_{\pi'}\) and \(p_{\pi''}\) the symmetric and antisymmetric states with respect to the plane containing the bent molecule. The adiabatic potential surfaces \(V_{\pi''}, V_{\sigma}, V_{\pi'}\) as well as \(E_{s\sigma}\) and \(E_{d\sigma}\) are known from \textit{ab initio} calculations [88] so that we can deduce the adiabatic coefficients \(\delta\) and \(\gamma\) from these equations. In the present method, the electronic Hamiltonian \(\hat{H}_{\text{elec}}(Q)\) is used to construct the \(5 \times 5\) short-range reactance matrix coefficients \(K_{i,i'}(Q)\) written in the same basis of electronic states as \(\hat{H}_{\text{elec}}(Q)\). For that matter, we first use the fact that \(\hat{K}(Q) = \tan(\pi \hat{\mu}(Q))\), where \(\hat{\mu}(Q)\) is the quantum defect matrix, to find the diagonal elements of the reactance matrix \(\hat{K}(Q)\) in the eigenchannels basis. We use quantum defects corresponding to principal quantum number \(n = 4\) for \(s\sigma\) state, and \(n = 3\) for the other adiabatic states. Finally, to obtain the reactance matrix in the same initial basis as \(\hat{H}_{\text{elec}}(Q)\) in (3.12), we simply use the unitary operator in (3.13) and apply it to the diagonal form of the reactance matrix.
3.2.4 Research of resonances: Rydberg states

Once the adiabatic states \( \Phi_{m_{\mu,l}}(R_{GH}; R_{CO}, \theta, \varphi) \), energies \( U^+_{m_{\mu,l}}(R_{GH}) \), and the reaction matrix \( K_{i,j'}(Q) \) are obtained, we take \( R_{GH} \) as the adiabatic coordinate and apply the quantum-defect approach that has been already used in a number of DR studies of triatomic and diatomic ions [77, 76].

![Resonant potential curves](image)

**Figure 3.8:** Resonant potential curves \( U_a(R_{GH}) \) of the neutral molecule state with magnetic quantum number \( M = 1 \). The ground ionic state potential, as well as the first and second excited ionic states, are shown by dash thick lines. The Rydberg states are very dense just below the ionic potentials. For clarity, we plotted these resonant states only for effective quantum number \( \nu < 40 \).

We first construct the reaction matrix \( K_{j,j'}(R_{GH}) \), where \( j \) denotes a vibrational and electronic angular momentum channel, using the vibrational frame transformation introduced
in Section 2.4:

\[
K_{(m_{\varphi},l_{\varphi}),l_{\varphi}'(R_{GH}) = \int \Phi_{m_{\varphi},l_{\varphi}}(Q)K_{l_{\varphi},l_{\varphi}'}(Q)\Phi_{m_{\varphi}',l_{\varphi}'}(Q)dQ,}
\]

(3.17)

where the integration is carried over the three internuclear coordinates, \( R_{CO} \), \( \varphi \), and \( \theta \) at fixed \( R_{GH} \). The reaction matrix \( K_{j,j'}(R_{GH}) \) thus obtained has many channels and parametrically depends on \( R_{GH} \). Then, we apply the procedure of channel elimination in the MQDT formalism (see Subsection 2.3.3). For each \( R_{GH} \) value, we obtain a number of resonances with energies \( U_a(R_{GH}) \) and widths \( \Gamma_a(R_{GH}) \). The resonances correspond to the autoionizing electronic states of the neutral molecule at frozen \( R_{GH} \). The fixed-\( R_{GH} \) width of the resonances is the reciprocal of the fixed-\( R_{GH} \) resonance autoionization lifetime, which of course is not an experimentally-observable resonance width since \( R_{GH} \) has not been quantized. The different resonances, with their corresponding ionic potentials, are presented in Fig. 3.8 only until the second excited vibrational state for clarity. In our treatment, we actually seek for resonant states attached to ionic potentials until the fourteenth excited state, for which convergence in the final cross section was reached.
Figure 3.9: Zoom on the spectrum over a region just below the first excited ionic state, where a few avoided crossings involving a Rydberg state associated to a highly excited ionic vibrational state are evident. These avoided crossings, sign of strong vibronic couplings (Renner-Teller or other vibrational-electronic couplings), represent ways for the system to dissociate (pre-dissociation) via adiabatic passage on the $R_{GH}$ coordinate, to a more excited ionic vibrational state.

3.3 Calculations of the final results

3.3.1 Dissociative recombination cross-section calculation

The energies and widths of the resonances are then used to calculate the cross-section for electron capture by the ion. We start with the cross section formula in the case of dissociative attachment to a neutral molecule, which applies equally to the process of DR considered here. Using a linear approximation for the stiff resonant state potential at the Franck-Condon
point (where the total energy crosses the resonant potential curve) and thus describing the
dissociative states by an Airy functions, the following formula was obtained in [77]

$$
\sigma = \sum_a 2\pi^2 \frac{k_o}{k_o^2} \frac{\Gamma_a(R_{GH})}{\left| U_a'(R_{GH}) \right|^2 |\chi_o^+(R_{GH})|^2 \rho(E)}.
$$

(3.18)

In equation (3.18), $k_o$ is the asymptotic wave number of the incident electron, which depends on the initial state $o$ of the target molecular ion, $\chi_o^+(R_{GH})$ is the initial vibrational wave function of the ion, $U_a'(R_{GH})$ and $\Gamma_a(R_{GH})$ are respectively the derivative of the potential and the width of autoionization of a resonant electronic potential labeled $a$ (all these parameters are evaluated at the Franck-Condon point). The factor $e^{-\rho(E)}$ represents the survival probability, which could be less than unity if the system has a substantial probability to autoionize before dissociation. For a system like HCO\(^+\), it is comparatively unlikely that the system will autoionize before finding its way for dissociation after electron capture (see Subsection 3.4.2) and therefore we assume $e^{-\rho(E)} \approx 1$.

The above formula is appropriate for capture in a resonant state that is energetically open for direct dissociation. In the present treatment, we have to consider both resonant states, either open or closed for dissociation. If a corresponding resonant state is closed, bound with respect to dissociation, the formula in (3.18) has to be modified. In [102], the formula of Bardsley [11] was adapted for the present situation of indirect DR. Let us consider the ion initially in its ground vibrational state and the incoming electron in a given partial wave state. Each resonant state $a$ has an autonionizing width $\Gamma_a(R_{GH})$ with respect to the

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ground ionic state, at a given $R_{GH}$. When the vibrational motion in the resonant state is quantized, with wave function $\chi^{\text{res}}(R_{GH})$, one should bear in mind that only a subset of the target vibrational levels will be energetically open. Each resulting quantized resonance acquires an autoionization width given by

$$\Gamma_a = \left| \int_0^\infty \chi^{\text{res}}(R_{GH}) \sqrt{\Gamma_a(R_{GH})} \chi_0^+(R_{GH}) dR_{GH} \right|^2. \quad (3.19)$$

The total line-width $\Gamma$ of this quantized resonance also includes its predissociation partial width $\Gamma_d$, in a way that $\Gamma = \Gamma_a + \Gamma_d$. On that account, the contribution to the total cross section can be expressed using the Wigner formula

$$\sigma^{\text{res}}(E) = \frac{\pi}{k_o^2} \frac{\Gamma_a \Gamma_d}{(E - E_{\text{res}})^2 + \frac{1}{4} \Gamma^2}. \quad (3.20)$$

Each energetically closed ionic vibrational state $c$ generates a series of Rydberg states with energy $\epsilon_{nc}$, numbered with the effective quantum number $n_c$. The cross section, averaged over the energy interval between two resonances with energies $\epsilon_n$ and $\epsilon_{n+1}$ is given by:

$$\langle \sigma(E) \rangle = \frac{1}{\Delta_n + \Delta_{n+1}} \int_{\epsilon_n - \Delta_n}^{\epsilon_{n+1} + \Delta_{n+1}} \sigma(E') dE', \Delta_{n+1} = \frac{\epsilon_{n+1} - \epsilon_n}{2} \quad (3.21)$$

If we extend the limit of this integral to infinity, we finally get:

$$\langle \sigma(E) \rangle \approx \frac{2\pi^2}{k_o^2} \left( \frac{\Gamma_a \Gamma_d}{\Gamma \Delta} \right). \quad (3.22)$$
where $\Delta = \Delta_{n+1} + \Delta_n \simeq \frac{1}{n_c^2}$. In (3.22), the quantity in parenthesis approaches a constant as $n_c$ increases in the appropriate channel $c$, since the total and partial widths should become proportional to $\Delta$ in that limit. The total cross section is finally obtained by summing over all Rydberg states associated with all closed ionic channels. In the limit where $\Gamma_d \gg \Gamma_a$, this gives

$$\sigma = \frac{2\pi^2}{k_o^2} \sum_c |\langle \chi_{c}^{\text{res}}(R_{GH}) | \sqrt{\Gamma_a(R_{GH})} | \chi_o^+(R_{GH}) \rangle |^2 n_c^3. \quad (3.23)$$

The total DR cross-section for HCO$^+$ is mainly determined by the sum in (3.23) (compared with the sum in (3.18)), because the electron is most likely captured into one of the lowest closed channels that cannot dissociate directly. As mentioned previously, the formulas above describe the cross-section for capture of the electron. It is equal to the DR cross-section only if the probability of subsequent autoionization is negligible compared to the dissociation probability, after the electron has been captured by the ion.

The projection $M = m_\varphi + \lambda$ of the total angular momentum on the CO molecular axis, where $\lambda$ is the projection of the electronic angular momentum on the CO axis, is a conserved quantity in our model. Therefore, the resonances and the cross-section are calculated separately for each value of $|M|$. Since $\lambda$ can only be 0 or $\pm 1$ in our model ($\sigma$ and $\pi$ states) and the initial vibrational state of the ion has $m_\varphi = 0$, the possible values of $|M|$ are 0 and 1. The total cross-section for electron capture by the ion in the ground vibrational level is given [102] by $\langle \sigma^{\text{total}} \rangle = \langle \sigma^{M=0} \rangle + 2\langle \sigma^{M=1} \rangle$. 

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3.3.2 Convolution procedure over experimental energy spreads

In storage ring experiments, the electron cooler (see Subsection 1.1.4) generates a nearly mono-energetic beam, merged with the stored ion beam, and whose resulting velocity spread can be described by the anistropic bi-Maxwellian distribution [6]

\[ f(\vec{v}_e) = \frac{m_e}{2kT_{e\parallel}} \sqrt{\frac{m_e}{2kT_{e\perp}}} \exp \left( -\frac{m_e v_{e\parallel}^2}{kT_{e\parallel}} - \frac{m_e (v_{e\parallel} - \bar{v}_{e\parallel})^2}{kT_{e\parallel}} \right), \]

(3.24)

where \( m_e \) is the electron mass, \( k \) is the Boltzmann constant, \( T_{e\parallel} \) and \( T_{e\perp} \) are respectively the longitudinal and transversal electron temperatures, with corresponding energy spreads \( \Delta E_{\parallel} = kT_{e\parallel} \) and \( \Delta E_{\perp} = kT_{e\perp} \), \( \vec{v}_e \) is the electron velocity vector, \( v_{e\parallel} \) and \( v_{e\perp} \) are the longitudinal and transversal electron velocity respectively and finally \( \bar{v}_{e\parallel} \) is the mean longitudinal velocity of the electron beam. The mean transverse velocity is not included since it is zero.

Denoting the electronic energy as \( E_e = m_e v_e^2 / 2 \), where \( v_e = |\vec{v}_e| \), and the mean longitudinal energy as \( \bar{E}_{\parallel} = m_e \bar{v}_{e\parallel} / 2 \), the final convoluted cross section over the velocity distribution is given by

\[ \langle \sigma_{E_{\parallel}} \rangle \bar{v}_{e\parallel} = \int v_e f(\vec{v}_e) \sigma(E_e) d^3 \bar{v}_e. \]

(3.25)

The obtained smooth merged beam cross section is presented in Fig. 3.10.
Figure 3.10: The figure shows the calculated DR cross-section for HCO$^+$ (solid line) as a function of the incident electron energy. The experimental [89] (cross symbols) and previous theoretical [102] (dashed line) cross-sections are also shown for comparison. The theoretical curves include a convolution over the experimental electron energy distribution according to the procedure described in [76] with $\Delta E_\perp = \Delta E_\parallel = 3$ meV.

### 3.3.3 Thermal rate

The thermal rate coefficient is actually another important quantity for plasma and interstellar studies. It is simply expressed as a convolution of the rate coefficient over all collision energies present at a temperature $T$. We start with the distribution in collision velocity given by

$$g(v_c) = 4\pi v_c^2 \left( \frac{m_e}{2\pi kT} \right)^{3/2} e^{-\frac{E_c}{kT}},$$

(3.26)
where \( v_c = |\vec{v}_c| \) is the absolute value of the collision velocity and \( E_c = m_e v_c^2 / 2 \) is the collision energy. Therefore we get for the thermal rate coefficient

\[
\alpha(T) = 4\pi \left( \frac{m_e}{2\pi kT} \right)^\frac{3}{2} \int_0^\infty v_c^3 \sigma(E_c) e^{-\frac{E_c}{kT}} dv_c.
\] (3.27)

Expressing the thermal rate coefficient solely in function of the collision energy, we finally obtain

\[
\alpha(T) = \frac{8\pi m_e}{(2\pi m_e kT)^\frac{3}{2}} \int_0^\infty E_c \sigma(E_c) e^{-\frac{E_c}{kT}} dE_c.
\] (3.28)

The thermal rate coefficient is shown in Fig. 3.11.

3.4 Discussion of the results and perspectives.

3.4.1 Interpretation of the results

Fig. 3.10 compares the present results with the experimental data from a merged-beam experiment [89] and with the previous theoretical study [102]. The theoretical results are almost identical (about 10% different) for electron energies below 0.1 eV. However they differ significantly at higher energies, where the present calculation gives a higher cross-section. Both curves are smaller than the experimental data by a factor of 2-3. Therefore, the approximation of the frozen C-O bond employed in [102] is apparently justified for low electron energies but appears to deteriorate at higher energies. This result can be
Figure 3.11: Theoretical (dashed lines) and experimental DR thermal rates for HCO⁺ and DCO⁺. The only available experimental data point for DCO⁺ is shown as a diamond symbol. The other symbols and the solid line represent data from experiments with HCO⁺.

rationalized as follows. For small electron energies, the CO vibration plays a negligible role because only a few resonances are associated with excited CO vibrational modes. In addition, normally, widths of these resonances are relatively small due to small relevant coupling in the corresponding reaction matrix elements. The largest coupling elements in the matrix are associated with the Renner-Teller coupling, which is active when $m_\phi$ is changed. However, when the total energy of the system becomes close to (but below) the first CO-excited level $\{00^01\}$ of the ion (0.3 eV above the ground vibrational level), the Rydberg series of resonances associated with the $\{00^01\}$ level becomes more dense and, more importantly,
they become mixed with the Rydberg series of the resonances associated with \( \{03^10\} \). The latter are coupled relatively strongly to the ground vibrational level \( \{00^00\} \) of the ion by the Renner-Teller coupling.

Fig. 3.11 shows the thermal rate coefficients obtained in the present study for HCO\(^+\) and DCO\(^+\) and compares them with available experimental data. Somewhat analogous to Fig. 3.10, the theoretical DR rate coefficient for HCO\(^+\) is smaller than the rate coefficient obtained from the merged-beam experiment \([89]\) by about a factor of three. The majority of the other experimental thermal rate coefficients shown in the figure are obtained in plasma experiments. These rates are significantly higher than the merged-beam experimental data \([89]\).

In the previous treatment \([102]\), the DR rate coefficient obtained for DCO\(^+\) was approximately 30% smaller than for HCO\(^+\). In the present study, the DCO\(^+\) coefficient is smaller than the one in HCO\(^+\) by only 10%. The only experimental data available for DCO\(^+\) is the rate coefficient \(2.6 \times 10^{-7}\) cm\(^3\)/s obtained at \(T=95\) K \([3]\). The same study provides the rate coefficient for HCO\(^+\), which is by 10% larger.

### 3.4.2 Discussion on autoionization

As we mentioned earlier, autoionization is not included in this treatment, which is equivalent of assuming, that once the electron is captured in a Rydberg state, it ultimately leads to the dissociation of the molecule. In reality, the captured electron could autoionize with
a probability equal to its capture probability (detailed balance principle). For this reason, it is highly desirable to estimate the order of magnitude of the autoionizing probability in order to have a qualitative idea of how much we overestimated the DR cross section. Such discussion is given in [102], for which the CO bond was frozen and we just outline here the main points that lead to an estimate of the autoionization. If we consider a resonant curve $U_a(R_{GH})$, its adiabatic autoionization width is $\Gamma_a(R_{GH}) = \sum_i \Gamma_a^{(i)}(R_{GH})$, where $\Gamma_a^{(i)}(R_{GH})$ represents the partial width into the $i$th open ionic channel. The higher widths are therefore generally related to resonant curves with a few nearest closed ionic channels. These curves are in general very similar in shape to their parent ionic channel when their effective quantum number is high, and the direct dissociation from these resonant curves is therefore impossible (the molecule merely vibrates in the same fashion than the stable ion does). In order to dissociate, the molecule must jump\(^5\) adiabatically to a more excited vibrational Rydberg state (adiabatically with respect to the dissociative coordinate). This process happens mainly at dissociative distances where avoided crossings occur (see Fig. 3.12). We can picture the electron, as descending into lower orbitals and thus exciting the vibrations of the ionic core. For the present resonant dissociative states, the molecule has a strong probability amplitude to be at large dissociative distance, where autoionization is impossible and the system irreversibly dissociates. The Landau-Zener model was used to estimate the predissociation probability. When the neutral molecule is vibrating along a $U_a(R_{GH})$ potential curve, it can jump to another curve $U_a'(R_{GH})$ via an adiabatic transition (adiabatic with respect to the

\(^5\)Process named predissociation in molecular spectroscopy.
dissociative coordinate $R_{GH}$) at an avoided crossing.

![Graph](image)

Figure 3.12: Another zoom on the spectrum over a region depicting a few avoided crossings. For convenience, the ionic ground state energy was subtracted from the data. The energy splittings are shown by arrows and are used in the Landau-Zener model to find the probability of adiabatic passage.

The probability of adiabatic passage is given by the Landau-Zener formula [86]:

$$P_{\alpha,\alpha'} = 1 - \exp\left(-\frac{2\pi \alpha^2}{\Delta F \sqrt{\frac{m}{2\Delta E}}}\right) \approx \frac{2\pi \alpha^2}{\Delta F \sqrt{\frac{m}{2\Delta E}}}$$

(3.29)

In this expression, $\alpha$ is the non diagonal coupling between diabatic states (states that would cross if the coupling was absent). Numerically, $\alpha$ is equal to half of the splitting between the adiabatic curves, $\Delta F$ is the absolute difference in slope (net classical slope) between
crossing diabatic curves, $\Delta E$ is the kinetic energy at avoided crossing and $m$ is the reduced mass of the system. Estimations of the order of magnitude of the different parameters were given in [102]. They found an order of magnitude of the Landau-Zener probability of about $10^{-4}$ at large $\Delta E$, for which the probability depends weakly on the kinetic energy. During a period of oscillation $\tau_{1/2}$, the system goes through a number of avoided crossing. This number of avoided crossing of a resonant curve was estimated to be around 10, which gives a predissoication probability of about 0.001-0.01. In the present case, where the CO bond is released, the number of avoided crossing is only slightly increased, compared with the previous study, by the presence of Rydberg curves corresponding to vibrational quanta of CO. Therefore the estimation of the predissoication probability should be of same order. On the other hand, the probability of autoionization during a period of oscillation $\tau_{1/2}$ is simply $P_{\text{auto}} \sim \tau_{1/2} \Gamma$, where $\Gamma$ is the autoionization width. The largest calculated $\Gamma$ was about $10^{-5}$ a.u, and $\tau_{1/2} = \pi/\omega$ where $\omega$ corresponds to the ground vibrational level frequency ($\hbar \omega/2=0.007$). Therefore this leads to an upper bound for the autoionization probability $P_{\text{auto}} \sim \pi \Gamma /\omega = 0.002$. Finally, the smallest ratio is $P_d/P_{\text{auto}} \sim 0.5$, where the upper bound autoionization probability was used. This ratio should more likely be around 2-3 and probably even higher in our case for which the CO bond is allowed to vibrate and more avoided crossings are present. This concludes our discussion on autoionization and gives a qualitative idea of how much our DR cross section is overestimated in the present study.
3.4.3 Conclusion and perspectives

The theoretical DR cross-section obtained in the previous study [102] was smaller by a factor 2-3 than the lowest measured experimental cross-section. However, the previous theory did not account for vibration along the CO coordinate, and the main purpose of the present study was to assess the validity of the frozen CO approximation employed there. It suggests that the CO vibration does not play a significant role in the DR process at energies below 0.1 eV, but starts to be important at higher energies, when the total energy of the ion+electron system approaches that of the first excited CO vibrational mode. This study suggests also that reduced dimensionality can be used in DR studies of small polyatomic ions as long as one includes (1) the dissociative coordinate and (2) the vibrational coordinates responsible for the highest probability of electron capturing. For HCO+ the dominant dissociative coordinate is the CH bond (or $R_{CH}$), whereas the vibrational coordinates responsible for the electron capture are $\theta$ and $\varphi$. Comparing with our previous study [102], the effect of the CO vibration seems to be larger for DCO+, which can be explained by a larger D/CO mass ratio.

In the present and previous theoretical studies, it was assumed that $s$- and $p$-wave-dominated eigenchannels are not mixed. This is justified to some extent by the fact that the \textit{ab initio} energies used here account for the mixing, at least, at static geometries of the ion. However, in the dynamical framework of electron-ion collisions, the energy eigenstates obtained in the \textit{ab initio} calculation could in principle be strongly mixed due to the perma-
nent dipole moment (∼3.9 debye) of HCO⁺. The effect of the ionic dipole interaction with the electron is studied in details in the next chapter.
CHAPTER 4
DISSOCIATIVE RECOMBINATION OF HCO$^+$ INCLUDING ITS PERMANENT DIPOLE MOMENT

4.1 Modeling the permanent dipole moment of HCO$^+$ ion

4.1.1 Aim of the study

The theoretical description of the DR process of HCO$^+$ has proved to be far from simple. In spite of the fact that the recent theoretical studies [102, 29] have (1) demonstrated that the non-Born-Oppenheimer Renner-Teller coupling plays an important role in DR of HCO$^+$ and (2) considered all internal degrees of freedom in the treatment (see Chapter 3), the obtained theoretical cross-section is still smaller than the lowest experimental results (especially at small incident electronic energy, as shown in Fig. 3.10). Although experimental data differ significantly from each other, it seems that existing DR theory is still missing some important effect(s) for the DR of HCO$^+$. One of the possible improvements proposed in the present chapter is to account for the relatively large permanent electric dipole moment of HCO$^+$, which has been estimated in several studies [135, 18, 136] with values ranging from 3.3 to 4.0 debye (1 debye is 0.393430 atomic units). We adopt the value $D = 3.9$ debye from
Therefore this study is devoted to (1) the development of a theoretical approach that accounts for the electron interaction with the electric dipole moment in addition to the usual Coulomb interaction between the ion and the electron and (2) an application of the approach to DR of HCO$^+$. One of the main theoretical techniques used in our study of DR is Multi-channel Quantum Defect Theory (MQDT) [119, 48, 68, 8], introduced in Section 2.3. The standard version of MQDT [119, 8] was initially developed for pure Coulomb potentials with centrifugal terms, i.e. potentials with asymptotic behavior $V(r) = -\frac{1}{r} + \frac{l(l+1)}{2r^2}$, where $r$ is the radial electronic coordinates and $l$ is an integer. A first generalization to the problem of combined Coulomb and attractive or repulsive dipole potentials was introduced by Bely [17] in the context of electron scattering from He$^+$, where the ionic dipole moment produces electron escape channels characterized by radial $r^{-2}$ potentials having non-integer or even complex values of $l$. Analytical studies [47, 50] have generalized MQDT to account for the interaction between colliding partners behaving asymptotically as $\alpha/r^p$, with arbitrary $\alpha$ and positive $p = 0, 1, \text{or } 2$. Subsequent studies [131, 100, 101, 38, 37, 22] have developed applications to a broader class of long-range potentials, e.g. with $p = 3, 4$ and 6, as well as to more general numerically-specified potentials. In particular, the generalized theory (GMQDT) is well-suited for the present problem, where we want to account for the dipole-electron interaction in addition to the regular Coulomb potential at large electronic distances. The GMQDT itself is developed in detail in [47, 50]. Thus, we only summarize the main formulas of GMQDT in the present chapter and describe the adaptations to the theory that are needed in order to represent
DR of molecular ions with a permanent electric dipole moment. As is shown below, the new theoretical DR method to account for the dipole moment is very similar to the one developed in Chapter 3, with comparatively small changes in the formulas for the reaction matrix \( \hat{K} \) and in the closed-channel elimination procedure. For this reason, we only remind succinctly the main steps of the approach, described in detail in Chapter 3, and rather stress the main differences between both studies.

Electron scattering from neutral polar molecules was treated in a frame transformation methodology by Clark [25] and tested quantitatively by Clark and Siegel [26]. The theoretical formulation and the subsequent work of Fabrikant [34] bears similarities to the present one, in that the combined dipole plus centrifugal potentials for the scattering electron are first diagonalized to find the scattering eigenchannels.

### 4.1.2 Hamiltonian of the problem

In order to model the DR process of HCO\(^+\), we write explicitly the Hamiltonian of the ion-electron system as \( \hat{H} = \hat{H}_{\text{ion}} + \hat{H}_{\text{elec}} \), where \( \hat{H}_{\text{ion}} \) is the ionic Hamiltonian and \( \hat{H}_{\text{elec}} \) describes the electronic Hamiltonian and the electron-ion interactions. Here, \( \hat{H}_{\text{ion}} \) is the vibrational Hamiltonian of the molecular ion expressed in (3.1) using a Jacobi system of coordinates \( Q = \{ R_{\text{CO}}, R_{\text{GH}}, \theta, \varphi \} \), where \( R_{\text{CO}} \) and \( R_{\text{GH}} \) represent respectively the distances C-O and G-H (\( G \) is the center of mass of the CO bond), \( \theta \) is the angle between the vectors \( \overrightarrow{OC} \) and \( \overrightarrow{GH} \), \( \varphi \) is the angle of azimuthal orientation of the bending. Here, we consider \( R_{\text{GH}} \) as an adiabatic
coordinate representing the dissociation path. In the approach developed in Chapter 3, we
neglected the rotational motion of the CO bond in space, but included relative rotation of H
and CO. This approximation\(^1\) is justified by a large CO/H mass ratio. As a result of the ap-
proxi mation, the projection \(m_\varphi\) of the angular momentum \(\hat{L}\) on the CO axis is conserved. We
solve the Schrödinger equation for the ionic Hamiltonian, keeping the \(R_{GH}\) coordinate fixed.
This procedure determines vibrational wave functions \(\Phi_{m_\varphi,l}(R_{GH}; R_{CO}, \theta, \varphi)\) and corres-
ponding adiabatic energies \(U_{m_\varphi,l}(R_{GH})\) that depend parametrically on \(R_{GH}\). Index \(l\) numerates
the ionic vibrational states for a given \(m_\varphi\).

For the electronic part \(\hat{H}_{\text{elec}}\) of the total Hamiltonian \(\hat{H}\), it was shown [88] that only
electronic states \(s\sigma, p\pi^-, p\sigma, \text{and } p\pi^+\) have a significant contribution to the HCO\(^+\) DR cross-
section. We include them into the treatment and include the \(d\sigma\) states in addition, although
they have a relatively small effect in DR of HCO\(^+\). Therefore, the electronic Hamiltonian
\(\hat{H}_{\text{elec}}(Q)\) for a fixed value of \(Q\) and integrated over all electronic coordinates can be written
as an infinite number (Rydberg series) of matrices \(5 \times 5\) (see equation (3.12)). In the matrix,
the Renner-Teller couplings between \(p\pi^-, p\sigma\) and \(p\pi^+\) states are explicitly taken into account
via the coupling coefficients \(\gamma\) and \(\delta\). On the other hand, no coupling\(^2\) between \(s\sigma, p\sigma\) and
d\(d\sigma\) states was accounted for, because these states are not coupled by the Coulomb field at
large distances \(r\) in the basis of electronic states with a definite angular momentum. Now, if
we include the electron-dipole interaction as well, it will introduce a coupling between states

\(^{1}\)However, the approximation may lead to an underestimated DR cross-section if the rotational auto-ion-
izing resonances in HCO play an important role in DR.

\(^{2}\)Except at short range in the \textit{ab initio} calculation of the potential surfaces.
with different electronic angular momenta. The coupling elements between the $s\sigma$, $p\sigma$ and $d\sigma$ states (integrated only over the electron angular coordinates) behaves as $1/r^2$ at $r \to \infty$. To account such a behavior in the framework of ordinary (Coulomb field only) MQDT, one would have to use energy-dependent non-diagonal matrix element of the quantum defect matrix. For this reason, we cannot use the specified basis of electronic states to represent the electronic Hamiltonian of the system. However, we adopt the logic of [25, 26, 34] and utilize a different electronic basis for which the non-diagonal coupling elements would vanish at large distances\(^3\). We stress the two approximations used here: (1) We consider the dipole moment for all possible geometries of HCO\(^+\) ion to be constant and equal to the permanent dipole moment $D$ of HCO\(^+\) at its equilibrium position (linear configuration, $\theta = 0$). (2) As we already mentioned, $d\sigma$ states have a minimal influence on the DR process, so that we can neglect any coupling with these states and concentrate our attention uniquely on

\[ V(r) = -\frac{1}{r} + \frac{D\cos \theta}{r^2} \]

Figure 4.1: Schematic representation of the effect of the large permanent dipole of HCO\(^+\) on a Rydberg electron.

\(^3\)More precisely, the non-diagonal coupling elements should at least decrease with $r$ faster than $1/r^2$. 

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the coupling between \( p\sigma \) and \( s\sigma \) states. In fact, we have verified the validity of the second approximation by comparing results with and without inclusion of couplings between \( p\sigma \) and \( d\sigma \) states, and we find that the inclusion of the coupling with the \( d\sigma \) states has a negligible effect on the final cross-section. To enhance the clarity of our presentation, we do not include the coupling with the \( d\sigma \) states in the discussion below. With the mentioned approximations, the \( s\sigma-p\sigma \) part of the electronic Hamiltonian \( \hat{H}_{\text{elec}}(Q, r) \) has the form

\[
\hat{H}_{\text{elec}}(Q, r) = \begin{pmatrix}
-\frac{1}{r} & \frac{<Y_0^0|D\cos\theta_d|Y_1^0>}{r^2} \\
\frac{<Y_1^0|D\cos\theta_d|Y_0^0>}{r^2} & -\frac{1}{r} + \frac{1}{r^2}
\end{pmatrix}.
\] (4.1)

The above matrix is coupled to the two \( p\pi^\pm \) states by the Renner-Teller coupling between \( p\pi \) and \( p\sigma \) states. The matrix elements for the coupling were given and discussed in Section 3.2.

Under the assumption that \( D \) is constant for any \( Q \), the numerator in the non-diagonal elements can be easily evaluated and we find \( \tilde{D} = <Y_0^0|D\cos\theta_d|Y_1^0> = \frac{D}{\sqrt{3}} \) (here the angle \( \theta_d \) is the azimuthal angle of the electron in the molecular coordinate system). When we diagonalize the \( 2 \times 2 \) Hamiltonian in (4.1), we find two new electronic states \( |\tilde{s}\sigma\rangle \) and \( |\tilde{p}\sigma\rangle \), which are superpositions of \( |s\sigma\rangle \) and \( |p\sigma\rangle \) with a projection of the angular momentum still equal to zero. The radial functions related to these new channel eigenstates are solutions of two Schrödinger equations with effective potentials different than for \( |s\sigma\rangle \) and \( |p\sigma\rangle \) states

\[
V_\pm(r) = -\frac{1}{r} + \frac{1 \pm \sqrt{1 + 4\tilde{D}^2}}{2r^2}.
\] (4.2)
Figure 4.2: Coulomb potentials $V_{l=0}(r)$ and $V_{l=1}(r)$ for integer values of the angular momenta $l = 0, 1$. The inclusion of the permanent dipole moment of HCO$^+$ produces two new eigenchannels $|\tilde{p}\sigma\rangle$ and $|\tilde{s}\sigma\rangle$, with associated potentials $V_+(r)$ and $V_-(r)$, respectively. On one hand, the centrifugal barrier increases for $V_+(r)$ potential, on the other hand, the potential $V_-(r)$ is more attractive than the corresponding potential for a usual spherical wave.

The potentials $V_+(r)$ and $V_-(r)$, presented in Fig. 4.2, are respectively related to the channels $|\tilde{p}\sigma\rangle$ and $|\tilde{s}\sigma\rangle$. The effective potential for $|\tilde{p}\sigma\rangle$ is more repulsive than the one for $|p\sigma\rangle$, the effective potential for $|\tilde{s}\sigma\rangle$ is more attractive than the one for $|s\sigma\rangle$. We use the notations $|\tilde{p}\sigma\rangle$ and $|\tilde{s}\sigma\rangle$ for the new channel states because the mixing between $p\sigma$ and $s\sigma$ states is not very strong so that the new states are still mainly composed from their respective original states (around 75%).

Changing electronic states from $|p\sigma\rangle$, $|s\sigma\rangle$ to $|\tilde{p}\sigma\rangle$ and $|\tilde{s}\sigma\rangle$, the $5 \times 5$ electronic Hamiltonian $\hat{H}_{\text{elec}}(Q)$ including the five states $|\tilde{p}\sigma\rangle$, $|\tilde{s}\sigma\rangle$, $|d\sigma\rangle$, and $|p\pi^\pm\rangle$ has the same form as the
one given in (3.12) if we change quantity $E_\sigma$ to $E_\tilde{\sigma}$ to keep consistency in notations. The coefficients $\gamma$ and $\delta$ are obtained from the \textit{ab initio} potential energy surfaces $V_{\pi',\pi'',\sigma}(Q)$ \cite{88} using the same formulas than in Chapter 3, where the states denoted as $p\pi'$ and $p\pi''$, are respectively symmetric and antisymmetric superposition of $|p\pi^+\rangle$ and $|p\pi^-\rangle$ with respect to reflexion in a plane containing the molecular axis. Therefore, the diagonalization of $\hat{H}_{\text{elec}}(Q)$ is accomplished by the same unitary matrix $\hat{U}$ than the one in (3.13).

4.1.3 Quantum defects and reaction matrix for the $-1/r \pm A/r^2$ potential

One more difference with the treatment of \cite{102, 29} is the way the quantum defects functions $\mu_i(Q)$ and the reaction matrix $\hat{K}(Q)$ are evaluated from the \textit{ab initio} potential surfaces of HCO. The evaluation of quantum defects $\mu_i(Q)$ in \cite{88, 102, 29} is made based on the Rydberg formula, which assumes an integer and non-negative partial wave quantum number and the asymptotic effective potential for the electron-ion interaction of the form $V(r) = -\frac{1}{r} + \frac{\lambda(\lambda+1)}{2r^2}$ with $\lambda$ an integer usually denoted $l$. From (4.2) it is clear that the corresponding values of $\lambda$ are not integer numbers: they are obtained from the equation $\lambda(\lambda + 1) = 1 \pm \sqrt{1 + 4\tilde{D}^2}$. Introducing the positive $\Delta_+ = 5 + 4\sqrt{1 + 4\tilde{D}^2}$ and negative $\Delta_- = 5 - 4\sqrt{1 + 4\tilde{D}^2}$ quantities,
the new "partial wave" quantum numbers are

\[
\lambda_{\rho\sigma} = \frac{-1 + \sqrt{\Delta}}{2},
\]
\[
\lambda_{\sigma\sigma} = \frac{-1 \pm i \sqrt{-\Delta}}{2}, \tag{4.3}
\]

where \(\lambda_{\rho\sigma}\) is real and \(\lambda_{\sigma\sigma}\) is complex. Therefore, the standard quantum defect treatment cannot be applied. Below, we summarize the main ingredients of the generalized quantum defect theory as formulated in [47, 50].

We start with a one-channel problem represented by the following equation, where \(\lambda\) is a complex number\(^4\)

\[
\left( -\frac{1}{2} \frac{d^2}{dr^2} + \frac{\lambda(\lambda + 1)}{2r^2} - \frac{1}{r} - \epsilon \right) f(\epsilon, \lambda, r) = 0. \tag{4.4}
\]

The equation has two independent solutions\(^5\) behaving asymptotically for \(\epsilon < 0\) as \(f^\pm(\epsilon, \lambda, r) \to e^{\pm \nu r} e^{\pm \nu}, \) where \(\nu = \frac{i}{\kappa} = (-2\epsilon)^{-1/2}.\) From these two functions, one can construct the regular and irregular solutions, respectively denoted \(f(\epsilon, \lambda, r)\) and \(g(\epsilon, \lambda, r)\). In our case, the only basic requirement for \(g(\epsilon, \lambda, r)\) is that it should lag 90° with respect to the regular solution \(f(\epsilon, \lambda, r)\). More generally, great care has to be taken to construct the irregular solution for certain types of potentials\(^6\), in a way that the solution remains independent on threshold effects. This construction procedure is discussed for instance in [50]. The asymptotic ex-

---

\(^4\)We stress that although \(\lambda\) can be complex, the factor \(\lambda(\lambda + 1)\) is always real, so that equation (4.4) can have real solutions.

\(^5\)For \(f^\pm\) we use definitions of [50]. See equation (3.7) of [50]. In contrast, \(f^\pm\) in [8] are defined differently, equation (2.38) in [8].

\(^6\)For instance pure dipole or repulsive Coulomb potential.
pansion of these solutions as a superposition of $f^{\pm}$ is obtained using the following general

formula, applied for instance on the regular $f(\epsilon, \lambda, r)$ function:

$$2ikf(\epsilon, \lambda, r) = W(f^-, f^+)(\epsilon, \lambda, r) - W(f^+, f^-)(\epsilon, \lambda, r). \tag{4.5}$$

The Wronskian $W(a, b)$ above is defined as

$$W(a, b) = a \frac{db}{dr} - b \frac{da}{dr}. \tag{4.6}$$

For the potential in equation (4.4), the solutions are confluent hypergeometric functions.

Using their asymptotic behavior at large $r$, we can write for $f$ [47] 

$$f(\epsilon, \lambda, r) = (\pi \kappa)^{-\frac{1}{2}} (\sin \beta D_\epsilon)^{-1} f^- - \cos \beta D_\epsilon f^+. \tag{4.7}$$

In the above expression, the factor $D_\epsilon$ is a monotonic function of $\epsilon$ that rescales the am-
plitudes of $f^{\pm}$ and the oscillating factors $\sin \beta$ and $\cos \beta$ are parameters responsible for the
energy-dependent mixing between the exponentially growing and decaying functions $f^{\pm}$.

The wave function for a bound state should decay exponentially at infinity. Therefore, the
condition for a bound state is simply $\sin \beta = 0$, or equivalently $\beta = \pi(n + 1)$ with $n = 0, 1, 2, ...$.

If $\lambda$ is a real number, $\beta$ is simply $\pi(\nu - \lambda)$. Specifically, if $\lambda$ is an integer $l$, it corresponds
to a pure Coulomb field with a centrifugal term and we recover the Rydberg formula for the
energy of bound states, namely $E = -0.5/(n + l + 1)^2$. In the general case when $\lambda = \lambda_R + i\alpha$
is a complex number, the formula for $\beta$ is more cumbersome [50]

$$\beta(\kappa, \lambda) = \pi(1/\kappa - \lambda_R) + \tan^{-1}[\tanh(\pi\alpha)\tan(y - \alpha \ln(2\kappa))],$$

(4.8)

where $y = \arg(\Gamma(2\lambda + 2)[\Gamma(\nu - \lambda)/\Gamma(\lambda + 1 + \nu)]^{1/2})$.

Having defined the regular solution, we can write the irregular solution using a similar procedure. The irregular solution $g(\epsilon, \lambda, r)$ is then given by

$$g(\epsilon, \lambda, r) = -(\pi\kappa)^{-1/2}(\cos \beta(D_\epsilon)^{-1}f^- + \sin \beta D_\epsilon f^+).$$

(4.9)

If we consider an additional short range potential in (4.4), the asymptotic solution will in general be written as a superposition of regular and irregular solutions $F(\epsilon, \lambda, r) = f(\epsilon, \lambda, r) - Kg(\epsilon, \lambda, r)$, where $K$ is a mixing coefficient. From (4.7) and (4.9) the asymptotic behavior of $F(\epsilon, \lambda, r)$ is easily derived. The requirement that the coefficient in front of the growing exponential must vanish in order for the solution to be physically acceptable determines $K$ as $K = -\tan(\beta)$.

Because HCO$^+$ has a dipole moment, evaluation of the reaction matrix $\hat{K}$ from ab initio energies has to be modified (in comparison with our previous study [102, 29]). Namely, the reaction matrix $\hat{K}$ in the diagonal form and at fixed nuclear positions is written in terms of $\beta(\kappa, \lambda)$ as $K_{ii} = -\tan(\beta_i(\kappa_i, \lambda_i))$ for each channel $i$ (we have five of them as discussed above). Index $i$ at $\beta_i$ means that we use different formulas depending on the asymptotic behavior of the potential in the corresponding channel. The value of $\kappa$ is obtained from the
of HCO and HCO$^+$ [88] with $n = 4$ for $\tilde{s}\sigma$ state and $n = 3$ for other states. The $\hat{K}(Q)$ matrix in the basis of states $\tilde{s}\sigma$, $p\pi^-$, $\tilde{p}\sigma$, $p\pi^+$ and $d\sigma$ is obtained using the unitary transformation as discussed in [102], namely $\hat{K}(Q) = U^\dagger \tan(-\hat{\beta})U$.

4.2 Results and discussion

4.2.1 Cross-section calculation

Similarly to our previous study, we solve the vibrational Schrödinger equation for HCO$^+$ fixing the adiabatic coordinate $R_{GH}$ and obtain the eigenenergies $U_{m,\ell}(R_{GH})$ (adiabatic potentials) and the corresponding eigenstates $\Phi_{m,\ell}(R_{GH}; R_{CO}, \theta, \varphi)$ (adiabatic states). Then, we use $\Phi_{m,\ell}(R_{GH}; R_{CO}, \theta, \varphi)$ to obtain the reaction matrix $\mathcal{K}_{\{m,\ell,i\},\{m',\ell',i'\}}(R_{GH})$

$$\mathcal{K}_{\{m,\ell,i\},\{m',\ell',i'\}}(R_{GH}) = \langle \Phi_{m,\ell} | K_{i,i'}(Q) | \Phi_{m',\ell'} \rangle,$$

(4.10)

where the integral in the above expression is taken over the three coordinates $R_{CO}$, $\varphi$, and $\theta$. The resulting reaction matrix $\mathcal{K}_{j,j'}$ ($j \equiv \{m,\ell,i\}$) is multichannel and depends parametrically on $R_{GH}$. It is then used to obtain for each $R_{GH}$, the value positions $U_a(R_{GH})$ and widths $\Gamma_a(R_{GH})$ of autoionizing resonances of the neutral HCO molecule. The procedure of resonance search is standard and is discussed, for example, in [77]. The only difference is how the quantity $\beta(\kappa, \lambda)$ is calculated for states with non-integer $\lambda$. $\beta(\kappa, \lambda)$ is needed to
perform the closed-channel elimination procedure and evaluation of closed-channel mixing coefficients (see Subsection 2.3.3). The quantity $\beta(\kappa, \lambda)$ should be calculated using equation (4.8) for channels with non-integer $\lambda$. The obtained widths and positions of autoionizing resonances are used to calculate the electron-ion recombination cross-section as described in [102].

![Graph](image)

Figure 4.3: Calculated DR cross section for HCO$^+$ including dipole contribution (solid line) and the DR cross section for HCO$^+$ without the dipole contribution as a function of the incident electron energy. The experimental [89] (cross symbols) and previous theoretical [102] (dashed line) cross sections are also shown for comparison. The theoretical curves include a convolution over the experimental electron energy distribution.
4.2.2 Interpretation

Fig. 4.3 shows the cross section obtained in the present study. The inclusion of the electric dipole moment of HCO\(^+\) leads to an overall increase of about 50% for the cross section. Thus, inclusion of the electric dipole moment seems to improve the agreement with experiment. The agreement between theory and experiment is particularly good for electron energies between 0.06 eV and 0.3 eV. For larger energies, the experiment seems to have a large error bar (the experimental error bar is large possibly because the measured cross-section is small at higher energies). At energies below 0.06 eV the theoretical cross-section is below the experimental one by a factor of two approximately. The reasons for the difference are not clear and are discussed in details in the concluding Chapter 8.

We would like to discuss in detail the reason of the increase of the cross section comparing with the results of the previous theoretical approach [102, 29]. With the effect of the HCO\(^+\) electric dipole moment included, it seems reasonable to expect a higher cross section due to an additional coupling between \(s\sigma\) and \(p\sigma\) states introduced by the dipole term. However, a more detailed analysis shows that the coupling is not directly responsible for the increase of the cross section, but it acts rather in an indirect way through the Renner-Teller effect as described below. The cross section in the present study is calculated using autoionizing resonances. Therefore, the cross section is increased if the density or/and widths of resonances become larger with the inclusion of the electric dipole moment. The density of resonances is expressed as \(\frac{1}{\pi} \frac{d\beta}{dE}\). Therefore, we can compare the density of resonances by evaluating this
quantity using the updated formula for $\beta$. For the $p$-states, the quantities $\beta$ for the pure Coulomb and Coulomb+dipole interactions differ from each other by an energy-independent term. Therefore, the density of resonances produced by closed $p$-wave channels is the same in both treatments. For the $s$-states, analysis of the derivative of new $\beta(E)$ in (4.8) gives only negligible differences for pure Coulomb and Coulomb+dipole interactions. Thus, the higher observed cross section is caused uniquely by an increase in widths of autoionizing resonances. By inspecting different resonances, we have indeed found that the increase in the cross section is related to larger widths of $p$-resonances.

To apprehend this result, we introduce the averaged cross section $\langle \sigma \rangle$ for the electron capturing, which was suggested in [102]. For this purpose, we use the element $\langle v', i' | \hat{S} | v, i \rangle$ of scattering matrix describing the $|v, i \rangle \rightarrow |v', i' \rangle$ scattering process and we obtain

$$\langle \sigma \rangle = \frac{\pi}{2E_{el}} \left| \langle v', i' | \hat{S} | v, i \rangle \right|^2. \quad (4.11)$$

In the above formula, $i$ and $i'$ denote the electronic state, $v$ is the ionic ground state and $v'$ any vibrational state. The brackets $\langle \rangle$ mean that we average over autoionization Rydberg resonances attached to a single vibrational state $v'$. The formula (4.11) is valid for electronic energy $E_{el}$ lower than the difference in energy between $v'$ and $v$. We now apply the frame transformation to obtain

$$\langle \sigma \rangle = \frac{\pi}{2E_{el}} \left| \int \langle v' | Q \rangle S_{i'i'}(Q) \langle Q | v \rangle dQ \right|^2. \quad (4.12)$$
The main contribution in (4.12) is given by the integration over the asymmetric degenerate coordinates \((\rho, \varphi)\) introduced in Subsection 3.2.2. For this reason, we only integrate over degenerate displacement around the equilibrium configuration at \(Q_0\). The integration over \(\varphi\) is trivial since the vibrational functions have \(e^{\pm im\varphi}\) dependence and the cross section is simply
\[
\langle \sigma \rangle \approx \frac{\pi}{2E_{el}} \left| \int \langle v' | \rho \rangle S_{v'i}(Q) \langle \rho | v \rangle d\rho \right|^2.
\] (4.13)

Let us express the averaged cross section in (4.12) using the reactance matrix \(\hat{K}(Q)\). The short-range scattering matrix is related to the quantum defect matrix by \(\hat{S}(Q) = \exp(2i\pi \hat{\mu}(Q))\) (Subsection 2.3.3) and the short-range reactance matrix is related to the quantum defect matrix by \(\hat{K}(Q) = \tan(\pi \hat{\mu}(Q))\). Since the non-diagonal elements of the quantum defects are small close to the linear geometry (they vanish at the linear configuration), and considering that the ion in its ground state is most likely to be found in a configuration close to linearity, we can expand \(\hat{S}(Q)\) in first order in the radial asymmetric displacement \(\rho\) (Subsection 3.2.2) with a good level of accuracy when reporting in (4.12). Therefore, we get for the short-range scattering matrix
\[
\hat{S}(Q) \approx \exp[2i\pi \hat{\mu}(Q_0)] \left[ \hat{I} + 2i\pi \left( \frac{\partial \hat{\mu}}{\partial \rho} \right) \rho \right].
\] (4.14)

The partial derivative in (4.14) is taken at \(Q_0\). The constant factor on the right side in (4.14) does not contribute into the cross section since \(v\) and \(v'\) are orthogonal. The second term is related to the non-diagonal elements of the reactance matrix for small displacements by \(K_{ii'}(\rho) \approx \rho \pi \partial \mu_{ii'}/\partial \rho\) and gives another purely non-diagonal matrix when multiplied by
exp[2iπ\(\tilde{\mu}(Q_0)\)], for which the non-diagonal coefficients are actually multiplied by complex numbers of modulus unity. We conclude that the cross section (4.13) can also approximatively be written in term of the non-diagonal elements of the reactance matrix as

\[
\langle \sigma \rangle \approx \frac{2\pi}{E_{el}} \left| \int \langle v' | \rho \rangle K_{\ell^i}(Q) \langle \rho | v \rangle d\rho \right|^2.
\] (4.15)

Because the widths are related to the non-diagonal elements of the reaction matrix \(K_{ii'}(Q, E)\), we can investigate the non-diagonal elements to understand the reason for the increase of the cross section. In the diagonalized form, the elements of the reaction matrix are \(K_{jj'} = \tan(\pi \mu_j) \delta_{jj'}\) where the quantum defects \(\mu_j\) are obtained directly from \textit{ab initio} calculation for every internuclear configuration \(Q\) using (4.8). The old quantum defect are also obtained from the same \textit{ab initio} data but using the Rydberg formula. The new and old quantum defect are shown for comparison in Fig. 4.4 as a function of the Jacobi angle \(\theta\). As it can be seen from the figure, the new quantum defect for the \(\tilde{s}\sigma\) and \(\tilde{p}\sigma\) states differ from each other by a simple translation. The translation, which has no direct effect on widths of the \(\tilde{s}\sigma\) resonances (they are basically just shifted), has a drastic effect on the \(\tilde{p}\sigma\) states coupled to the \(p\pi\) states by the Renner-Teller effect.

It is possible to show that changing the basis for the reaction matrix from the eigenbasis (diagonal form of \(\tilde{K}(Q)\)) to the basis of the five states \(|\tilde{p}\sigma\rangle, |\tilde{s}\sigma\rangle, |d\sigma\rangle, \) and \(|p\pi^\pm\rangle\) discussed above, introduces a non-diagonal term \(K_{ii'}\) between \(\tilde{p}\sigma\) and \(p\pi^\pm\) that is directly proportional to the difference \(\tan(\mu_{\tilde{p}\sigma}) - \tan(\mu_{p\pi^\pm})\). From Fig. 4.4, it is evident that the difference
Figure 4.4: The figure shows quantum defects for the new states $\tilde{s}\sigma$ and $\tilde{p}\sigma$ calculated from the \textit{ab initio} electronic energies using $\beta$ of equation (4.8) as well as the old quantum defect (calculated using $\beta$ determined by a pure Coulomb potential) as a function of the Jacobi angle $\theta$. The two other Jacobi coordinates $R_{CO} = 2.00$ a.u. and $R_{GH} = 3.27$ a.u are fixed at their equilibrium positions for $\theta = 0$.

is increased for the new $\tilde{p}\sigma$ state comparing with the difference for the old (without dipole contribution) $p\sigma$ state. The coupling element between $p\pi^+$ and $p\pi^-$ are only slightly affected by the translation of the quantum defect. The latter effect is a rather familiar feature of the quantum defect formalism. The presence of the dipole moment induces a strong anistropy in the electronic potential, which reflects in an increase of the difference in quantum defects and stronger electronic couplings.

The approximate width for the two coupling elements in the new and old treatments can be estimated using equation (4.15). The result is shown in Fig. 4.5. The coupling between $\tilde{p}\sigma$ and $p\pi^\pm$ is clearly enhanced compared with the previous treatment by about 50%. On
Figure 4.5: The figure shows the absolute value square of the non-diagonal elements $|K_{ii'}(Q,E)|^2$ of the reaction matrix as a function of the bending angle $\theta$ around equilibrium values of $R_{CO}(2.00 \, a.u)$ and $R_{GH} (3.27 \, a.u)$.

The other hand, the coupling between the $p\pi^+$ and $p\pi^-$ states is changed only a little (less than 5%). Thus, we conclude that the increase of the coupling between $\tilde{p}\sigma$ and $p\pi^\pm$ states is responsible for the higher cross-section in the present approach including the electric dipole moment of HCO$^+$. Finally, we see that such a rough estimation of the increase in resonance widths is compatible with the overall increase of the final cross section obtained from the full calculation. The latter fact reflects the validity of the interpretation.
4.2.3 Concluding remarks

We have investigated the role of the permanent electric dipole moment of HCO$^+$ in the dissociative recombination of the ion with low energy electrons. We found that the inclusion of the dipole moment increases significantly the coupling between the $p\sigma$ and $p\pi^\pm$ states and only a little the coupling between $p\pi^+$ and $p\pi^-$. This leads to an increase of the cross section for all collision energies below 1 eV by about 50%. The obtained theoretical cross section agrees well with the experimental data of [89] for energies between 0.06 and 0.3 eV. Although, the cross section is also increased for low energies ($< 0.06$ eV), the theoretical result is still below the experiment by about a factor of two. More theoretical and experimental work has to be done to clarify the reason for the remaining difference and we give a brief discussion on the perspectives and possible explanations for the discrepancies between our calculations and the experimental data in Chapter 8.

Finally, in the present study we assumed that the permanent dipole moment $D(Q)$ of HCO$^+$ does not depend on the geometry of the ion and is fixed at the value $D_0$ of $D(Q)$ at the equilibrium geometry. In a more accurate treatment, the variation of the dipole moment $D$ in (4.1) with coordinates $Q$ would give a slightly different $Q$-dependence of $\beta$ in (4.8) and the reaction matrix. The interval of relevant geometries that has to be considered for the variation of $D$ is limited to the geometries of the ground and the first excited vibrational levels of HCO$^+$. The expectation value of $D$ calculated for the ground and first excited vibrational levels would be very similar to each other and to $D_0$: The ground and first excited
states of HCO$^+$ are well described by the harmonic oscillator approximation. Therefore, the inclusion of the $Q$-dependence would give a much smaller effect on the total cross-section than the effect from $D_0$. The relative ratio of the two effects (from the $Q$-dependence and $D_0$) would be proportional in the present model to the degree of anharmonicity of the HCO$^+$ potential surface and, therefore, cannot explain the remaining difference between theory and experiment.
CHAPTER 5
SIMPLER APPROACH TO STUDY DISSOCIATIVE RECOMBINATION IN HIGHLY SYMMETRICAL POLYATOMIC MOLECULAR IONS: STUDY OF H$_3$O$^+$ AND H$_3^+$

5.1 Simplified model for electronic capture and calculated cross section

5.1.1 Introducing the model

The theoretical approach developed in recent years for DR in triatomic molecular ions takes into account vibrational, rotational, and nuclear spin degrees of freedom. The resulting cross-sections or rate coefficients provide detailed information about the way the DR process occurs, which rotational and vibrational states of the molecule participate and what are the final distribution of products. However, the numerical method is very demanding. The calculation of DR cross-sections for each new molecular ion is rather complicated and requires significant changes in the numerical code. It is thus desirable to capitalize on the insights gleaned about DR mechanisms, to formulate a simpler method that is able to give a correct
order of magnitude estimate for the DR cross-section in polyatomic ions. The attempts to use a simpler approach in triatomic molecules, that would still keep ingredients essential for the correct description of the vibronic interactions ions have been made in recent publications devoted to DR in HCO$^+$ and H$_3^+$ [102, 28, 70, 71, 30] and [77]. The present study is another step in developing a predictable theory of DR in polyatomic ions, but is similar in spirit to the ideas developed in [77, 102, 30, 70, 71], in which one makes simplified assumptions about the DR pathways and uses the normal mode approximation for the low-lying vibrational levels. The starting point of the approach$^1$ is the ab initio potential surfaces $U^+(Q)$ of the H$_3$O$^+$ ion close to its equilibrium geometry and of several excited electronic molecular states of the neutral molecule H$_3$O. More precisely, we need molecular states which are predominantly responsible for the largest probability for the capture of an incident electron to form the autoionizing resonances of H$_3$O. We know from our previous study (Chapter 3) that the knowledge of accurate ab initio potential surfaces should in most cases be sufficient to describe the DR process and to obtain the DR cross-sections and rate coefficients.

Studies of DR in H$_3^+$ [77, 36] showed that at temperatures $T > 100$ K, the overall (averaged over resonances) DR rate is mainly determined by the capture of the electron into Rydberg states attached to excited vibrational levels of the molecular ion. Inclusion of the rotational structure at modestly higher temperatures does not appreciably change the overall DR rate. Therefore we only account for vibration of the ion (i.e., neglecting rotation) in the simplified method and assume that the excited vibrational modes are responsible for the electron

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$^1$The approach is similar to [77, 102, 28] but different from [70, 71] where experimental data was used.
capture. For molecules heavier than H$_2^+$, the approach should be valid even for temperatures less than 100 K. In this approach, we also assume that the predissociation is much faster than the autoionization once the electron is captured by the ion. This appears to be justified for all polyatomics at low energies, which in our view reflects the fact that there are so many vibrational modes that can be excited, that predissociation is a more probable outcome (for the Rydberg electron recollisions to pump energy into vibration) than for the electron to find that tiny phase space where it can vibrationally autoionize and escape from the ion. Using these assumptions, it is possible to find a simple way to estimate the DR cross section.

5.1.2 Calculation of the cross section

We assume that the ion is initially in the ground vibrational level $v$ and we neglect its rotation. The energy of the ground vibrational level is chosen to be the origin of the total energy. The incident electron with kinetic energy $E_{el}$ has an initial angular momentum projection $\Lambda$ on the molecular symmetry axis of the ion. Using the approximation suggested in [102] and already introduced in equation (4.11), we calculate the cross section $\langle \sigma \rangle$ for the electron capturing, where $\langle \sigma \rangle$ means that we evaluate the cross section averaged over autoionization Rydberg resonances attached to the vibrational state $v'$. For this purpose, we use the element $\langle v', \Lambda' | \hat{S} | v, \Lambda \rangle$ of scattering matrix describing the $|v, \Lambda \rangle \rightarrow |v', \Lambda' \rangle$ scattering process

$$
\langle \sigma \rangle = \frac{\pi}{2E_{el}} \left| \langle v', \Lambda' | \hat{S} | v, \Lambda \rangle \right|^2 \Theta((E_{v'} - E_v) - E_{el}).
$$

(5.1)
The Heaviside function in equation (5.1) means that the electron can only be captured into a Rydberg state attached to the vibrational state $v'$ with energy $E_{v'}$, if the total energy $E_v + E_{el}$ is smaller than $E_{v'}$. This leads to a sharp drop of the cross-section once the energy of the incident electron reaches the vibrational threshold\footnote{This effect has been experimentally observed for several triatomic molecules.}. If there are several vibrational states that can contribute to the total cross-section for the capturing, then a corresponding sum over $v'$ should be evaluated. The above formula allows us to estimate quickly the DR cross-section, if there is experimental spectroscopic [71] or \textit{ab initio} data, which can be used to obtain the scattering amplitude in equation (5.1). As it is demonstrated in [102, 70, 71] and below, it provides a reasonable agreement with the experiment for several molecular ions that we have considered so far.

In the next step, we apply the vibrational frame transformation

$$
\langle \sigma \rangle = \frac{\pi}{2E_{el}} \left| \int \langle v'|Q S_{N',\Lambda}(Q)\langle Q|v \rangle dQ \right|^2 \Theta((E_{v'} - E_v) - E_{el}) ,
$$

(5.2)

where $Q$ represents compactly the coordinates of all nuclei and $S_{N',\Lambda}(Q)$ are elements of the clumped-nuclei scattering matrix $\hat{S}(Q)$. The matrix $\hat{S}(Q)$ depends on $Q$ and can be written in terms of the quantum defect matrix as $\hat{S}(Q) = \exp [2i\pi \hat{\mu}(Q)]$. For small vibrations, we can expand the quantum defect matrix to first order over small displacements $Q_i$ around $Q = 0$,

$$
\hat{\mu}(Q) = \hat{\mu}(0) + \sum_i \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right) Q_i .
$$

(5.3)
Here and below, all partial derivatives are assumed to be taken at the equilibrium position of the ion. Then, the scattering matrix is expressed as

\[ \hat{S}(Q) = \exp[2i\pi \hat{\mu}(0)] \exp \left[ 2i\pi \sum_i \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right) Q_i \right] . \] (5.4)

We expand the exponential term on the right side to first order

\[ \hat{S}(Q) = \exp[2i\pi \hat{\mu}(0)] \left( \hat{I} + 2i\pi \sum_i \left( \frac{\partial \hat{\mu}}{\partial Q_i} \right) Q_i \right) , \] (5.5)

where we introduced the identity matrix $\hat{I}$. In (5.2), the ionic vibrational functions in the bracket are orthogonal to each other. Therefore, the constant terms in equation (5.5) for the $\hat{S}(Q)$ matrix is not contributing into the cross section of equation (5.2). Furthermore, in the case of degenerate electronic energies at equilibrium geometry of the ion, the matrix $\exp[2i\pi \hat{\mu}(0)]$ is proportional to $\hat{I}$, with a coefficient of proportionality of modulus unity. Hence, combining (5.2) and (5.5), we finally obtain

\[ \langle \sigma \rangle = \frac{2\pi^3}{E_{el}} \sum_i \left( \frac{\partial \mu_{\Lambda \Lambda'}}{\partial Q_i} \right) \langle v'|Q_i|v \rangle^2 \Theta(E'_v - E_v - E_{el}) . \] (5.6)

Equation (5.6) is quite general and can be used to calculate the electron capturing cross section for different molecular ions with degenerate electronic states at equilibrium geometry. The above simple formula for the DR cross-section allows us to estimate the accuracy $\Delta \sigma/\sigma$ of the theoretical result, i.e. from the accuracy of $ab\ initio$ calculation of the potential surfaces.
(quantum defects): \( \Delta \sigma / \sigma \sim 2 \Delta \mu'_Q / \mu'_Q \sim \Delta \epsilon'_Q / \epsilon'_Q \), where the primes mean the derivatives (actually, the gradients for multidimensional vibrations) with respect to \( Q \), \( \epsilon \) is the energy difference between the ionic and neutral potential surfaces of the molecule. The above formula linking the accuracy of \textit{ab initio} and cross-section calculation is quite important. It shows that for cross-section calculation, the relative, not the absolute, accuracy of \textit{ab initio} calculations is important. The accuracy of \textit{ab initio} calculation of gradients of potential surfaces is usually significantly better than the accuracy of energies \( \Delta \epsilon \).

The actual DR cross-section is in general smaller than the cross-section for the electron capturing obtained in the way described above. The reionization should decrease\(^3\) it. Once the electron is captured, the branching ratio between predissociation and autoionization probabilities determines the actual DR cross-section. The predissociation probability is determined by the strength of coupling between the state \( |1_i, \Lambda'\rangle \) formed in the collision with other states \( |v''_i, \Lambda''\rangle \). Our approach based on the normal mode and the S-matrix analysis gives a good estimate of the predissociation probability, which is similar in spirit to the one described in (5.1) for the electron capture. We view the vibrating molecule (after the electron is captured) as a set of harmonic oscillators with one mode excited by the electron impact. The modes are coupled to each other by a coupling which is derived from the variation of the quantum defects.

\(^3\)On the other hand, the “complex multichannel resonance phenomenon”, familiar from multichannel Rydberg spectroscopy (MQDT) [69, 8], can lead to enhancements significantly higher than the simple excitation of unperturbed Rydberg resonances attached to the first excited state.
5.2 The Jahn-Teller effect

We already discussed the Renner-Teller effect in Subsection 3.2.2, where we presented the DR process of the linear triatomic ion HCO$^+$. We now introduce another non Born-Oppenheimer effect that occurs in highly symmetric molecules. More precisely, we study the closed shell H$_3^+$ and H$_3$O$^+$ ions when they recombine with a low energy electron, to form the unstable molecules H$_3^*$ and H$_3$O$^*$. We use H$_3^+$ to illustrate\textsuperscript{4} the Jahn-Teller effect, since its symmetry is more obvious to apprehend than the symmetry of H$_3$O$^+$. The point group of the H$_3^+$ molecule is $D_{3h}(M)$ (see Chapter 6), with two doubly degenerate irreducible representation $E'$ and $E''$. Therefore, at the equilateral equilibrium configuration of the three hydrogen atoms, the point group representing the electronic Born-Oppenheimer Hamiltonian is also $D_{3h}(M)$ and the electronic states can be degenerate. In our case, these degenerate states are Rydberg states of the outside electron with either positive or negative projections of the angular momentum on the symmetrical axis of the molecule. Still, one should bear in mind that, in contrary to the study on HCO$^+$, the projection of the angular momentum on the symmetry axis of the system is not a good quantum number, even at the symmetric configuration of the ion. Nevertheless, if we restrict the study to the sub-space of $p$-electrons, the $p\pi^+$ and $p\pi^-$ states are degenerate at the $D_{3h}(M)$ configuration. If the nuclei are displaced from equilibrium in an asymmetrical way (thus breaking the equilateral triangular geometry of the molecule), the group $D_{3h}(M)$ is not anymore the symmetry group of the electronic Born-Oppenheimer Hamiltonian. On that account, the level of symmetry is lowered, and the new point group

\textsuperscript{4}The Jahn-Teller effect in H$_3$O$^+$ is introduced in Subsection 5.3.2.
becomes $C_s(M)$, with two one dimensional irreducible representations $A'$ and $A''$. Hence, the degeneracy is broken and the electronic energies are splitted. We understand the reason why the Born-Oppenheimer approximation is very poor in this situation. We mentioned earlier that the energies between two electronic states have to be relatively large compared to the separation in vibrational energies for the Born-approximation to be valid. This can obviously not be the case when degenerate electronic states are present, since the electronic energies are situated close to each other, even at distorted geometry. We have already studied such a case in Chapter 3 for the linear chain molecule HCO\(^+\), via the Renner-Teller effect. In contrary to the Renner-Teller effect, for which the rotational term $\hat{T}_{\text{rot}}$ was dominant, the dominant term in the Jahn-Teller effect is the vibrational kinetic operator $\hat{T}_{\text{vib}} = \frac{1}{2} \sum_r \hat{P}_r^2$, where the summation runs over the different normal modes. In the following development, we introduce a simplified model suggested by Moffit and Liehr [104] and Longuet-Higgins [91], in which a parametrized Hamiltonian describing the coupled states is introduced.

First, we start with the pair of real adiabatic degenerate electronic states $(\psi^{(a)}_{\text{elec}}, \psi^{(b)}_{\text{elec}})$ at the equilibrium configuration of the nuclei. Then, we construct the following linear combinations

\[
\psi^{(\pm)}_{\text{elec}} = \frac{1}{\sqrt{2}} (\psi^{(a)}_{\text{elec}} \pm i \psi^{(b)}_{\text{elec}}).
\]  

(5.7)
The transformation properties are then simply

\[ C_3 \psi_{\text{elec}}^{(\pm)} = \exp(\mp i2\pi/3)\psi_{\text{elec}}^{(\pm)} \]  

(5.8)

\[ \sigma_v \psi_{\text{elec}}^{(\pm)} = \psi_{\text{elec}}^{(\mp)} \]  

(5.9)

where \( C_3 \) is the rotation by \( 2\pi/3 \) around the molecular symmetry axis of the ion, and \( \sigma_v \) is the reflection through a plane containing this axis of symmetry. Using solely symmetry arguments, we can now determine how the energies of the degenerate electronic states split when the molecule is distorted asymmetrically from equilibrium. Assuming that the degenerate electronic energy at the symmetrical configuration is not close from any other electronic energies, we can consider to a good approximation that the two states \( \psi_{\text{elec}}^{(+)} \) and \( \psi_{\text{elec}}^{(-)} \) perturb one and another to form the correct adiabatic states at displaced geometry. Considering this fact, the electronic Hamiltonian \( \hat{H}_{\text{elec}} \) in this basis would have coefficients of the form

\[ V_{++} = \int \psi_{\text{elec}}^{(\pm)\ast} \hat{H}_{\text{elec}} \psi_{\text{elec}}^{(\pm)} dq ; \quad V_{--} = \int \psi_{\text{elec}}^{(\pm)\ast} \hat{H}_{\text{elec}} \psi_{\text{elec}}^{(\pm)} dq, \]

\[ V_{+-} = \int \psi_{\text{elec}}^{(\pm)\ast} \hat{H}_{\text{elec}} \psi_{\text{elec}}^{(\mp)} dq ; \quad V_{++} = \int \psi_{\text{elec}}^{(\pm)\ast} \hat{H}_{\text{elec}} \psi_{\text{elec}}^{(\pm)} dq, \]  

(5.10)

where \( q \) denotes compactly all electronic coordinates. The latter coefficients depend of course on the position of the nuclei, but the Hamiltonian \( \hat{H}_{\text{elec}} \) remains totally symmetric under the operations of the \( D_{3h}(M) \) group. From equations (5.8) and (5.10), we deduce that \( C_3 \) leaves \( V_{++} \) and \( V_{--} \) unchanged, multiply \( V_{+-} \) by \( \omega^2 \) and \( V_{++} \) by \( \omega \) (\( \omega = e^{2i\pi/3} \)). The operation \( \sigma_v \) interchanges \( V_{++} \) and \( V_{--} \) on one hand and \( V_{+-} \) and \( V_{++} \) on the other hand. We can
expand these later coefficients in Taylor series truncated to order two in the degenerate normal coordinates. We consider the set of normal coordinates \((Q_+, Q_-)\), which transform according to the \(E\) irreducible representation of \(D_{3h}(M)\) in the following way:

\[
C_3Q_+ = \omega^2 Q_+ ; \quad \sigma_v Q_+ = Q_- \quad \text{(5.11)}
\]
\[
C_3Q_- = \omega Q_- ; \quad \sigma_v Q_- = Q_+ \quad \text{(5.12)}
\]

Using these transformations, it is easy to see that the following form of the electronic matrix elements satisfy the above symmetry requirements

\[
V_{++} = V_{--} = V_0 + V_{++}^+ Q_+ Q_- \quad \text{(5.13)}
\]
\[
V_{+-} = V_{+}^+ Q_- + V_{+}^- (Q_+)^2 \quad \text{(5.14)}
\]
\[
V_{-+} = V_{+}^+ Q_+ + V_{+}^- (Q_-)^2 \quad \text{(5.15)}
\]

where \(V_0, V_{+}^+, V_{++}^+\) and \(V_{+-}^-\) are molecular parameters that can be calculated by differentiating the matrix elements of (5.10) with respect to \(Q_+\) and \(Q_-\). When we diagonalize the matrix, we obtain two eigenvalues

\[
U_{a,b} = V_0 + V_{++}^+ \rho^2 \pm \rho \sqrt{(V_{+-}^+)^2 + (V_{+-}^-)^2 \rho^2 + 2V_{+-}^+ V_{+-}^- \rho \cos 3\varphi} \quad \text{(5.16)}
\]

In the latter expression, \(a\) corresponds to + sign and \(b\) to – sign. Also, we introduced the module \(\rho\) and the angle \(\varphi\) in such a way that \(Q_{\pm} = \rho e^{i\pm\varphi}\). The eigenenergies in (5.16) have
corresponding electronic eigenfunctions

\[ \phi_{\text{elec}}^{(a)} = \frac{1}{\sqrt{2}}(e^{i\theta}_1 \psi_{\text{elec}}^{(+)} + e^{-i\theta}_1 \psi_{\text{elec}}^{(-)}) , \quad (5.17) \]

\[ \phi_{\text{elec}}^{(b)} = \frac{i}{\sqrt{2}}(e^{i\theta}_2 \psi_{\text{elec}}^{(+)} - e^{-i\theta}_2 \psi_{\text{elec}}^{(-)}) , \quad (5.18) \]

where we introduced the geometry dependent phase factor \( e^{i\theta} = V_{++}/|V_{+-}| \). If we express the non-diagonal element \( V_{+-} \) in (5.15) as a function of \( \rho \) and \( \varphi \), we obtain

\[ V_{+-} = V_{+-}^+ \rho e^{i\varphi} + V_{+-}^- \rho^2 e^{-2i\varphi} . \quad (5.19) \]

Now, restricting the non-diagonal element in (5.19) to first order in \( \rho \), we obtain \( \theta = \varphi \) in (5.17) and (5.18), as well as \( U_{a,b} = V_o \pm |V_{+-}^+| \rho \) in (5.16), where \( V_o \) is the electronic energy at equilateral geometry (\( \rho = 0 \)). First, the eigenenergies in (5.16) and the electronic eigenfunctions in (5.17) and (5.18) should correspond to the adiabatic energies and to the real Born-oppenheimer electronic functions, respectively. Therefore, their form can be compared with actual \( \textit{ab initio} \) calculations (Sections 5.3 and 5.4). Second, we notice that at small displaced geometry \( U_b < V_o \), which implies that the symmetry geometry is not anymore the equilibrium configuration. This important result comes from the fact that the Jahn-Teller effect is linear, in contrary with the quadratic Renner-Teller effect for which the equilibrium geometry could still possibly remain at the linear configuration\(^5\). The general form of the potential in (5.16) is depicted in Fig. 5.1 as a function of \( \rho \) and \( \varphi \). Notice the conical in-

\(^5\)The equilibrium configuration can also be shifted for linear molecules, as we saw for the lowest 2p state potential of HCO in Fig. 3.2.
intersection at \( \rho = 0 \). If we continue increasing the coordinate \( \rho \), the potential \( U_b \) in equation (5.16) will raise its energy above the potential \( V_o \), which suggests that \( U_b \) should have at least one minimum. It can indeed be derived from (5.16) that the potential \( U_b \) have three minima, occurring at a particular value of \( \rho \) when \( \varphi \) changes from 0 to \( 2\pi \). This phenomenon is the so-called \textit{Jahn-Teller instability}, and comes from the instability on the \( U_b \) potential surface. The degenerate normal coordinates \( Q_+ \) and \( Q_- \) are said to be \textit{Jahn-Teller active}. Roughly speaking, the ion is vibrating around its equilibrium symmetric configuration in its ground rovibronic state until it recombines with a low energy scattering \( p \)-electron. Then, the Jahn-Teller instability is responsible for the distortion of the molecule away from its initial equilibrium geometry. Of course, such instability through the Jahn-Teller active degenerate normal mode could lead to the dissociation of the molecule.

In a general study of Jahn-Teller effect in molecules, one calculates the eigenenergies of the vibronic wave function, solving the Jahn-Teller Hamiltonian

\[
\hat{H}_{JT} = \hat{T}_{vib} + \hat{H}_{elec}. \tag{5.20}
\]

In practice, one seeks for a vibronic solution of the form

\[
\Psi = \chi^{+}_v(Q)\psi_{elec}^{(+)}(q) + \chi^{-}_v(Q)\psi_{elec}^{(-)}(q). \tag{5.21}
\]
Figure 5.1: The potential surfaces of the $2p\pi_1$ and $2p\pi_2$ states of $H_3^+$, as well as the $2p\sigma$ state potential. The $p\pi$ states potentials demonstrate the conical intersection around the equilateral geometry of $H_3^+$ ($\rho=0$), induced by Jahn-Teller splitting. The position of the three minima can be seen through the surface projection on the $(Q_x,Q_y)$ plane.
For this purpose, one diagonalizes the Hamiltonian $\hat{H}_{JJ}$ in the basis

$$|\psi_{\text{elec}}^{(+)}\rangle|\nu_1\rangle|\nu_2\rangle|\nu_{n+1}, l_{n+1}\rangle|\nu_{n+2}, l_{n+2}\rangle|\nu_{n+1}, l_{n+1}\rangle|\nu_{n+2}, l_{n+2}\rangle..., \quad (5.22)$$

where the different state functions $|\nu_1\rangle, |\nu_2\rangle, ...$ represent vibrational normal mode of the system in consideration. In the present DR study, we adopt a similar approach, except that we are only interested in states that are coupled to the ground ionic vibrational state by Jahn-Teller interaction.

## 5.3 DR of H$_3$O$^+$

### 5.3.1 Vibrational modes of the H$_3$O$^+$ ion

In its equilibrium position, the H$_3$O$^+$ ion is pyramidal and thus described by the $C_{3v}(M)$ symmetry point group. However, the barrier for tunneling for the oxygen atom through the plane of the three hydrogen nuclei is quite weak so that the $D_{3h}(M)$ symmetry point group can be used for the qualitative analysis of vibrational modes\footnote{For the $D_{3h}(M)$ group, the expressions for vibrational normal modes do not depend on actual force constants of H$_3$O$^+$, on the hand the $C_{3v}(M)$ normal modes do depend on the force constants.}. In this picture, the oxygen atom is situated in the middle of the equilateral triangle formed by the three hydrogen nuclei, at a distance $R_{OH} = 1.039\text{Å}$. The normal modes in the $D_{3h}(M)$ configuration are given in [111], and for the equivalent case of the ammonia molecule in [132]. Following the notations
of Weeks in [132], the normal coordinates take the form:

\begin{align*}
U_1 &= \sqrt{\frac{1}{12}} (-2x_1 + x_2 + x_3 + \sqrt{3}y_2 - \sqrt{3}y_3) \quad A_1', \\
U_2 &= \sqrt{\frac{3m}{M + 3m}} z_o - \sqrt{\frac{M}{3(M + 3m)}} (z_1 + z_2 + z_3) \quad A_2'',
U_3 &= \sqrt{\frac{1}{12}} (2x_1 - x_2 - x_3 - \sqrt{3}y_2 + \sqrt{3}y_3) \quad E'_x,
U_4 &= \sqrt{\frac{1}{12}} (2y_1 - y_2 - y_3 + \sqrt{3}x_2 - \sqrt{3}x_3) \quad E'_y,
U_5 &= \sqrt{\frac{3m}{M + 3m}} x_o - \sqrt{\frac{M}{3(M + 3m)}} (x_1 + x_2 + x_3) \quad E'_x,
U_6 &= \sqrt{\frac{3m}{M + 3m}} y_o - \sqrt{\frac{M}{3(M + 3m)}} (y_1 + y_2 + y_3) \quad E'_y. 
\end{align*}

In the above expressions, we used the Cartesian coordinates \((x_i, y_i, z_i)\) of the three hydrogen atoms \(i = 1, 2, 3\) with mass \(m\), and the oxygen atom with coordinates \((x_o, y_o, z_o)\) and mass \(M\). Also, we labeled each of the normal modes with their corresponding irreducible representation in the \(D_{3h}(M)\) point group. The normal mode \(U_1\) corresponds to the symmetric stretch of the triangle formed by the three hydrogens, \(U_2\) is the distance of the oxygen atom from the plane formed by the hydrogens. The degenerate normal mode \(U_3\) and \(U_4\) correspond to asymmetric stretch of the triangle formed by the three hydrogens, and finally the degenerate mode \(U_5\) and \(U_6\) correspond to motion of the oxygen atom parallel to the plane formed by the hydrogen atoms at equilibrium, with a corresponding tipping of the hydrogen triangle.

The geometrical actions of these modes are shown in Fig. 5.2.
In the study, we consider the $\text{H}_3\text{O}^+$ ion vibrating near its equilibrium configuration. Therefore we need the normal coordinates at that specific configuration in the $C_{3v}(M)$ point group symmetry. These normal modes are decomposed as $2A_1 \oplus 2E$ in the $C_{3v}(M)$ configuration and we denote the two symmetric modes by $Q_1$ and $Q_3$, and the two degenerates modes by $Q_2 = (Q_{2x}, Q_{2y})$ and $Q_4 = (Q_{4x}, Q_{4y})$. 

On one hand, $Q_1$ and $Q_3$ are linear combinations of $U_1$ and $U_2$, on the other hand, $Q_{2x}$ and $Q_{4x}$ are linear combinations of $U_3$ and $U_5$, and $Q_{2y}$ and $Q_{4y}$ are linear combinations of $U_4$ and $U_6$. All the coefficients in the combinations depend on the actual force constant of
H$_3$O$^+$. However, the mixing between $U_3$ and $U_5$ on one hand and between $U_4$ and $U_6$ on the other hand for H$_3$O$^+$ is small. On that account, the characteristics of the degenerate modes at $C_{3v}(M)$ geometry is mainly determined by their expressions in (5.23). It is important to stress here that in the present study, the H$_3$O$^+$ modes are obtained numerically by the standard normal modes analysis using the MOLPRO package. The expressions in (5.23) are provided just to give an idea about the character of the modes.

Table 5.1: Frequencies (in cm$^{-1}$) of H$_3$O$^+$ normal modes obtained in our study compared to the energies for the lowest vibrational states obtained by a direct diagonalization of the vibrational Hamiltonian by Bowman et al. [19].

<table>
<thead>
<tr>
<th>Representation</th>
<th>Present calculations</th>
<th>Bowman et al. [19]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_1$</td>
<td>$A_1$</td>
<td>900</td>
</tr>
<tr>
<td>$\omega_2$</td>
<td>$E$</td>
<td>1704</td>
</tr>
<tr>
<td>$\omega_3$</td>
<td>$A_1$</td>
<td>3609</td>
</tr>
<tr>
<td>$\omega_4$</td>
<td>$E$</td>
<td>3705</td>
</tr>
</tbody>
</table>

The frequencies of the four $2A_1 \oplus 2E$ normal modes of H$_3$O$^+$ are given in Table 5.1. The frequencies have been obtained from ab initio calculations using the MOLPRO package [133] and are compared with accurate (beyond normal mode approximation) calculations by Bowman et al. [19], who used an implementation of the MULTIMODE code. The results agree well, with relative error less than 10%. In order of increasing frequencies, the first symmetric normal mode, denoted $Q_1$, is the so-called umbrella mode, the second doubly degenerate mode $Q_2 = (Q_{2x}, Q_{2y})$ represents the deformation, the third mode $Q_3$ represents the O-H symmetric stretch, and finally, the fourth degenerate mode $Q_4 = (Q_{4x}, Q_{4y})$ is the antisymmetric O-H stretch.
5.3.2 Jahn-Teller in $\text{H}_3\text{O}^+$

We now introduce the vibronic Jahn-Teller coupling in the $\text{H}_3\text{O}$ radical. The $\text{H}_3\text{O}$ electronic Rydberg states with non-zero projection $\Lambda$ (more precisely with $\Lambda \neq 0(\text{mod } 3)$) of the electronic angular momentum on the symmetry axis of the molecule are doubly degenerate at the equilibrium position of the ion (and any equilateral configuration of the three hydrogen nuclei). Such states with $\Lambda \neq 0(\text{mod } 3)$ belong to the $E$ irreducible representation of the $C_{3v}(M)$ point group. For any geometry different than equilateral, energies of the two electronic states split apart. The energy splitting between the two electronic states is linear with respect to $Q_{2x}, Q_{2y}, Q_{4x},$ and $Q_{4y}$ [91], as we discussed in Section 5.2. Because the splitting between the two states is small or zero near the equilateral geometry, the non-Born-Oppenheimer interaction (Jahn-Teller coupling) between the vibrational and electronic motions is large or infinite. This coupling is responsible for the large probability of capturing the incident electron into an excited vibrational level. We include the Jahn-Teller coupling into the DR treatment using the parametrization Hamiltonian describing the coupled states suggested by Moffit and Liehr [104] and Longuet-Higgins [91]. The parametrized Hamiltonian is obtained in the way described in Section 5.2, except that $\text{H}_3\text{O}^+$ has two active normal modes. If, instead of the real normal coordinates $(Q_{2x}, Q_{2y})$ and $(Q_{4x}, Q_{4y})$, we use polar normal modes $\rho_i$ and $\varphi_i$ ($Q_{ix} = \rho_i \cos \varphi_i, Q_{ix} = \rho_i \sin \varphi_i$) with $i = 2, 4$, we obtain the following form for the matrix $\hat{H}_{\text{elec}}$ in the basis of the two degenerate electronic states
(ψ_{elec}^{(+)} \psi_{elec}^{(-)}) defined in equation (5.7)

\[ \hat{H}_{elec} = W_0 \hat{I} + \hat{H}_{elec,Q_2} + \hat{H}_{elec,Q_4}, \]  

(5.24)

with

\[ \hat{H}_{elec,Q_2} = \begin{pmatrix} \frac{1}{2} k_2 \rho_2^2 & f_2 \rho_2 e^{-i\varphi_2} + g_2 \rho_2^2 e^{2i\varphi_2} \\ f_2 \rho_2 e^{i\varphi_2} + g_2 \rho_2^2 e^{-2i\varphi_2} & \frac{1}{2} k_2 \rho_2^2 \end{pmatrix}, \]  

(5.25)

and with the similar expression for \( \hat{H}_{elec,Q_4} \) depending on \( \rho_4 \) and \( \varphi_4 \). In equation (5.24), \( \hat{I} \) is the \( 2 \times 2 \) identity matrix and \( W_0 \) is the energy of \( \text{H}_3\text{O} \) at the equilateral geometry. In equation (5.25), the coefficients \( f_2 \) and \( g_2 \) correspond respectively to the coefficients \( V_+^- \) and \( V_+^+ \) introduced in (5.19). The one-dimensional normal modes \( Q_1 \) and \( Q_3 \) do not participate in the coupling between the degenerate electronic states. Therefore, the solutions of two-state vibronic Hamiltonian can be written

\[ \Psi = \eta_1(Q_1) \eta_3(Q_3)(\eta^+(Q_2,Q_4)\phi_+(q) + \eta^-(Q_2,Q_4)\phi_-(q)). \]  

(5.26)

If we set the coordinate \( \rho_4 = 0 \) (thus \( \hat{H}_{elec,Q_4} = 0 \)), but not \( \rho_2 \), and diagonalize the electronic Hamiltonian in (5.24), we obtain electronic Born-Oppenheimer surfaces which form was given in (5.16), and electronic eigenstates given in (5.17). In a similar way, the Born-Oppenheimer energies and eigenstates can be obtained for the \( Q_4 \) degenerate mode.

If plotted as functions of the two coordinates \( Q_{2x} \) and \( Q_{2y} \), the potential surfaces exhibit a conical intersection near the equilateral geometry \( \rho_2 = 0 \) with the minimum of energy
situated at $f_2^2/2k_2$ below the energy of the intersection. The electronic potential surfaces obtained by \textit{ab initio} calculations exhibit the same behavior. This allows fitting of the \textit{ab initio} data to the analytical behavior of (5.16). Therefore, the parameters $k_i$, $f_i$, $g_i$, and $W_0$ of the Jahn-Teller coupling can be obtained from the \textit{ab initio} energies of excited electronic states of $\text{H}_3\text{O}$.

![Effective quantum number as a function of $Q_{2a}$ coordinate (left) and $Q_{4a}$ coordinates (right). The electronic states are labeled at the equilibrium configuration of $\text{H}_3\text{O}^+$ with data from [92]](image)

We will use the quantum defect theory to calculate the DR cross-section. In this approach it is convenient to represent the \textit{ab initio} potential energy surfaces in the form of effective...
quantum numbers \( \nu(Q) \) or quantum defects \( \mu(Q) \) that are related to the potential energies \( U(Q) \) according to (in atomic units - a.u.)

\[
U(Q) = U^+(Q) - \frac{1}{2[\nu(Q)]^2} = U^+(Q) - \frac{1}{2[n - \mu(Q)]^2},
\]

where \( U^+(Q) \) denotes the ionic potential and \( n \) is the principal quantum number associated with the corresponding electronic state (with energy \( U(Q) \)). For excited electronic states the quantum defects \( \mu(Q) \) are only weakly-dependent on \( n \).

Fig. 5.3 shows the \( Q_{2x} \) and \( Q_{4x} \)-dependence of effective quantum numbers obtained from \textit{ab initio} potential energy surfaces calculated in this study. The results at the equilibrium geometry of \( \text{H}_3\text{O}^+ \) are compared with \textit{ab initio} data from [92]. According to quantum defect theory, the quantum defects and the Jahn-Teller splitting for the excited electronic states should not depend on the principal quantum number. The results shown in the figure are in agreement with it. Because the electron is initially captured into a highly excited Rydberg states during the DR process, we need to use the Jahn-Teller parameters obtained from the excited Rydberg states.

5.3.3 Cross section calculation

We now apply equation (5.6) to DR in \( \text{H}_3\text{O}^+ \) using the parameters of the Jahn-Teller coupling obtained above. These parameters are used below to construct the scattering matrix \( \hat{S}(Q) \).
Thus, they determine the $\text{H}_3\text{O}^+$ DR cross section. We consider the symmetric normal modes $Q_1$ and $Q_3$, as well as the doubly degenerate normal modes $Q_2 = (\rho_2, \varphi_2)$ and $Q_4 = (\rho_4, \varphi_4)$ as the vibrational coordinates. We start with an electronic state with potential

$$U(Q) = U^\Lambda(Q) - \frac{1}{2(n - \mu(Q))^2}.$$  \hspace{1cm} (5.28)

If we take derivative with respect to $Q_i$, we obtain

$$\left( \frac{\partial \mu}{\partial Q_i} \right) = -\left( \frac{\partial \nu}{\partial Q_i} \right) = -\nu^3 \left( \frac{\partial U}{\partial Q_i} \right).$$ \hspace{1cm} (5.29)

The potential does not depend to first order on $Q_1$ or $Q_3$, i.e. $\partial \mu_{\Lambda,\Lambda'}/\partial Q_1 = \partial \mu_{\Lambda,\Lambda'}/\partial Q_3 = 0$, for any electronic states $\Lambda$ and $\Lambda'$. In the same way, using equation (5.16), we find that the potentials do not depend to first order on $\varphi_2$ and $\varphi_4$ near the equilateral geometries, i.e. $\partial \mu_{\Lambda,\Lambda'}/\partial \varphi_2 = \partial \mu_{\Lambda,\Lambda'}/\partial \varphi_4 = 0$. Hence, in the first order of approximation, the only non-vanishing terms in (5.6) are the ones that depend on $\rho_2$ and $\rho_4$. Therefore, the main contribution into the electron capturing is due to the Jahn-Teller coupling.

We assume that the incident electron has projection $\Lambda = -1$ on the molecular axis (equations (5.26) and (5.24)), the final electronic state has projection $\Lambda' = 1$ once the electron is captured into a Rydberg state attached to an excited vibrational level of the ionic core. For the cross section calculation, we need to evaluate the derivatives $\partial \mu_{\Lambda',\Lambda}/\partial \rho_i$ at the equilibrium of the ion. Because the diagonal elements of $\hat{\mu}(Q)$ are the same, the derivative $\partial \mu_{\Lambda',\Lambda}/\partial \rho_i$ is equal to the derivative of eigenvalues $\mu_a(Q)$ and $\mu_b(Q)$ of $\hat{\mu}$. The derivatives
\( \partial \mu_a / \partial \rho_i \) and \( \partial \mu_b / \partial \rho_i \) are obtained from \textit{ab initio} calculations shown in Fig. 5.3 or directly using (5.16) and (5.27) from the potential energy surfaces of the excited electronic states of H\(_3\)O that are coupled by the Jahn-Teller interaction,

\[
\left( \frac{\partial \mu_{1,-1}}{\partial \rho_2} \right) = \left| \frac{\partial U_a}{\partial \rho_2} \right| \nu_3^3 \quad \text{and} \quad \left( \frac{\partial \mu_{1,-1}}{\partial \rho_4} \right) = \left| \frac{\partial U_a}{\partial \rho_4} \right| \nu_3^3.
\]  

(5.30)

At the last step of the treatment, we consider the vibrational states of H\(_3\)O\(^+\) in the normal mode approximation and label them as \( |v_1 v_2 v_3 v_4 \rangle \), where \( l_2 \) and \( l_4 \) are the vibrational angular momenta associated with the degenerate normal modes. The ion is initially in its ground vibrational state, so that \( |v\rangle = |0000\rangle \) in equation (5.6). The only non vanishing terms in the cross section (5.6) are \( \langle 01^1 00^0 | \rho_2 | 00^0 00^0 \rangle = 1/\sqrt{2\omega_2} \) and \( \langle 00^0 01^1 | \rho_4 | 00^0 00^0 \rangle = 1/\sqrt{2\omega_4} \) (mass-scaled normal coordinates are used in these expressions). The frequencies \( \omega_i \) are given in Table 5.1. Hence, in this approximation, the electronic capture can only occur into these two final vibrational states. Also, the cross section in equation (5.6) has to be multiplied by two because the final vibrational state is doubly degenerate. It gives the final DR cross section

\[
\langle \sigma \rangle = \frac{2\pi^3}{E_d \omega_2} \left( \frac{\partial \nu_a}{\partial \rho_2} \right)^2 \Theta(h \omega_2 - E_d) + \frac{2\pi^3}{E_d \omega_4} \left( \frac{\partial \nu_a}{\partial \rho_4} \right)^2 \Theta(h \omega_4 - E_d).
\]  

(5.31)

The derivatives \( \partial \nu_a / \partial \rho_i \) are obtained from the dependencies \( \nu_a(\rho_i) \) such as shown in Fig. 5.3. There are several electronic \( E \) states that are doubly-degenerate at the equilaterial configuration and that are split by the Jahn-Teller coupling once the \( C_{3v} \) symmetry is lifted. These states can be considered as different superpositions of the hydrogen-like states \( p\pi, d\pi, \)
$d\delta$. As it is clear from Fig. 5.3, the Jahn-Teller coupling is not negligible between $d\pi$ states. Therefore, the electron can be captured into these states. In equation (5.31) we account separately for the contribution from each such Jahn-Teller pair of electronic states. The final cross-section is plotted in Fig. 5.4 and we also show the experimental DR cross section obtained in the CRYRING storage ring [109].

![Graph](image-url)

**Figure 5.4:** Theoretical DR cross section of $\text{H}_3\text{O}^+$ ion convoluted with energy spread $\Delta E_\perp = 2\text{meV}$ and $\Delta E_\parallel = 0.1\text{meV}$ and compared with experimental data by Neau et al. [109].
5.4 DR of $\text{H}_3^+$

5.4.1 Vibrational modes of the $\text{H}_3^+$ ion and Jahn-Teller effect

The $\text{H}_3^+$ ion has equilateral geometry at its equilibrium position. Displacements around this equilibrium position are described by the symmetric stretch normal mode $Q_1$ and the degenerate asymmetrical stretch mode, with corresponding real normal coordinates $Q_{e_x}$ and $Q_{e_y}$.

The normal coordinates are expressed as follows

$$
Q_1 = \sqrt{\frac{1}{12}} (-2x_1 + x_2 + x_3 + \sqrt{3}y_2 - \sqrt{3}y_3)
$$

$$
Q_{ex} = \sqrt{\frac{1}{12}} (2x_1 - x_2 - x_3 - \sqrt{3}y_2 + \sqrt{3}y_3)
$$

$$
Q_{ey} = \sqrt{\frac{1}{12}} (2y_1 - y_2 - y_3 + \sqrt{3}x_2 - \sqrt{3}x_3).
$$

We denote the vibrational state of the $\text{H}_3^+$ ion as $|v_1, v_2^{(2)}\rangle$. As explained in Section 5.3 for the case of $\text{H}_3\text{O}^+$ ion, the electron can only be captured in Rydberg states corresponding to the vibrational states $|01^{\pm1}\rangle$. Therefore we only need the energy of the first excited degenerate mode. We use the value $\hbar\omega=2527.1\text{cm}^{-1}$ from [103].

From the same study [103], the actual Jahn-Teller coefficients $\lambda$ were evaluated for $np_x$ and $np_y$ orbitals\(^7\) by asymmetric displacements. The coefficient $\lambda$ corresponds to the Jahn-Teller splitting for quantum defects, therefore we have $\lambda = f\nu^5$ (see equation (5.29)), where

\(^7\)Jahn-Teller coefficients were evaluated for $p$ orbitals up to principal quantum number $n=5$. 

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5.4.2 Cross section calculation

We have calculated the DR cross-section using the value $\lambda = 11950\text{cm}^{-1}$ corresponding to the $5p$ orbital. Following the same principle as in Section 5.3, the final cross-section is given by

$$\sigma_i(E_{el}) = \frac{2\pi^3}{\omega E_{el}} \lambda^2 \Theta(h\omega - E_{el}).$$  \hspace{1cm} (5.33)$$

Using only the two parameters $h\omega$ and $\lambda$, and after averaging on energy spread, we finally obtain the final cross section presented in Fig. 5.6. Our estimation is in good agreement with
Figure 5.6: Cross section calculation for $\text{H}_3^+$ molecular ion using a simplified model. The results are compared with a previous theoretical study [36] and TSR and CRYRING experiments.

Theoretical results by [36] and CRYRING experimental data, as well as another estimated cross section of $\text{H}_3^+$ calculated by Jungen and Pratt in [71], who used experimental data for the Jahn-Teller interaction.

5.5 Discussion of the results and perspectives

We investigated the DR cross section of $\text{H}_3\text{O}^+$ and $\text{H}_3^+$ using a simplified model for which electronic capture is assumed to be the decisive step. The Jahn-Teller effect was considered as the key ingredient for capture in one of the excited state of the two degenerate vibrational
normal modes (harmonic approximation). The results are in good agreement with storage ring experimental data by Neau et al. [109], which suggest that reionization should be small during predissociation. On the other hand, electronic capture\footnote{Capture in highly excited vibrational states is usually small but could be none negligible.} in other excited vibrational states, which is not taken into account in this model could enhance the overall cross section. Therefore, no definite conclusions on how the DR process precisely occurs can be made from this model. As a conclusion, we wish to propose an improvement to the model. Our treatment relies on the harmonic approximation to describe the vibrational states. Actually, anharmonic terms in the electronic ionic potential of H$_3$O$^+$ exist and can be easily obtain via \textit{ab initio} calculations. For instance, these anharmonicities in the potential could couple the second excited state of the degenerate normal modes (as well as other excited states) to their first excited states. This would probably not change the cross section at low energies in a noticeable way, but it has the advantage to allow the determination of the cross section at energies beyond $\hbar \omega_4$. 

\footnotetext[8]{Capture in highly excited vibrational states is usually small but could be none negligible.}
CHAPTER 6

MOLECULAR SYSTEM COMPOSED WITH THREE IDENTICAL ATOMS

6.1 The general approach

6.1.1 Aim of the study

Quantum systems of three identical atoms have attracted a considerable interest during the last years, principally due to recent experimental and theoretical advances in the field of ultra-cold degenerate gases. One such example of the recent experimental advances is the observation of three-body Efimov states [33] in ultra cold gas of cesium [80]. Another motivation to study quantum few-body problems is due to recent experiments with interacting atoms and molecules trapped in optical lattices. The interaction between a few atoms (or molecules) in optical traps can be changed by an appropriately chosen external field. Understanding and controlling the interaction between atoms (and molecules) in optical lattice contributes into the progress in the domain of quantum information and quantum computing.

One aspect of the interaction in the three-body system is the selection rules determining allowed and forbidden final states of the system after the scattering process. For three
identical atoms, there are three possible configurations before, during and after a collision. Namely, (1) the three atoms are far from each other and do not interact at all, (2) two of the three atoms are close and interact with each other, but the third atom is situated far from them and therefore can be considered as free, and (3) the three atoms are close to each other such that the interaction between them cannot be neglected. For each of these configurations, one can assign a set of appropriate quantum numbers. Before and after a collision, the configuration may change. Therefore, the set of quantum numbers may also be different before and after the collision. However, there are relationships between the sets corresponding to different configurations. In addition, some quantum numbers are the same in the three sets and are therefore conserved during the collision. Such correlations between the three sets of quantum numbers are the consequence of the conservation of symmetry of the total wave function of the system. The symmetry of rotational and vibrational wave functions of the system of three indistinguishable atoms has been studied previously by several authors [7, 31, 95, 107, 113, 134]. However, there was no systematic description of the correlation between quantum numbers appropriate for all the three possible configurations. In this article, we discuss the three sets of appropriate quantum numbers and derive the rules describing the correlations between different quantum numbers in the three sets. Since there exist some selection rules regarding the change in the quantum numbers, we derive and discuss them in detail.

In Section 6.1.2, we will give a brief overview of symmetry properties of the three identical atoms and general rules for construction of wave functions. Then, in Section 6.2, we present
wave functions and the corresponding quantum numbers appropriate for each of the three configurations of the system. In Section 6.3, we derive the scattering selection rules and represent them by diagrams of correlation between the three sets of quantum numbers, similar to the case of diatomic molecules [129]. Finally, Section 6.4 contains our conclusions.

6.1.2 System and symmetry

The group $S_3$ of permutations of three identical particles is isomorphic to the point group of symmetry $C_{3v}$. Geometrically, the system with the $C_{3v}$ symmetry can be represented by a flat equilateral triangle containing the six following elements: three reflexions $\sigma_v$ through three vertical planes perpendicular to the plane of the triangle, two rotations $C_3$ by $2\pi/3$ in the plane of the triangle and the identity operator $E$ [86, 21]. Adding to $S_3$ the operator of inversion $E^*$, the new group $S_3 \otimes \{E, E^*\}$ becomes isomorphic to the point group $D_{3h}$, which itself can be represented as $D_{3h} = C_{3v} \otimes \{\sigma_h, E\}$ where $\sigma_h$ is the reflection through the symmetry plane. Relative motion of three structureless particles is characterized by the $C_{3v}$ group. If rotation of the whole system in a space-fixed coordinate frame needs to be accounted for, then, the symmetry of the system is represented by the $D_{3h}$ group. In our discussion we will be using the same notations for elements $\hat{R}$ of the group $D_{3h}$ as in [21]; the 12 elements $\hat{R}$ are $E, (12), (13), (23), (123), (132)$ without inversion plus the same elements with the inversion $E^*$. 

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Each eigenstate of the Hamiltonian of the system is transformed in the $D_{3h}$ group according to one of the six irreducible representations: $A'_1, A''_1, A'_2, A''_2, E', E''$. The representations $E'$ and $E''$ are two-dimensional. For convenience, we define bases in the $E'$ and $E''$ representations. Namely, in the two-dimensional space of $E'$ we use two orthogonal basis states, $E'_+$ and $E'_-$, whose properties are such that

\begin{align}
(123)E'_\pm &= e^{i\omega}E'_\pm, \\
(12)E'_\pm &= E'_\mp,
\end{align}

where $\omega = 2\pi/3$. The basis states turn into each other through operator (12). The basis states, $E''_+$ and $E''_-$ in the $E''$ representation are defined in the same way.

Table 6.1: Coefficients $\chi^\Gamma_R$ in the projector formula (6.3) for $E'_\pm$ and $E''_\pm$ basis states. Coefficients $\chi^\Gamma_R$ for one-dimensional irreducible representations of the $D_{3h}$ group are equal to the corresponding characters [21]. Operators $E$ and $E^*$ are the identity and inversion operators correspondingly.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$E'$</th>
<th>$(123)$</th>
<th>$(132)$</th>
<th>(12)</th>
<th>(23)</th>
<th>$E^*$</th>
<th>$(123)^*$</th>
<th>$(132)^*$</th>
<th>(12)$^*$</th>
<th>(23)$^*$</th>
<th>$(13)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E'_\pm$</td>
<td>1</td>
<td>$e^{\pm i\omega}$</td>
<td>$e^{\pm i\omega}$</td>
<td>1</td>
<td>$e^{\pm i\omega}$</td>
<td>$e^{\pm i\omega}$</td>
<td>1</td>
<td>$e^{\mp i\omega}$</td>
<td>$-e^{\mp i\omega}$</td>
<td>1</td>
<td>$-e^{\pm i\omega}$</td>
</tr>
<tr>
<td>$E''_\pm$</td>
<td>1</td>
<td>$e^{\pm i\omega}$</td>
<td>$e^{\pm i\omega}$</td>
<td>1</td>
<td>$e^{\pm i\omega}$</td>
<td>$e^{\mp i\omega}$</td>
<td>-1</td>
<td>$-e^{\mp i\omega}$</td>
<td>$e^{\pm i\omega}$</td>
<td>-1</td>
<td>$-e^{\pm i\omega}$</td>
</tr>
</tbody>
</table>

Having defined the bases in $E'$ and $E''$, we can represent an arbitrary state $\psi$ of the system as a superposition of eight functions, each transforming as $A'_1, A''_1, A'_2, A''_2, E'_+, E'_-, E''_+, E''_-$. Each term in the superposition can formally be obtained by projecting the state $\psi$ on the corresponding function. The projector operator on the basis state $\Gamma$ was given in equation
(2.10) and act on an unsymmetrized function \( \psi \) in the following way:

\[
\hat{P}_\Gamma \psi = \sum_{\hat{R} \in D_{3h}} \chi^\Gamma_{\hat{R}} \hat{R} \psi.
\]

(6.3)

Here, the sum is taken over all 12 elements \( \hat{R} \) of the \( D_{3h} \) group. This formula is just the regular projector on a one-dimensional irreducible representation \( \Gamma \) of \( D_{3h} \). Therefore, in the above equation, \( \chi^\Gamma_{\hat{R}} \) are the well-known characters [21] if \( \Gamma \) is an one-dimensional irreducible representation. Coefficients \( \chi^\Gamma_{\hat{R}} \) for the states \( E'_\pm \) or \( E''_\pm \) are given in Table 6.1.

For simplicity, we will only consider the coordinate part of total wave function of the system. The electronic and nuclear spin statistics of three identical atoms can be described using a similar approach, which is briefly discussed in our conclusion.

We are interested in selection rules in the collision process, which starts with a given state \( \psi \) of the system. The state \( \psi \) is usually specified by a set of quantum numbers that are appropriate for the initial configuration of the system. These quantum numbers are in general not conserved during the scattering process. However, they are sufficient to decompose the state into the sum of irreducible representation of the group \( D_{3h} \). A given irreducible representation is conserved during the collision and can be viewed as a good quantum number, allowing the characterization of the possible final states of the system. Therefore, decomposition of initial states into irreducible representations of \( D_{3h} \) allows us to derive the selection rules, i.e. to point out which final states (characterized by other set of quantum numbers) are not accessible from that given initial state; if the operator \( \hat{P}_\Gamma \)
acting on $\psi$ gives identically 0, it means that final states transforming according to $\Gamma$ are not accessible from the initial state $\psi$.

6.2 The different configurations

6.2.1 Short distances: A bound triatomic system

We consider that the three atoms are situated at short distances from each other if the potential of interaction in each pair of the atoms is much larger than the rotational energy of the relative motion. We define the short range region in this way to be able to separate vibrational and rotational motion of the system and use vibrational and rotational quantum numbers of the three atoms. Therefore, the total wave function is written as a product of rotational $R$ and vibrational $\phi$ factors:

$$\psi = R(\alpha, \beta, \gamma)\phi(Q_1, Q_x, Q_y), \quad (6.4)$$

where $\alpha, \beta, \gamma$ are the Euler angles defining orientation of the plane of the three atoms in the space-fixed coordinate frame; $Q_1$ is the symmetric normal coordinate and $(Q_x, Q_y)$ are the asymmetric degenerate normal coordinates, representing altogether three independent vibrational coordinates defining relative positions of the three atoms. The rotational wave
function of the system is described by the symmetric top eigenstates [86]

$$\mathcal{R}(\alpha, \beta, \gamma) = \left[ \frac{2J + 1}{8\pi^2} \right]^{1/2} \left[ D_{M,K}^J(\alpha, \beta, \gamma) \right]^*, \quad (6.5)$$

where $J$ is the total angular momentum of the system, $M$ and $K$ are respectively its projections on the space-fixed and molecular axes. These numbers are constants of motion of the symmetric top and sufficient to define completely the rotational state of the system. The correspondence between the quantum numbers $J, M, K$ and the irreducible representations of such rotational functions is summarized in Table 6.2, which is obtained from the symmetry properties of the Wigner functions $D_{M,K}^J(\alpha, \beta, \gamma)$ [21, 106] in the $D_{3h}$ group and from the coefficients $\chi^\Gamma(\hat{R})$ of (6.3).

In the rigid rotor approximation, the vibrational wave function depending on three coordinates is transformed according to the irreducible representations of the $C_{3v}$ group. If such vibrational states are obtained numerically (usually one uses hyperspherical coordinates [67], whose definitions are given in Sec. [6.2.2]), their irreducible representations are determined by their symmetry properties. If the normal mode approximation is used for the vibrational states, one can assign to each vibrational state the label of an irreducible representation based on three vibrational quantum numbers $v_1, v_2$ and $l_2$ describing the three-dimensional harmonic oscillator of the $C_{3v}$ symmetry. We use notation $|v_1, v_2^l\rangle$ to specify the corresponding wave function. The quantum number $v_1$ describes the symmetric stretch mode, which preserves the equilateral configuration of the system. The value of $v_2$ indicates the
number of asymmetric radial vibrational quanta. The quantum number $l_2$ indicates the number of quanta in the vibrational angular momentum mode and can only take values $-v_2, -v_2 + 2 \ldots v_2 - 2, v_2$. The transformation properties of these vibrational functions are well known (see, for example, [21, 66, 74]) and depend only on the quantum number $l_2$ (see Table 6.3).

Table 6.2: Allowed quantum numbers for the rotational wave function $R(\alpha, \beta, \gamma)$.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$K$</th>
<th>$J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'_{1}$</td>
<td>0</td>
<td>even</td>
</tr>
<tr>
<td>$A'_{2}$</td>
<td>0</td>
<td>odd</td>
</tr>
<tr>
<td>$A'<em>{1} \oplus A'</em>{2}$</td>
<td>0 (mod 3) ∧ (≠ 0) ∧ (even)</td>
<td></td>
</tr>
<tr>
<td>$A''<em>{1} \oplus A''</em>{2}$</td>
<td>0 (mod 3) ∧ (odd)</td>
<td></td>
</tr>
<tr>
<td>$E'_{\pm}$</td>
<td>≠ 0 (mod 3) ∧ (even)</td>
<td></td>
</tr>
<tr>
<td>$E''_{\pm}$</td>
<td>≠ 0 (mod 3) ∧ (odd)</td>
<td></td>
</tr>
</tbody>
</table>

An example of the system where normal mode approximation works well for several low-lying vibrational states is the $H_3^+$ ion. For instance, the $H_3^+$ wave functions and the corresponding normal mode quantum numbers are shown and discussed in [74]. The bound state component of three-body resonances could also possibly be represented using the normal mode approximation. However, the approximation cannot be used for the continuum component of the resonances and for scattering states of the three atoms. They have to be calculated numerically.
Table 6.3: The table summarizes the $C_3v$ symmetry properties of the vibrational wave functions obtained in the normal mode approximation.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$l_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>0</td>
</tr>
<tr>
<td>$A_1 \oplus A_2$</td>
<td>$0 \pmod{3} \land (\neq 0)$</td>
</tr>
<tr>
<td>$E$</td>
<td>$\neq 0 \pmod{3}$</td>
</tr>
</tbody>
</table>

6.2.2 Three free atoms

The total Hamiltonian depends here on six coordinates (the motion of the center of mass is separated): three hyperspherical coordinates and the three Euler angles [95, 67]. For the case of a system of three identical atoms, the hyperspherical radius $\rho$ and the hyperspherical angles $\varphi$ and $\theta$ are simply defined in a way that:

\[
\begin{align*}
    r_1 &= 3^{-\frac{1}{4}} \rho \sqrt{1 + \sin \theta \sin (\varphi + \frac{2\pi}{3})}, \\
    r_2 &= 3^{-\frac{1}{4}} \rho \sqrt{1 + \sin \theta \sin (\varphi - \frac{2\pi}{3})}, \\
    r_3 &= 3^{-\frac{1}{4}} \rho \sqrt{1 + \sin \theta \sin \varphi},
\end{align*}
\]  

(6.6)

where $r_1$, $r_2$ and $r_3$ are the three internuclear distances. Using this system of coordinates, the total Hamiltonian takes the following form [95]:

\[
\hat{H} = -\frac{1}{2\mu} \left[ \frac{1}{\rho^5} \frac{\partial}{\partial \rho} \left( \rho^5 \frac{\partial}{\partial \rho} \right) - \frac{\hat{L}^2}{\rho^2} \right].
\]  

(6.7)
In (6.7), $\hat{\Lambda}^2$ is the operator of grand angular momentum, so that the term $\hat{\Lambda}^2/\rho^2$ represents a generalized angular momentum barrier. Its expression depending on the three Euler angles and the two hyperangles $\theta$ and $\varphi$ is

$$
\hat{\Lambda}^2 = -\frac{4}{\sin 2\theta} \frac{\partial}{\partial \theta} \sin 2\theta \frac{\partial}{\partial \theta} - \frac{4}{\sin^2 \theta} \frac{\partial^2}{\partial \varphi^2} + \frac{4i \cos \theta \hat{J}_y}{\sin^2 \theta} \frac{\partial}{\partial \varphi} + \frac{2\hat{J}_x^2}{1-\sin \theta} + \frac{2\hat{J}_z^2}{1+\sin \theta} + \frac{\hat{J}_y^2}{\sin^2 \theta} \tag{6.8}
$$

where $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$ are the angular momentum operators in the body-fixed coordinate system, which coincide with the principal moments of inertia. The symmetry of the eigenfunctions of the Hamiltonian is entirely determined by eigenfunctions $F^{\Lambda,\nu,J,M,\mu}(\alpha,\beta,\gamma,\varphi,\theta)$ of $\hat{\Lambda}^2$

$$
\hat{\Lambda}^2 F^{\Lambda,\nu,J,M,\mu} = \Lambda(\Lambda + 4) F^{\Lambda,\nu,J,M,\mu}. \tag{6.9}
$$

The functions $F^{\Lambda,\nu,J,M,\mu}$ are characterized by five quantum numbers $\Lambda, \nu, J, M, \mu$, each corresponding to an operator [95]:

(i) the grand angular momentum squared $\hat{\Lambda}^2$ with eigenvalues $\Lambda(\Lambda + 4)$ where $\Lambda = 0, 1, 2, \ldots$;

(ii) the operator $\hat{S} = i2\partial/\partial \varphi$, which determines the property of $F^{\Lambda,\nu,J,M,\mu}$ with respect to binary and cyclic permutations of the atoms and has eigenvalues $\nu = \Lambda, \Lambda - 2, \ldots, -\Lambda + 2, -\Lambda$;

(iii) the square of angular momentum $\hat{J}^2$ with eigenvalues $J(J + 1)$ where $J \leq \Lambda$;

(iv) the projection $\hat{J}_z$ of angular momentum on a space fixed axis with eigenvalues $M = -J, -J + 1, \ldots, J - 1, J$.
the operator lifting the degeneracy for linearly independent solutions still existing for
given values of $\Lambda, \nu, J, M$ with the quantum number $\mu$.

Functions $F$ are written as the finite sum [95]:

$$F^{\Lambda,\nu,J,M,\mu}(\alpha, \beta, \gamma, \varphi, \theta) = e^{-i\frac{\nu}{2}\varphi} \sum_{|N| \leq J} D^J_{M,N}(\alpha, \beta, \gamma) g_N^{\Lambda\nu\mu}(\theta). \quad (6.10)$$

Since the hyperangle $\theta$ is unchanged by permutations, the explicit description of the
function $g_N^{\Lambda\nu\mu}(\theta)$ is not important for our discussion. Using the symmetry of the Wigner
functions and the transformation of the hyperangle $\varphi$, one obtains transformations of the
function $F$ under the operations of $D_{3h}$

$$E^a F^{\Lambda,\nu,J,M,\mu} = (-1)^{\Lambda} F^{\Lambda,\nu,J,M,\mu}, \quad (6.11)$$

$$F^{\Lambda,\nu,J,M,\mu} = (-1)^{J} F^{\Lambda,-\nu,J,M,\mu}, \quad (6.12)$$

$$F^{\Lambda,\nu,J,M,\mu} = e^{-i\omega \nu} F^{\Lambda,\nu,J,M,\mu}. \quad (6.13)$$

The symmetry properties of functions $F^{\Lambda,\nu,J,M,\mu}$ are summarized in Table 6.4.

Since the three atoms do not interact with each other, instead of hyperspherical coordi-
nates, one can also use spherical coordinates for each atom separately $\vec{r}_1, \vec{r}_2, \vec{r}_3$. Then, the
total wave function is written as a product

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \phi_a(\vec{r}_1) \phi_b(\vec{r}_2) \phi_c(\vec{r}_3), \quad (6.14)$$
where indices $a, b,$ and $c$ specify one-atom states. To obtain definite irreducible representations of $D_{3h}$ from the product above one has to apply (6.3). The allowed irreducible representations depend on the quantum numbers $a, b,$ and $c$: If angular momenta $l_a, l_b, l_c$ are defined for each state $a, b,$ and $c,$ the parity of the whole system is definite and given by $(-1)^{l_a+l_b+l_c}$. If any two of the three states $a, b,$ and $c$ are not equal to each other, all three irreducible representations, $A_1, A_2,$ or $E$ of the allowed parity are possible (the sum of (6.3) does not vanish). If two of the three indices $a, b,$ and $c$ are equal to each other, only $A_1$ and $E$ are possible. Finally, if all three indices are the same, only $A_1$ irreducible representation is allowed.

Table 6.4: Allowed quantum numbers for three free atoms.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>$\upsilon$</th>
<th>$\Lambda$</th>
<th>$J$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'_1$</td>
<td>0</td>
<td>even</td>
<td>even</td>
</tr>
<tr>
<td>$A''_1$</td>
<td>0</td>
<td>odd</td>
<td>even</td>
</tr>
<tr>
<td>$A'_2$</td>
<td>0</td>
<td>even</td>
<td>odd</td>
</tr>
<tr>
<td>$A''_2$</td>
<td>0</td>
<td>odd</td>
<td>odd</td>
</tr>
<tr>
<td>$A'_1 \oplus A'_2$</td>
<td>$0 \pmod{3}$</td>
<td>even</td>
<td>even</td>
</tr>
<tr>
<td>$A''_1 \oplus A''_2$</td>
<td>$0 \pmod{3}$</td>
<td>odd</td>
<td>odd</td>
</tr>
<tr>
<td>$E'$</td>
<td>$\neq 0 \pmod{3}$</td>
<td>even</td>
<td>odd</td>
</tr>
<tr>
<td>$E''$</td>
<td>$\neq 0 \pmod{3}$</td>
<td>odd</td>
<td>odd</td>
</tr>
</tbody>
</table>

6.2.3 A diatomic and a free atom

We start with the non-symmetrized case, let say, atoms 1 and 2 form a dimer, atom 3 is far from the dimer. The interaction between the dimer and atom 3 is negligible. Here, we use the
mass-scaled Jacobi coordinates defined as \( \vec{r} = (3/4)^{1/4}(\vec{r}_2 - \vec{r}_1) \) and \( \vec{R} = (4/3)^{1/4}(\frac{\vec{r}_1 + \vec{r}_2}{2} - \vec{r}_3) \) [7]. In these coordinates, the kinetic energy operator has the simple form:

\[
\hat{T} = -\frac{\hbar^2}{2\mu} (\Delta \vec{r} + \Delta \vec{R}) ,
\]

with the 3-body reduced mass \( \mu = m/\sqrt{3} \). Thus, the Hamiltonian is

\[
\hat{H} = -\frac{\hbar^2}{2\mu} \Delta \vec{R} + \hat{H}_{12},
\]

where \( \hat{H}_{12} \) describes internal motion of the dimer. The conserved quantities for this case are the two angular momenta \( j_r \) and \( J_R \) and their projections \( m_r \) and \( M_R \) associated with \( \vec{r} \) and \( \vec{R} \) correspondingly, the vibrational state \( v \) of the dimer and the kinetic energy \( \epsilon \) associated with motion along \( R \). The wave function of the system (excluding the factor describing motion of center of mass) has the form

\[
\phi_{v,j_r}(r)Y_{j_r,m_r}(\Omega_r)u_{J_R,\epsilon}(R)Y_{J_R,M_R}(\Omega_R)/R ,
\]

where \( Y_{j,m}(\Omega) \) is a spherical harmonic depending on two angles collectively called \( \Omega \), \( \phi_{v,j_r}(r) \) is the vibrational state of the dimer, \( u_{J_R,\epsilon}(R) \) is the \( R \)-radial part corresponding to the free motion, i.e. the usual Bessel function. For us it is more convenient to construct the state
with a definite total angular momentum \( \vec{J} = \vec{j}_r + \vec{J}_R \) from the states of (6.17) as in [7]

\[
\psi_{v,j_r,J_R}^{J,M} (\vec{r}_1, \vec{r}_2, \vec{r}_3) = \mathcal{Y}_{J_r,J_R}^{J,M}(\Omega_r, \Omega_R) \phi_{v,j_r}(r) u_{J_R,\epsilon}(R) / R,
\]

(6.18)

where the bipolar spherical harmonic \( \mathcal{Y}_{J_r,J_R}^{J,M}(\Omega_r, \Omega_R) \) is

\[
\mathcal{Y}_{J_r,J_R}^{J,M}(\Omega_r, \Omega_R) = \sum_{m_r,M_R} C_{J_r,m_r,J_R,M_R}^{J,M} Y_{m_r}^{j_r}(\Omega_r) Y_{M_R}^{J_R}(\Omega_R).
\]

(6.19)

The wave function of (6.18) does not belong to a definite irreducible representation. Again, (6.3) is used to project the wave function on any of the one-dimensional irreducible representations or to basis states \( E_{\pm}' \) and \( E_{\pm}'' \) of \( D_{3h} \). In this case, it is more convenient to rewrite (6.3) in the form where operators (123) and (132) are written as products (23)(12) and (31)(12):

\[
\hat{P}_\Gamma = E + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(12) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12) + \chi_{(12)}^\Gamma(23) + \chi_{(23)}^\Gamma(31) + \chi_{(31)}^\Gamma(31) + \chi_{(13)}^\Gamma(12),
\]

(6.20)

where ’+p.t.’ means that we add all previous terms multiplied with the inversion operator \( E^* \). The effect of operator \( E^* \) and (12) is easily evaluated: The only factor in (6.18) that changes under \( E^* \) and (12) is the bipolar harmonic. The operator \( E^* \) acting on the \( \Omega_R \) part in (6.19) gives the same factor multiplied with \((-1)^{J_R}\), acting on the \( \Omega_r \) part gives an
additional factor \((-1)^{j_r}\). The operator \((12)\) changes only the \(\Omega_r\) factor, so that

\[
(12) \psi^{J,M,\epsilon}_{v,j_r,J_R} = (-1)^{j_r} \psi^{J,M,\epsilon}_{v,j_r,J_R},
\]

\[
E^* \psi^{J,M,\epsilon}_{v,j_r,J_R} = (-1)^{J_R+j_r} \psi^{J,M,\epsilon}_{v,j_r,J_R}.
\]

Therefore, we can rewrite \((6.20)\) as:

\[
\hat{P}_\Gamma \psi^{J,M,\epsilon}_{v,j_r,J_R} = (1 + \chi^{\Gamma}_{(23)}(23) + \chi^{\Gamma}_{(31)}(31)) \left(1 + (-1)^{j_r} \chi^{\Gamma}_{(12)}(12)\right) \left(1 + (-1)^{J_R+j_r} \chi^{\Gamma}_{E^*}\right) \psi^{J,M,\epsilon}_{v,j_r,J_R}.
\]

The above combination is identically zero if either the second or the third factor is zero. Thus, we obtain the combinations of \(J_R\) and \(j_r\) allowed for states transforming as \(\Gamma\). The results are summarized in Table 6.5.

Table 6.5: Allowed quantum numbers for the dimer+free-atom configuration. The trivial \(A_1'\) state with \(j_r = J_R = 0\) is not included this table.

<table>
<thead>
<tr>
<th>(\Gamma)</th>
<th>(j_r)</th>
<th>(J_R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1' \oplus E')</td>
<td>even</td>
<td>even</td>
</tr>
<tr>
<td>(A_1'' \oplus E'')</td>
<td>even</td>
<td>odd</td>
</tr>
<tr>
<td>(A_2' \oplus E')</td>
<td>odd</td>
<td>odd</td>
</tr>
<tr>
<td>(A_2'' \oplus E'')</td>
<td>odd</td>
<td>even</td>
</tr>
</tbody>
</table>
6.3 Correlations between configurations

The correlations between quantum numbers appropriate at different configurations of the three atoms are derived from conservation of the symmetry, i.e. irreducible representation of the state of three atoms. The possible correlations for several values of quantum numbers are summarized in Figs. 6.1 and 6.2 for total angular momentum \( J = 0 \) and \( J = 1 \). Since the symmetry depends only on the quantum numbers \( K \) and \( l_2 \) at small distances, on \( \Lambda \) and \( v \) for the non-interacting atoms, and on \( j_r \) and \( J_R \) for the dimer+atom configuration, only these quantum numbers are specified in Figs. 6.1 and 6.2.

With help of Figs. 6.3 and 6.4, we give an example of how the selection rules can be applied. Fig. 6.3 shows several adiabatic hyperspherical curves for a three-body model system. Such curves are obtained diagonalizing the rovibrational Hamiltonian in the space of the hyperangles, treating the hyper-radius as a continuous parameter. Rotational degrees of freedom (Euler angles) are also quantized. The particular example we consider is the actual \( \text{He}_3 \) potential [10] multiplied uniformly with an factor to obtain a deeper potential well for the trimer. The origin of the energy corresponds to the energy of the three atoms at infinite separation from each other. For simplicity of the discussion, we consider that the total angular momentum \( J \) of the system is zero. Therefore, the symmetry of the rotational part of the wave function is \( A'_{1} \). In Fig. 6.3, asymptotically-large values of the hyper-radius correspond to three-free-atom configuration if the energy of the system is positive and to the dimer+atom configuration if the total energy is negative. The lowest possible energy in
the asymptotic region is the energy of the dimer in the ground rovibrational state. For the considered model system, the dimer has only one possible vibrational state \( v = 0 \) and four rotational levels \( j_r = 0, 1, 2, \) and 3.

The selection rules could be applied to collisions of three atoms or to the decay of a quasi-bound three-body state (half-collision). As an example, we consider the decay of a quasi-bound state with the total energy larger than zero. After the decay, the system may end up in the three-free-atoms configuration or in the dimer+atom configuration. For example, if the initial state has symmetry \( A'_1 \), the dimer+atom configuration is possible only if \( j_r \) is an even number. This is clearly seen in Fig. 6.3: adiabatic curves of the \( A'_1 \) symmetry correlate at large hyper-radii only with dissociation thresholds with \( j_r = 0 \) and 2, which is consistent with the correlation diagram shown in Fig. 6.2. Similar analysis can be done for the \( E' \) initial state. However, \( E' \) short-range states can end up with all possible values of \( j_r \). There is no quasi-bound states of the \( A'_2 \) symmetry for the considered three-body potential. However, if we assume having the three free atoms collide in an \( A'_2 \) initial state, after such a collision only dimers with odd angular momenta \( j_r \) can be produced: \( A'_2 \) curves in Fig. 6.3 correlate only with odd \( j_r \) at large distances. Such initial arrangement of the three colliding identical atoms can be produced experimentally, for example, in ultra-cold gas of fully polarized fermionic atoms, such as \(^{40}\text{K}\).

As mentioned above, the irreducible representation of wave functions in hyperspherical coordinates is determined by the behavior of the functions along the hyper-angle \( \varphi \) and Euler angle \( \gamma \). In the considered example, the dependence on \( \gamma \) is trivial, since \( J = 0 \). Fig. 6.4
demonstrates the dependence of the wave functions on $\theta$ and $\varphi$ obtained numerically for three qualitatively different hyper-radii: (i) short hyper-radius, where the system behaves approximately as a rigid rotor, (ii) the intermediate region, and (iii) large hyper-radius, where one can approximate the system by three non-interacting atoms or the dimer+atom configuration. In the intermediate region no approximation may be applied. As it is clear from the figure, the symmetry of the wave functions is determined by a single variable $\varphi$. The binary permutations (12), (23) and (13) are equivalent, respectively, to refexions of the functions about the three axes going through the center of each plot in Fig. 6.4 at angles $\varphi = \pi/6$, $\varphi = 5\pi/6$ and $\varphi = -\pi/2$, whereas the cyclic permutations (123) and (132) are respectively equivalent to change of the hyperangle from $\varphi$ to $\varphi + \pi/3$ and $\varphi - \pi/3$.

6.4 Summary and conclusions

We have considered the sets of quantum numbers of three indistinguishable atoms for three different possible configurations: three non-interacting atoms, the pair of two interacting atoms and the third one being far from the pair, and finally, three interacting atoms. Some of the quantum numbers from the three sets are the same in the three configurations, others are appropriate only for the given configuration. During the process of collision of the three indistinguishable atoms, all three configurations are involved. The quantum numbers that are the same for the three configurations, are conserved during the collision, others are transformed. We analyzed the correspondence between quantum numbers from the three
sets and derived certain selection rules between them. The selection rules for several values of the quantum numbers are schematically presented in Figs. 6.1 and 6.2 as correlation diagrams similar to the correlation diagrams derived for diatomic molecules [129]. If needed, correlation diagrams for other values of the quantum numbers can be easily obtained from Tables 6.2, 6.3, 6.4, and 6.5. The derived correlation diagrams can be useful in analysis of experiments with ultra-cold degenerate atomic gases studying such processes as three-body recombination, formation and decay of three-body resonances [80, 78, 79, 60, 126], or thermalization of the degenerate gas.

Concluding, we would like to discuss briefly how the spin statistics can be included in the selection rules. Treating the nuclear and electronic spin parts of the total wave function separately from the rovibrational part, we neglected the interaction of the rovibrational motion with (electronic and/or nuclear) spins of the atoms. Hence, we assumed that the spin $\hat{H}_s$ Hamiltonian is separable from the the rovibrational Hamiltonian and the total wave function of the system is constructed as a product of the spin and spatial factors. The symmetry group of $\hat{H}_s$ is the subgroup $C_{3v}$ of $D_{3h}$.

Correspondingly, spin eigenstates transform in $D_{3h}$ according to one of the $A'_1, A'_2$, or $E'$ irreducible representations. The effect of the total spin of the system on the symmetry of total wave functions can be accounted using well-known tables of products of the $D_{3h}$ irreducible representations. An example of relationships between nuclear spin quantum numbers and irreducible representations for the system of three identical atoms is given in [74] for the case of $H_{3}^{+}$ (spin-$\frac{1}{2}$ atoms) and $D_{3}^{+}$ (spin-1 atoms).
Figure 6.1: Correlation diagram between the dimer+free-atom and three-free-atoms configurations. The quantum numbers used in this diagram are defined in Sections 6.2.3 and 6.2.2.
Figure 6.2: Correlation diagram between the dimer+free-atom and three-free-atoms configurations. The quantum numbers used in this diagram are defined in Sections 6.2.3 and 6.2.1.
Figure 6.3: Adiabatic curves for the model three-body potential discussed in the text. The total angular momentum $J = 0$. All coordinates except the hyper-radius are quantized. Since the irreducible representational is determined by the symmetry of the wave functions with respect to the (hyper-)angles $\varphi$ and $\gamma$, each curve is labeled with the index of an irreducible representation. For $J = 0$, only positive parity ($A_1', A_2'$, or $E'$) is allowed.
Figure 6.4: Hyperangular wave functions of three irreducible representations $A_1$, $A_2$, and $E$. $E$ is represented by its two components $E_a = \text{Re}al(E_+)$, and $E_b = \text{Im}(E_+)$. Here, the parity is defined (positive) but not specified since it is controlled by $\gamma$, that cannot be shown. In the left column the hyper-radius is $\approx 9$ a.u., in the middle column it is $\approx 20$ a.u., and in the right column it is $\approx 30$ a.u. The wave functions are shown as contour plots depending on $\theta$ and $\varphi$. The three upper functions are shown for only two values of contour cuts: 0.5 and 0.75. The other functions are shown for values $\pm 0.5$ and $\pm 1$. 
CHAPTER 7

SYMMETRY IN MOLECULAR SYSTEM COMPOSED WITH

FOUR IDENTICAL ATOMS

7.1 The general approach

Following the previous study on correlation diagrams in collisions of three identical atoms (Chapter 6), we describe the symmetry of a quantum system of four identical atoms in any possible large-distance configuration. As for the case of three identical atoms, we consider possible fragmentation channels for the system of four colliding atoms. Namely, we study the following rearrangements: (1) two dimers, (2) a trimer and a free atom and (3) a dimer and two free atoms. The case of four free atoms is not considered.

The main interest of this study is to derive selection rules for the scattering process from an initial state of a given four-body fragmentation rearrangement into a final state of a different rearrangement. An example of this kind of process is rearrangement collisions of four ultra-cold alkaline atoms such as Cs₃+Cs→Cs₂+Cs₂ or Cs₂+Cs+Cs→Cs₃+Cs. Although the derivation of the selections rules does not require complex numerical calculations, it involves a laborious analytical work to determine and classify in a clear way the allowed symmetries of the wave function depending on the constants of motions in each fragmentation
channel. For this reason, the following results can be considered as a general basis for studying collisions involving four identical atoms at low energies. The derived selection rules are applicable for processes at temperature significantly lower than the typical energy splitting between quantum states in the incident channel. At such low temperatures, the symmetry of the system plays a role and determines allowed transitions. Furthermore, we assume that the spin-orbit interaction is small, so that the complete Hilbert space of the four-atom Hamiltonian can be written as a tensorial product of spatial and spin spaces. The symmetry of each part of this tensorial space can be studied separately.

We start by considering the total group of symmetry of a molecular system, already introduced in equation (2.13)

\[ G_{\text{Full}} = G_T \otimes K(\text{spatial}) \otimes S_n^e \otimes G_{\text{CNP}} \otimes \varepsilon. \]  

(7.1)

In the above formula, \( G_{\text{Full}} \) is the total group of symmetry of the system expressed through the translational group \( G_T \), the rotational group \( K(\text{spatial}) \), the electron permutation group \( S_n^e \), the complete nuclear permutation group \( G_{\text{CNP}} \), and the inversion group \( \varepsilon = \{ E, E^* \} \) (\( E \) and \( E^* \) denote respectively the identity and parity operator). The wave functions transforming irreducibly in \( G_{\text{Full}} \) are the ones that simultaneously transform irreducibly in each of the former groups. In our study, we consider the irreducible representations related to the complete nuclear permutation inversion (CNPI) group of four identical particles \( G_{48} = S_4 \otimes \varepsilon \), where \( S_4 \) is the group of permutations of four elements. It is actually more convenient to
express the CNPI group using the point group of the tetrahedron $T_d(M)$ in the equivalent form $G_{48} = T_d(M) \otimes \varepsilon$. It allows use of the familiar notations for the irreducible representations of $T_d(M)$ to describe those of $G_{48}$, except that the latter have an even or odd character under inversion (respectively denoted by prime and double-prime symbols).

The group $G_{48}$ describes the general symmetry of a system of four identical particles as each of its element commutes with the molecular Hamiltonian. If we consider the system as divided in two or more fragments at large distances from each other, the interaction between the fragments can be discarded. This allows us to classify possible quantum states of the system using quantum numbers appropriate for isolated fragments. On the other hand, considering the system as isolated fragments ultimately decreases the symmetry of the Hamiltonian, which is not described anymore by the full group $G_{48}$. Because each fragment consists of one, two, or three particles only, its group of symmetry\textsuperscript{1} $G$ is a sub-group of $G_{48}$. Therefore, any eigenspace of the approximate Hamiltonian can be considered as a representation $\Gamma$ of $G$ and be decomposed in irreducible representations $\Gamma_i$ of $G$ in such that

$$\Gamma = \oplus a_i \Gamma_i. \quad (7.2)$$

Using the standard formula [86], the coefficients of the decomposition are

$$a_i = \frac{1}{|G|} \sum_{R \in G} \chi^{(i)}(R) \chi (R). \quad (7.3)$$

\textsuperscript{1}Since parts of the Hamiltonian are neglected, some elements of $G_{48}$ do not commute with the approximate Hamiltonian.
In the above formula, the number \( h \) is the order of the group \( G \), \( \chi^{(i)}(\hat{R}) \) are the characters of each irreducible representation for a particular element \( \hat{R} \) of the group and \( \chi(\hat{R}) \) are the different characters of each element \( \hat{R} \) for the reducible representation \( \Gamma \). Hence, each eigenspace related to a set of conserved quantum numbers of the system will be decomposed into irreducible representations of the group \( G \).

During the collision process, the fragments approach close to each other and the approximate Hamiltonian becomes inapplicable. One has to consider the symmetry of the exact Hamiltonian described by \( G_{48} \). Therefore, it is important to know how the lower-symmetry representations in \( G \) are transformed in the full group \( G_{48} \). In other words we have to know how lower-symmetry representations are reduced into \( G_{48} \) irreducible representations. In our approach, the role of the group \( G \) is not only to label clearly the different symmetries of an initial or final state, but also to give a useful intermediate of calculation towards the decomposition of an eigenspace of the system in irreducible representations of \( G_{48} \). Instead of using directly equation (7.3) on a subspace of the group \( G_{48} \) (which could be a cumbersome calculation as the symmetry of \( G_{48} \), despite the one of \( G \), is not well suited for the constants of motion of the system at large distances), we can use equation (7.3) on any irreducible representation of \( G_{48} \) and decompose it as irreducible representations of \( G \). This calculation is straightforward using table of characters of the groups. When the decomposition is derived, it can be be inverted to find the decomposition of eigenspace of \( G \) in irreducible representations of \( G_{48} \).
Table 7.1: Characters of the irreducible representations of the group $T_d(M)$.

<table>
<thead>
<tr>
<th></th>
<th>$T_d$</th>
<th>E</th>
<th>(123)</th>
<th>(12)(34)</th>
<th>(1234)*</th>
<th>(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$F_1$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$F_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

As already mentioned, the group $G_{48} = T_d(M) \otimes \varepsilon$. Hence, we can study the symmetry of $G_{48}$ by considering separately the symmetry of $T_d(M)$ and of $\varepsilon$. For clarity we also choose the groups $G$ to be sub-groups of $T_d(M)$ such that our approach relies systematically on the characteristics of symmetry of the point group of the tetrahedron$^2$ $T_d(M)$. The $T_d(M)$ group, equivalent to the permutation group of four identical elements $S_4$, has five irreducible representations [86, 21]: $A_1$ and $A_2$ (one dimensional), $E$ (two dimensional) and $F_1$ and $F_2$ (three dimensional). The characters of $T_d(M)$ are given in Table 7.1. When the decompositions are found for both reducible representations of space and spin, the decomposition of the total reducible representation (product of spin and spatial parts) can be easily obtained using the table of products of irreducible representations (Table 7.2). For example, one concludes from this table that the totally antisymmetric irreducible representation can only be obtained by three of the ten different products: $E \otimes E$, $F_1 \otimes F_2$ and $A_1 \otimes A_2$.

We stress the following point inherent to our treatment. When considering a large distance configuration, we choose at first the sub-group $G$ of $T_d(M)$, which describes the best the symmetry of the system. In the next step, we apply equation (7.3) to find the decom-

$^2$For instance, the molecules CH$_4$ and NH$_4^+$ are described by the point group $T_d(M)$ if tunneling from an equilibrium configuration to another is neglected.
Table 7.2: Products of irreducible representations of the group $T_d$.

<table>
<thead>
<tr>
<th></th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$E$</th>
<th>$F_1$</th>
<th>$F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>$A_1$</td>
<td>$A_2$</td>
<td>$E$</td>
<td>$F_1$</td>
<td>$F_2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$A_2$</td>
<td>$A_1$</td>
<td>$E$</td>
<td>$F_2$</td>
<td>$F_1$</td>
</tr>
<tr>
<td>$E$</td>
<td>$E$</td>
<td>$E$</td>
<td>$A_1 \oplus A_2 \oplus E$</td>
<td>$F_1 \oplus F_2$</td>
<td>$F_1 \oplus F_2$</td>
</tr>
<tr>
<td>$F_1$</td>
<td>$F_1$</td>
<td>$F_2$</td>
<td>$F_1 \oplus F_2$</td>
<td>$A_1 \oplus E \oplus F_1 \oplus F_2$</td>
<td>$A_2 \oplus E \oplus F_1 \oplus F_2$</td>
</tr>
<tr>
<td>$F_2$</td>
<td>$F_2$</td>
<td>$F_1$</td>
<td>$F_1 \oplus F_2$</td>
<td>$A_2 \oplus E \oplus F_1 \oplus F_2$</td>
<td>$A_1 \oplus E \oplus F_1 \oplus F_2$</td>
</tr>
</tbody>
</table>

Position of the irreducible representations of $G_{48}$ in irreducible representations of $G$ and we invert this decomposition to find the allowed decomposition of the irreducible representations of $G$ in irreducible representations of $T_d(M)$. However, it is in general not true that this decomposition will describe exactly the representation space in $T_d(M)$. Nevertheless, it always provides the forbidden irreducible representations of $T_d(M)$ for the representation under consideration. Let us note $h_G$ and $h_T$ the respective orders of the groups $G$ and $T_d(M)$. We also introduce the integer\(^3 d = h_T/h_G\) and a representation space\(^4 \xi \) of $G$. If, when we apply all the elements of $T_d(M)$ on the basis wave functions of $\xi$, we create a new reducible space $\xi'$ of dimension $d$ times the dimension of $\xi$, then the decomposition of $\xi'$ in irreducible representations of $T_d(M)$ is exactly described by the procedure discussed above.

It means that the elements of the group $T_d(M)$ will create $d$ times new independent functions so that all the irreducible representations in the decomposition will be allowed. The latter point will become more clear when we discuss practical cases below. We will see that the spatial part of the total wave function always fulfill this requirement. On the other hand, it is not true if we consider the spin part of the wave function, for which Young tableaux

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\(^3\)From group theory, one can show that $d$ is always an integer if $G$ is a sub-group of $T_d(M)$.

\(^4\)Thus, $\xi$ is stable under all the elements of $G$ but unstable under the elements of $T_d(M)$.
represent the adequate way to find the symmetry. Despite this fact, for only four atoms, simple considerations and knowledge of the allowed representations in $T_d(M)$ are sufficient to find the exact decomposition.

7.2 Two dimers at large distance

Let us at first focus on the configuration for which two dimers are at relative large distances from each other. In this configuration the dimers are weakly interacting (or not interacting at all) through a potential depending solely on the distance between the centers of mass of the dimers. In the center of mass referential system, Jacobi coordinates are appropriate to describe such a configuration. The canonical transformations\(^5\) from the initial system of coordinates $\{\vec{r}_i, \vec{p}_i\}$ for $i = 1, 2, 3$ and 4, to the new system of coordinates $\{\vec{r}_{12}, \vec{p}_{12}, \vec{r}_{34}, \vec{p}_{34}, \vec{R}, \vec{P}\}$ can be written in the following form

\[
\begin{align*}
\vec{r}_{12} &= \vec{r}_1 - \vec{r}_2; \quad \vec{r}_{34} = \vec{r}_3 - \vec{r}_4; \quad \vec{R} = \frac{1}{2} (\vec{r}_3 + \vec{r}_4 - \vec{r}_1 - \vec{r}_2) \\
\vec{p}_1 &= -\frac{\vec{P}}{2} + \vec{p}_{12}; \quad \vec{p}_2 = -\frac{\vec{P}}{2} - \vec{p}_{12}; \quad \vec{p}_3 = \frac{\vec{P}}{2} + \vec{p}_{34}; \quad \vec{p}_4 = \frac{\vec{P}}{2} - \vec{p}_{34}.
\end{align*}
\]  

(7.4)  

(7.5)

These coordinates are depicted schematically in Fig. 7.1.

If we label with $m$ the mass of each of the four atoms, define the reduced masses of the two dimers $\mu_{12} = \mu_{34} = \mu = m/2$, the reduced mass $\mu_{\vec{R}} = m$ for the dimer-dimer system

\(^5\)These transformations and transformations below are obtained using the condition that the center of mass is at the origin, thus $\vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \vec{r}_4 = 0$. 

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and introduce $r_{12} = |\vec{r}_{12}|$, $r_{34} = |\vec{r}_{34}|$ and $R = \vec{R}$, the Hamiltonian in the new system of coordinates has the form

$$\hat{H} = \frac{1}{2\mu} \vec{p}_{12}^2 + V^k_{12}(r_{12}) + \frac{1}{2\mu} \vec{p}_{34}^2 + V^{k'}_{34}(r_{34}) + \frac{1}{2\mu R} \vec{P}^2 + V_{dd}(R) + \hat{H}_{\text{spin}}. \quad (7.6)$$

In the above expression, the potentials $V^k_{12}$ and $V^{k'}_{34}$ represent the Born-Oppenheimer electronic potentials characterizing the interaction of two atoms in each dimer with electronic states labeled respectively $k$ and $k'$, $V_{dd}$ is the radial potential of interaction between the two dimers at large distance. The operators associated with these new variables satisfy standard commutation relations as $[\hat{r}_{12}, \hat{p}_{12}] = i\hbar$ or $[\hat{r}_{12}, \hat{p}_{34}] = 0$. The Hamiltonian of the system can be expressed as the sum of independent Hamiltonians as $\hat{H} = \hat{H}_{12} + \hat{H}_{34} + \hat{H}_R + \hat{H}_{\text{spin}}$, where $\hat{H}_{\text{spin}}$ represents the spin part of the total Hamiltonian. Thus, we can treat the spatial part separately from the spin part. The solution of the Schrödinger equation is written as the

![Diagram](image)

Figure 7.1: Configuration: two dimers at large distance.

\footnote{In this study, the potential $V_{dd}$ has to be either set to zero at large distances, or at most be radial, in order to find a simple form for the solution of the Schrödinger equation. For instance, $V_{dd}$ could be a dimer-dimer potential averaged over the rovibrational states of the two dimers.}
following product

$$\Psi_{a,b}^{L,M,\varepsilon} = f_{n_a,l_a}^k (r_{12}) Y_{l_a}^{m_a} (r_{12}) f_{n_b,l_b}^{k'} (r_{34}) Y_{l_b}^{m_b} (r_{34}) F_{\varepsilon,L} (R) Y_{L}^{M} (\vec{R}).$$ \hspace{1cm} (7.7)

In (7.7), $l_a$ and $l_b$ represent the angular momenta of the dimers, $L$ is the angular momentum of the two dimers relative motion with associated reduced mass $\mu_{\vec{R}}$ and vector position $\vec{R}$. The quantum numbers $m_a$, $m_b$ and $M$ are the projections of these angular momenta on a fixed laboratory axis, $n_a$ and $n_b$ are principal quantum numbers describing the vibrational state of each dimer, and $\varepsilon$ is the energy related to the relative motion of the two dimers. The functions $f^k$, $f^{k'}$ and $F$ represent respectively the different radial parts of the wave function in the potential $V_{12}^k$, $V_{34}^{k'}$ and $V_{dd}$. To simplify the notations, we introduced $a = \{n_a, l_a, m_a\}$ and $b = \{n_b, l_b, m_b\}$ in the expression of the wave function (7.7).

Table 7.3: Character table of the sub-group $G_1$ (isomorphic to the point group $C_{2v}(M)$) for the case of two dimers in different electronic states.

<table>
<thead>
<tr>
<th>$G_1$</th>
<th>$E$</th>
<th>$(12)^*$</th>
<th>$(12)(34)$</th>
<th>$(34)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

We consider a very general case when the two potentials $V_{12}^k$ and $V_{34}^{k'}$ are different ($k \neq k'$). Physically, it means that the two dimers are distinguishable and we can label the dimer composed with the atoms 1 and 2 by the set of quantum numbers $a$ and the other dimer by $b$. The sub-group of $T_d(M)$ that describes the best the symmetry of this Hamiltonian is the group $T_d(M)$. \hspace{1cm} 200
$G_1 = \{E, (12)^*, (34)^*, (12)(34)\}$, isomorphic to the point group $C_{2v}(M)$ (water molecule) and composed of four classes (one element in each class). We choose the usual convention of naming the irreducible representations of $G_1$ by their corresponding names in the point group $C_{2v}(M)$. On that account, $G_1$ has $A_1$, $A_2$, $B_1$ and $B_2$ irreducible representations.

Table 7.3 gives the characters of the group $G_1$. We now apply the operators of the group $G_1$ on the wave function (7.7) and obtain

\begin{align*}
(12)^*\Psi^{L,M,\varepsilon}_{a,b} &= (-1)^{l_b + L} \Psi^{L,M,\varepsilon}_{a,b} \\
(34)^*\Psi^{L,M,\varepsilon}_{a,b} &= (-1)^{l_a + L} \Psi^{L,M,\varepsilon}_{a,b} \\
(12)(34)\Psi^{L,M,\varepsilon}_{a,b} &= (-1)^{l_a + l_b} \Psi^{L,M,\varepsilon}_{a,b} \\
E^*\Psi^{L,M,\varepsilon}_{a,b} &= (-1)^{l_a + l_b + L} \Psi^{L,M,\varepsilon}_{a,b}.
\end{align*}

We can use the formula (7.3) to find the irreducible representations of the one dimensional space defined by the set of quantum numbers $\{a, b, L, M, \varepsilon\}$. When this procedure has been performed, we can use again formula (7.3) on the irreducible representations of the group $T_d(M)$ to find their decompositions in irreducible representations of $G_1$. When we invert these results, we obtain the decomposition of an irreducible representations of $G_1$ on the irreducible representations of $T_d(M)$. This decomposition is exact. Indeed, the ratio $h_{T_d}/h_{G_1}$ equals six and the representation space in $G_1$ is one dimensional\(^8\). On the other hand, six independent wave functions are produced by applying the elements of $T_d(M)$ on (7.7), so

\(^7\)The symmetry transformations are obtained using solely the well know transformation of spherical harmonics, namely $Y_m^l(-\vec{r}) = (-1)^l Y_m^l(\vec{r})$, where $\vec{r}$ is any position vector.

\(^8\)The elements of the group $G_1$ do not create new independent functions when apply on (7.7).
that the representation space in $T_d(M)$ has dimension six. Finally, we consider the parity operator as well to obtain the actual total sub-group $G_1 \otimes \varepsilon$ of the group of symmetry $G_{48}$. The results\(^9\) are listed in Table 7.4.

Table 7.4: Decomposition in irreducible representations of $G_1 \otimes \varepsilon$ (two different electronic states), $G_2 \otimes \varepsilon$ (same electronic states, different rovibronic states) and $G_{48}$ for the space part of two dimers at far distance.

<table>
<thead>
<tr>
<th>$l_a$</th>
<th>$l_b$</th>
<th>$L$</th>
<th>Dec. in $G_1 \otimes \varepsilon$</th>
<th>Dec. in $G_2 \otimes \varepsilon$</th>
<th>Dec. in $G_{48}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>even</td>
<td>even</td>
<td>$A'_1$</td>
<td>$A'_1 \oplus B'_2$</td>
<td>$A'_1 \oplus E'' \oplus F''_2$</td>
</tr>
<tr>
<td>odd</td>
<td>odd</td>
<td>odd</td>
<td>$A''_1$</td>
<td>$A''_1 \oplus B''_2$</td>
<td>$A''_1 \oplus E'' \oplus F''_2$</td>
</tr>
</tbody>
</table>
| even  | even  | odd  | $B'_2$                          | $A'_2 \oplus B'_1''$           | $A'_2 \oplus E' 
\oplus F'_1''$ |
| odd   | odd   | even | $B''_2$                         | $B'_2$                         | $E''$           |
| even  | odd   | odd  | $A''_2$                         | $E''$                         | $F''_1 \oplus F''_2$ |
| odd   | even  | even | $A''_2$                         | $E''$                         | $F''_1 \oplus F''_2$ |

Let us now consider the case where the two dimers are in the same electronic state ($k = k'$). Physically, the dimers are indistinguishable and their Born-Oppenheimer electronic potentials are equal. For this reason, the symmetry of the Hamiltonian of the system in (7.6) is increased as we are allowed to perform exchange of the dimers. Therefore the sub-group of $T_d(M)$ that describes the best the symmetry of the Hamiltonian is the group $G_2$ that contains the elements of the group $G_1$, as well as the new elements of exchange of dimers $(1423)^*$, $(1324)^*$, $(14)(23)$ and $(13)(24)$. This group is isomorphic to the point group $D_{2d}(M)$ used for example, to describe the allene molecule ($C_3H_4$) without torsional tunneling. Again we name

\(^9\)These results have been obtained for fixed value of the projections of the different angular momenta. They are still true if one instead constructs a wave function with definite values of the total angular momentum, of $l_a$, $l_b$ and $L$, since the symmetry does not depend on the projections of $\vec{l}_a, \vec{l}_b$ and $\vec{L}$. 

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the irreducible representations of $G_2$ using the irreducible representation of the corresponding point group $D_{2d}(M)$. This group has four one-dimensional irreducible representations $A_1$, $A_2$, $B_1$, $B_2$ and a two-dimensional irreducible representation $E$. Table 7.5 gives characters of this group.

Table 7.5: Character table of the sub-group $G_2$ for the case of two dimers in the same electronic states. $G_2$ is isomorphic to the point group $D_{2d}(M)$.

<table>
<thead>
<tr>
<th>$G_2$</th>
<th>$E$</th>
<th>(1423)$^*$</th>
<th>(12)(34)</th>
<th>(13)(24)</th>
<th>(34)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

If we consider at first the general case for which $\{n_a,l_a\} \neq \{n_b,l_b\}$, we can apply our general procedure on the reducible space defined by the set $\{a,b,L,M,\varepsilon\}$. In order to find the characters of each operator of $G_2$, we consider the result of (7.8) as well as the actions of the new operators in $G_2$:

\[
(13)(24)\Psi_{a,b}^{L,M,\varepsilon} = (-1)^L\Psi_{b,a}^{L,M,\varepsilon}
\]

\[
(1423)^*\Psi_{a,b}^{L,M,\varepsilon} = (-1)^{l_a}\Psi_{b,a}^{L,M,\varepsilon}
\]

\[
(1324)^*\Psi_{a,b}^{L,M,\varepsilon} = (-1)^{l_b}\Psi_{b,a}^{L,M,\varepsilon}.
\]

It is easy to see that the representation space is now two-dimensional. If $l_a$ and $l_b$ have different parities, the space can only be the $E$ irreducible representation of $G_2$ (as the
character of \((34)^*\) is for example zero). On the other hand, if \(l_a\) and \(l_b\) have the same parity, the space has to be the sum of two one dimensional irreducible representations. Also, it is easy to see that the decomposition is also exact using similar arguments than the ones introduced in the previous case. These results are listed in Table 7.4 as well. The final decompositions in \(T_d(M)\) are the same in both cases.

Table 7.6: Correspondence between the irreducible representations of \(G_2\) and \(T_d(M)\).

<table>
<thead>
<tr>
<th>(\Gamma) in (G_2)</th>
<th>Dec. in (T_d(M))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>(A_1 \oplus E)</td>
</tr>
<tr>
<td>(B_1)</td>
<td>(A_2 \oplus E)</td>
</tr>
<tr>
<td>(A_2)</td>
<td>(F_1)</td>
</tr>
<tr>
<td>(B_2)</td>
<td>(F_2)</td>
</tr>
<tr>
<td>(E)</td>
<td>(F_1 \oplus F_2)</td>
</tr>
</tbody>
</table>

It is worth mentioning here the relation between true and accident degeneracies. For the case when the integers \(l_a\) and \(l_b\) are of same parity, the two states of the different one-dimensional irreducible representations have the same energy at the limit of an infinite separation between the dimers. This is an accidental degeneracy. At finite inter-dimer separations a weak interaction between the dimers lifts the accidental degeneracy: the states of the one-dimensional irreducible representations (for the same pair \(l_a\) and \(l_b\)) become non-degenerate. However, for the case of the two-dimensional irreducible representation (when \(l_a\) and \(l_b\) have different parities), the degeneracy is true because it is given by the symmetry properties of equations (7.8) and (7.9), which are true for infinite and finite separations. Therefore, when \(l_a\) and \(l_b\) have different parities, the degeneracy of the two states is not lifted at finite inter-dimer separations.
Concluding, at given \( a \) and \( b \), the particular irreducible representation of the eigenspace is the only relevant information to describe the eigenstates. Thus, no other physical constants of the system can label one-dimensional irreducible representations of \( G_2 \) at large distances. It is important to know how any irreducible representations of \( G_2 \) is decomposed into irreducible representations of \( T_d(M) \). The correspondence is given in Table 7.6. We stress the fact that symmetry does not depend on particular values of \( m_a, m_b \) nor \( M \). For this reason, any superposition of these states will have the same symmetry.

We also need to consider a special case for which the two dimers are in the same rovibronic states, namely \( \{n_a, l_a\} = \{n_b, l_b\} = \{n, l\} \). If the projections \( m_a \) and \( m_b \) are the same, the reducible space becomes one dimensional and should be treated differently. However, instead of separating this case from the others, it is more appropriate\(^{10} \) to introduce the new quantum numbers \( \vec{l}_{ab} = \vec{l}_a + \vec{l}_b \) and its projection \( m_{ab} \) on an arbitrary axis of the laboratory. We construct the new wave function

\[
\Phi_{l,\vec{l}_{ab},m_{ab}}^{L,M,\varepsilon} = \sum_{m_a, m_b} C_{l,m_a,l,m_b}^{\vec{l}_{ab},m_{ab}} \Psi_{a,b}^{L,M,\varepsilon}.
\]

Only transformations corresponding to the exchange of the two dimers have to be modified. Using the symmetry property of the Clebsh-Gordan coefficients

\[
C_{l,m_a,l,m_b}^{\vec{l}_{ab},m_{ab}} = (-1)^{l_{ab}} C_{l,m_b,l,m_a}^{\vec{l}_{ab},m_{ab}}.
\]

\(^{10}\text{This is the usual way to treat composition of three angular momenta.}\)
we find the following form for the transformations:

\[(13)(24)\Phi_{l_{ab},m_{ab}}^{L,M,\varepsilon} = (-1)^{L+l_{ab}}\Phi_{l_{ab},m_{ab}}^{L,M,\varepsilon}\]

\[(1423)^*\Phi_{l_{ab},m_{ab}}^{L,M,\varepsilon} = (-1)^{l_{ab}+l_{ab}}\Phi_{l_{ab},m_{ab}}^{L,M,\varepsilon}\]

\[(1324)^*\Phi_{l_{ab},m_{ab}}^{L,M,\varepsilon} = (-1)^{l_{ab}+m_{ab}}\Phi_{l_{ab},m_{ab}}^{L,M,\varepsilon}.
\]

From the action of the operators we establish the correspondence between the quantum numbers participating in the symmetry \(\{l, L, l_{ab}\}\) and the irreducible representations of \(G_2\) via formula (7.3). Using Table 7.6, we find the desired results that are listed in Table 7.7.

Here, the particular symmetry does not depend on the quantum numbers \(m_{ab}\) and \(M\) so that any superposition of these states (for example to construct the total angular momentum of the system) has the same symmetry.

Table 7.7: Decomposition in irreducible representations of \(G_2 \otimes \varepsilon\) and \(G_{48}\) for the space part of two dimers at far distance in the same electronic and rovibronic states.

<table>
<thead>
<tr>
<th>(l)</th>
<th>(L)</th>
<th>(l_{ab})</th>
<th>Dec. in (G_2 \otimes \varepsilon)</th>
<th>Dec. in (G_{48})</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>even</td>
<td>even</td>
<td>(A'_1)</td>
<td>(A'_1 \oplus E')</td>
</tr>
<tr>
<td>odd</td>
<td>odd</td>
<td>odd</td>
<td>(A''_1)</td>
<td>(A''_1 \oplus E'')</td>
</tr>
<tr>
<td>even</td>
<td>odd</td>
<td>odd</td>
<td>(B'_1)</td>
<td>(A'_2 \oplus E')</td>
</tr>
<tr>
<td>odd</td>
<td>even</td>
<td>even</td>
<td>(B''_1)</td>
<td>(A''_2 \oplus E'')</td>
</tr>
<tr>
<td>even</td>
<td>odd</td>
<td>even</td>
<td>(A''_2)</td>
<td>(F''_1)</td>
</tr>
<tr>
<td>odd</td>
<td>even</td>
<td>odd</td>
<td>(A'_2)</td>
<td>(F'_1)</td>
</tr>
<tr>
<td>even</td>
<td>odd</td>
<td>odd</td>
<td>(B''_2)</td>
<td>(F''_2)</td>
</tr>
<tr>
<td>odd</td>
<td>even</td>
<td>even</td>
<td>(B'_2)</td>
<td>(F'_2)</td>
</tr>
</tbody>
</table>
The spin Hamiltonian (7.6) can also be described by the group \( G_2 \), considered\(^{11} \) as a sub-group of \( S_4 \). The group \( S_4 \) is equivalent to \( T_d(M) \) so that all previous decompositions relating irreducible representations of \( T_d(M) \) to \( G_2 \) are equivalently valid between \( S_4 \) and \( G_2 \). The constants of motion introduced to describe this system are \( S_a, S_b \) and \( S_{\text{tot}} \), which represent respectively the spins of each dimer, the total spin of the system, and their respective projections \( M_a, M_b \) and \( M_{\text{tot}} \) on a laboratory axis. The spin wave function has the following form:

\[
\Psi^{S_{\text{tot}},M_{\text{tot}}}_{S_a,S_b} = \sum_{M_a,M_b} C^{S_{\text{tot}},M_{\text{tot}}}_{S_a,M_a,S_b,M_b} |S_a,M_a\rangle |S_b,M_b\rangle.
\]  

(7.13)

The action of the operators of \( G_2 \) on the wave function (7.13) are straightforward. On the other hand, the general procedure to obtain the decomposition of the representation spaces into irreducible representations of \( S_4 \) does not always provide the exact decomposition. Let us treat each case separately.

We start with the two-dimensional space \( S_{\text{tot}} = 0 \), which can be formed from the compositions of \( S_a \) and \( S_b \) either by \( 0 \otimes 0 \) or by \( 1 \otimes 1 \). Both of these compositions are one-dimensional in \( G_2 \), but form together only a two dimensional representation in \( S_4 \). We conclude that \( S_4 \) does not create enough independent functions for the decomposition procedure adopted previously to be exact. Still, this decomposition reveals the only possible irreducible repre-

\(^{11}\)We still use symbol \( G_2 \) for this sub-group to avoid introduction of new notations. Any superscript corresponding to the inversion operation in the operators of \( G_2 \) in Table 7.5 should now be discarded.
sentations that decompose this space in $S_4$. In order to find the correct decomposition, we do the following.

Table 7.8: Decomposition in irreducible representations of the spin part for two dimers. The spaces with $E$ and $F_1 \oplus F_2$ decompositions in $S_4$ are separately formed by superposition of spin states of two corresponding rows in the table.

<table>
<thead>
<tr>
<th>$S_a$</th>
<th>$S_b$</th>
<th>$S_{tot}$</th>
<th>Dec. in $G_2$</th>
<th>Dec. in $S_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$A_1$</td>
<td>$E$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>$B_1$</td>
<td>$E$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$B_2$</td>
<td>$F_2$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>$E$</td>
<td>$F_1 \oplus F_2$</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>$E$</td>
<td>$F_1 \oplus F_2$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>$A_1$</td>
<td>$5A_1$</td>
</tr>
</tbody>
</table>

Bearing in mind the trivial property of exchange symmetry of the spin in a diatomic and considering the symmetry property of the Clebsh-Gordan coefficients, we can show using Table 7.5, that the spaces $0 \otimes 0$ and $1 \otimes 1$ are reduced respectively to $A_1$ and $B_1$ in $G_2$. Using Table 7.6, we conclude that the spaces $0 \otimes 0$ and $1 \otimes 1$ are reduced respectively to $A_1 \oplus E$ and $A_2 \oplus E$ in $S_4$. In this case, the two dimensional space $S_{tot} = 0$ can only be of $E$ irreducible representation in $S_4$ because it is the only irreducible representation allowed for both spin compositions. Considering the case $S_{tot} = 1$ from the $1 \otimes 1$ space, we find that it is only formed by $B_2$ irreducible representations of $G_2$ so that it is bound to be of $F_2$ symmetry in $S_4$ (thus corresponding to the three projections of the total spin). The other space with $S_{tot} = 1$ formed by either $0 \otimes 1$ or $1 \otimes 0$ can only be $E$ in $G_2$, so that the decomposition is $F_1 \oplus F_2$ in $S_4$. One can check that the total number of independent functions created by action of $S_4$ on the two dimensional space is six, so that this decomposition is complete.
Finally, the space $S_{tot} = 2$ has to be formed by the $A_1$ symmetry in $S_4$. Its decomposition is $5A_1$ considering the five different projections of the spin. These results are listed in Table 7.8.

7.3 A bound triatomic and a free atom and a diatomic and two free atoms

7.3.1 A trimer and a free atom

We study for this configuration, a trimer and a free atom in their center of mass coordinate system. Towards this aim, we introduce appropriate coordinates \{\vec{r}_i', \vec{p}_i\}, i=1,2,3 and \{\vec{R}, \vec{P}\}. This set of coordinates is schematically depicted in Fig.(7.2) and defined by the
following canonical transformations:

\[
\vec{R} = \vec{r}_4 - \frac{\vec{r}_1 + \vec{r}_2 + \vec{r}_3}{3}; \quad \vec{r}_i' = \vec{r}_i - \frac{\vec{R}}{4}, i = 1, 2, 3
\]  
(7.14)

\[
\vec{P} = \vec{p}_4; \quad \vec{p}_i' = \vec{p}_i + \frac{\vec{P}}{3}, i = 1, 2, 3.
\]  
(7.15)

In the above transformations, we identify the couples \(\{\vec{r}_i', \vec{p}_i'\}\) for \(i = 1, 2, 3\), as the positions and momenta of the three atoms relative to the center of mass of the trimer. Introducing the reduced mass \(\mu = \frac{3m_4}{4}\), the Hamiltonian expressed with this new set of variables takes the following form

\[
\hat{H} = \frac{1}{2m} \sum_{i=1}^{3} \vec{p}_{i'}^2 + V_{123}^k(\vec{r}_1', \vec{r}_2', \vec{r}_3') + \frac{1}{2\mu} \vec{P}^2 + V(R) + \hat{H}_{\text{spin}}.
\]  
(7.16)

In this expression, \(V_{123}^k\) represents the internal potential of the trimer in a given electronic state \(k\). From equation (7.16), it can be easily seen that the spatial part of the quantum Hamiltonian is the sum of two independent Hamiltonians \(\hat{H} = \hat{H}_{\text{trimer}} + \hat{H}_{\vec{R}}\), where \(\hat{H}_{\text{trimer}}\) represents the Hamiltonian of the trimer in its own coordinate system, and \(\hat{H}_{\vec{R}}\) is the Hamiltonian of a fictive particle of mass \(\mu\) and position vector \(\vec{R}\) moving in a central potential \(V(R)\), where \(R = |\vec{R}|\). The sub-group \(G_3 = \{E, (12)^*, (23)^*, (13)^*, (123), (132)\}\) of \(T_d(M)\) describes the best the symmetry of the Hamiltonian. This group is isomorphic to the point group \(C_{3v}(M)\), which has two one-dimensional irreducible representations \(A_1\) and \(A_2\) and the two dimensional irreducible representation \(E\). The character table of \(C_{3v}(M)\) is given for example in [21]. If we consider small internal distances for the atoms of the trimer and
apply the rigid-rotor and harmonic approximations (see Subsection 2.2.1.2) for the potential around equilibrium, the spatial wave function of the system takes the following general form

$$\Psi_{N,K,M,v_1,v_2,l_2}^{L,M_L,\varepsilon} = R_{K,M}^N(\alpha, \beta, \gamma)\varphi_{v_1,v_2}^{l_2}(Q_1, Q_x, Q_y)f_{\varepsilon,L}(R)Y_{M_L}^{M}(\vec{R}).$$

(7.17)

The variables $\alpha$, $\beta$ and $\gamma$ are the Euler angles related to the rotation of the trimer. The quantum numbers $N$, $K$ and $M$ are respectively the angular momentum of the rigid trimer, its projection along the main axis of symmetry of the trimer and its projection on a laboratory-fixed axis. Also, $Q_1$ on one hand, and $Q_x$ and $Q_y$ on the other hand, are respectively the normal coordinates of symmetric stretch mode associated with the quanta of vibration $v_1$, and asymmetric stretch mode associated with the quanta of vibration $v_2$ and the projection $l_2$ of the angular momentum about the main symmetry axis of the trimer generated by vibration [74] ($l_2$ can have values $-v_2, -v_2 - 2, ..., v_2 - 2, v_2$). The quantum numbers $\varepsilon$, $L$ and $M_L$ are respectively the energy, angular momentum of trimer-atom relative motion and its projection on a laboratory-fixed axis, $\mu$ and $\vec{R}$ are respectively the reduced mass and radius vector of relative motion.

The actions of the operators of $G_3$ on the wave function (7.17) are easily found because the symmetry of the functions $R_{K,M}^N$ (proportional to the Wigner function) and $\varphi_{v_1,v_2}^{l_2}$ are well known [74]. Furthermore, the action of the parity operator is straightforward. We thus simply need to use these results, as well as the actions of the operators on the spherical
harmonic $Y^M_L(\vec{R})$ to find the correct decomposition in irreducible representations of $G_3$

\[(12)^*|K, l_2\rangle = s_2(-1)^{(L+K+N)}| - K, l'_2\rangle\]

\[(13)^*|K, l_2\rangle = s_2(-1)^{(L+K+N)}w^{2(l'_2+K)}| - K, l'_2\rangle\]

\[(23)^*|K, l_2\rangle = s_2(-1)^{(L+K+N)}w^{4(l'_2+K)}| - K, l'_2\rangle\] \quad (7.18)

\[(123)|K, l_2\rangle = w^{2(l'_2+K)}|K, l_2\rangle\]

\[(132)|K, l_2\rangle = w^{2(l_2-K)}|K, l_2\rangle.\]

In the above expressions, while showing the global actions of the operators of $G_3$, we label the wave function (7.17) only with the quantum numbers $K$ and $l_2$ in order to simplify the notations and show the non-diagonal operations. Also, we introduced the complex number $w = e^{i\pi/3}$ and followed the conventions of [74], where for $l_2 = 3m$, with $m$ integer, the number $l'_2 = l_2$ and for $l_2 \neq 3m$ we have $l'_2 = -l_2$. If $l_2 = 3m$, the states with $A_1$ and $A_2$ symmetries are distinguished by giving respectively a positive or negative value to the quantum number $l_2$. This appears in the transformations by the mean of the number $s_2$, which is 1 for state with $l_2 \geq 0$ and $-1$ if $l_2 < 0$. In the view of (7.18), the reducible space generated by the wave function (7.17) by the actions of the operators of $G_3$ is of dimension one if $K = 0$ and $l_2 = 3m$, of dimension two if either $l_2 \neq 3m$ or $K \neq 0$ and of dimension four if $K \neq 0$ and $l_2 \neq 3m$. Using again (7.3), we can determine the decomposition as irreducible representations of $G_3$.

The elements of $T_{d}(M)$ create three times more independent functions\footnote{A new independent function is created by each exchange (14)*, (24)* and (34)*.} than the basis set.
Table 7.9: Decomposition in irreducible representations of $G_3$ and $T_d(M)$ for the space part of a trimer and a free atom in a rovibronic and harmonic approximations valid for low energy states.

<table>
<thead>
<tr>
<th>$K$</th>
<th>$l_2$</th>
<th>$L + N$</th>
<th>Dec. in $G_3$</th>
<th>Dec. in $T_d(M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$3m; m \geq 0$</td>
<td>even</td>
<td>$A_1$</td>
<td>$A_1 \oplus F_2$</td>
</tr>
<tr>
<td>0</td>
<td>$3m; m &lt; 0$</td>
<td>odd</td>
<td>$A_1$</td>
<td>$A_1 \oplus F_2$</td>
</tr>
<tr>
<td>0</td>
<td>$3m; m \geq 0$</td>
<td>even</td>
<td>$A_2$</td>
<td>$A_2 \oplus F_1$</td>
</tr>
<tr>
<td>0</td>
<td>$3m; m &lt; 0$</td>
<td>odd</td>
<td>$A_2$</td>
<td>$A_2 \oplus F_1$</td>
</tr>
<tr>
<td>0</td>
<td>$\neq 3m$</td>
<td>$3m$</td>
<td>$E$</td>
<td>$F_1 \oplus F_2 \oplus E$</td>
</tr>
<tr>
<td>0</td>
<td>$\neq 3m$</td>
<td>$\neq 3m$</td>
<td>$A_1 \oplus A_2 \oplus E$</td>
<td>$A_1 \oplus A_2 \oplus E \oplus 2(F_1 \oplus F_2)$</td>
</tr>
<tr>
<td>$3n; n \neq 0$</td>
<td>$= 3m$</td>
<td>$A_1 \oplus A_2$</td>
<td>$A_1 \oplus A_2 \oplus F_1 \oplus F_2$</td>
<td></td>
</tr>
<tr>
<td>$3n; n \neq 0$</td>
<td>$\neq 3m$</td>
<td>$2A_1 \oplus 2A_2$</td>
<td>$2(A_1 \oplus A_2 \oplus F_1 \oplus F_2)$</td>
<td></td>
</tr>
</tbody>
</table>

of the representation space in $G_3$, meaning that the decomposition is exact. The results are listed in Table 7.9, where we voluntary present only the decomposition in $G_3$ and $T_d(M)$ because the even or odd character of the irreducible representations in $G_{18}$ depends only on the parity of the quantum numbers $K$.

Table 7.10: Decomposition in irreducible representations of the spin part of a trimer and a free atom.

<table>
<thead>
<tr>
<th>$S_{tot}$</th>
<th>$S_{tri}$</th>
<th>Dec. in $G_3$</th>
<th>Dec. in $T_d(M)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>$E$</td>
<td>$E$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$A_1$</td>
<td>$F_2$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$E$</td>
<td>$F_1 \oplus F_2$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$A_1$</td>
<td>$5A_1$</td>
</tr>
</tbody>
</table>

Considering the spin part of the wave function, we treat again the example of a system of four identical fermions of spin $\frac{1}{2}$. Since we neglect any spin-spin interactions between the trimer and the free atom, we conclude that the good quantum numbers to describe the
symmetry of the wave function are simply the total spin of the system $S_{\text{tot}}$ and the spin of the trimer $S_{\text{tri}}$. As the operations of $G_3$ act only on the trimer, whose spin symmetry is known and described for instance in [74], it becomes easy to relate the set $S_{\text{tot}}, S_{\text{tri}}$ to the irreducible representations of $G_3$. On the other hand, the group $S_4$ does not produce enough independent functions for the decomposition to be complete. Using considerations similar than for the spin of a dimer-dimer system and with the help of Table 7.8, we obtain the final results listed in Table 7.10.

### 7.3.2 A dimer and two free atoms

The configuration with a dimer and a free particles is obviously of very low symmetry. We can treat it in a very easy way, if we consider that we are in the limiting case of the configuration with two free dimers, where one of the dimer is actually not considered anymore as a bound system, but consists at present of two free particles. Therefore the Hamiltonian has the same form as (7.6) with the potential $V_{34}^{K'} = 0$ and the wave function has the same form as (7.7), where $a$ labels the dimer and $b$ the system of the two free particles.

Let us at first focus on the case where the two free atoms are in the same electronic states. The Hamiltonian is thus described by the group $G_1$ in Section 7.2 and the symmetries are simply given by Tab. 7.4. On the other hand, if the atoms are in different electronic states, the permutation $(34)^*$ (labeling of the free particles) is not allowed anymore and the approximative Hamiltonian at large distances has a poor degree of symmetry, only described...
by the sub-group \( G_4 = \{ E, (12)^* \} \) with only irreducible representations \( A_1 \) and \( A_2 \). Now the action of the operator \((12)^*\) has already been shown in (7.8), therefore the symmetry depends only on the parity of the sum \( L + l_b \), where \( l_b \) is the angular momentum of the system of two particles relative to their center of mass. Using the general procedure, we find the decomposition in \( G_4 \) and in \( T_d \). We see that due to the low level of symmetry of this configuration, all the symmetries are practically allowed for any sets \( \{ l_b, L \} \) and in particular the symmetry does not depend in any case on the quantum number \( l_a \) representing the angular momentum of the dimer.

Table 7.11: Decomposition in irreducible representations of the space part of a trimer and a free atom.

<table>
<thead>
<tr>
<th>( L + l_b )</th>
<th>Dec. in ( G_4 )</th>
<th>Dec. in ( T_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>even</td>
<td>( A_1 )</td>
<td>( A_1 \oplus E \oplus 2F_1 \oplus F_2 )</td>
</tr>
<tr>
<td>odd</td>
<td>( A_2 )</td>
<td>( A_2 \oplus E \oplus F_1 \oplus 2F_2 )</td>
</tr>
</tbody>
</table>

7.4 Miscellaneaous of the results

We want finally to present how these results on symmetry can be used to (1) help constructing realistic large-distance state of the system considering different kinds of couplings, (2) find selections rules from initial to final states in a process of collision (possible short-distance couplings), and (3) find allowed quantum numbers depending on the nature of the atoms.

In general, the zeroth order total wave function of our system is written as follow
\[ \Psi_{\text{total}} = \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{elec}} \psi_{\text{spin}}. \] (7.19)

In this expression, \( \psi_{\text{vib}}, \psi_{\text{rot}} \) and \( \psi_{\text{spin}} \) are respectively the vibrational, rotational and spin part of the nuclei wave function and \( \psi_{\text{elec}} \) is the electronic wave function. The separation of the different degrees of freedom in the total wave function has been obtained using at first a Born-Oppenheimer approximation by neglecting any spin-orbit couplings and any rotation-vibration interactions. In the present study, we determined on one hand the symmetry of the product \( \psi_{\text{vib}} \psi_{\text{rot}} \), and on the other hand, the symmetry of \( \psi_{\text{spin}} \) for spin \( \frac{1}{2} \) nuclei. In general, one computes the electronic wave function in the molecular system of coordinates and neglect in the Hamiltonian any rovibronic couplings on the electrons due to the rotation of the molecule. One obtains in this way the electronic wave function that depends parametrically on the position around equilibrium of each nuclei and expressed in a system of coordinates related to the position of the molecule in space. Therefore, this electronic wave functions has also a specific symmetry under nuclei permutations and parity operation. For each configuration of the system, we have to find at first which sub-group characterizes our system. For two free dimers, this is the sub-group \( G_1 \), the sub-group is obviously \( G_3 \) for a trimer and a free electron and for a dimer and a free nucleus, the sub-group is \( \{ E, E^*, (12), (12)^* \} \) equivalent to the sub-group \( G_1 \). Finally, when the symmetry of the electronic wave function for the separated fragments (dimer or trimer) is known, it is easy to find the irreducible representation in the appropriate sub-group for the electronic wave function of the total system. It gives the irreducible representation of each independent part \( \Gamma_{\text{vib}}, \Gamma_{\text{rot}}, \Gamma_{\text{spin}} \) and
\( \Gamma_{\text{elec}} \) of the total wave function in the appropriate sub-group. If one wants to consider possible couplings between different degrees of freedom, the new total wave function can always be written as:

\[
\Psi_{\text{total}}^{(j)} = \sum_n C_{j,n} \Psi_n^{\text{total}}
\] (7.20)

The index \( j \) labels the different eigenstates, \( n \) labels the basis of zero order wave function and \( C_{j,n} \) are the expansion coefficients. If one considers rotation-vibration interactions, this can only occur between states having the same \( \Gamma_{\text{vib}} \otimes \Gamma_{\text{rot}} \) irreducible representation, vibronic interactions for the same \( \Gamma_{\text{vib}} \otimes \Gamma_{\text{elec}} \) irreducible representation and so on. Here, we consider the irreducible representations of the sub-group only, because at large distance it is the group characterizing the symmetry of the Hamiltonian. On the other hand, at shorter distances, the approximate large-distance Hamiltonian is not representative of the interactions anymore. Each of the irreducible representation of the sub-group splits in irreducible representation of \( G_{48} \) as described in the different tables.

Only state with same irreducible representation in \( G_{48} \) can interact and we can thus predict possible final states or equivalently set up selections rules. We can construct diagram of correlations as in Chapter 6 to show the correspondence in a clear way. Finally, the total wave function in (7.19) should be of \( A_1 \) symmetry for bosons and \( A_2 \) symmetry for fermions and thus, allowed quantum numbers can be derived from these symmetry considerations.
CHAPTER 8
CONCLUSION

8.1 Dissociative recombination of HCO$^+$

8.1.1 Results of the thesis

Previous theoretical study of DR in HCO$^+$ have failed to explain relatively large DR rate observed in experiment. In fact, no consensus still exists between results from afterglow plasma and merged beam experiments. A past theoretical study [88] estimated a cross section an order of magnitude smaller than the lowest experimental data. The inclusion of the Renner-Teller coupling [102] in the model has shown to be a decisive factor in electron capturing and better agreement was reached between theory and experiment. The calculated cross section in [102] was only smaller by a factor 3-4 than the experimental results. In the latter study, the CO bond was frozen at its equilibrium value because the main channel for dissociation is H + CO, thus meaning that CO vibrations should not play a significant role in the DR process.

In Chapter 3, we apply a model similar than [102], but include all internal vibrations of the ion by allowing the CO bond to vibrate. The results show that the approximation of
frozen CO is indeed correct at low energy, but the vibrations of CO start to play a role for electron capturing at incident energies above 0.1eV. As the electron energy reaches values of the order of the first excited vibrational level of CO, the family of Rydberg resonances associated with excited CO vibrations becomes accessible. The direct coupling between vibrationally excited states and the ground electronic state is quite weak. On the other hand, the first excited vibrational level of CO is strongly coupled to excited degenerate vibrational modes of HCO+, which are themselves strongly coupled to the ionic ground vibrational state. Therefore, the cross section reproduces the previous theoretical results with frozen [102] at small electronic energies with a relative difference of only 10%. On the other hand, the cross section is significantly larger when the electron capturing via excitation of CO vibration becomes possible. At these energies, allowing the CO bond to vibrate leads to better agreement with the experiment by Lepadellec et al. [89].

In Chapter 4, we improve the model by including the very large dipole moment (4 Debyes) of HCO+. We investigate its possible effect on the recombination process. The GMQDT allows to consider a modified Coulomb potential, superposition of a pure Coulomb and a dipole potential. This work represents to our knowledge, the first DR study including the dipole moment of the ion. We found that including the dipole of HCO+ in the formalism indeed enhances the cross section by about 50% in the whole energy spectrum. The results are in overall better agreement with experimental data. More precisely, they reproduce the experimental data for electron incoming energy higher than 0.06eV and are only smaller by a factor of 2 than the data from [89] at low incident electron energies. The difference in
cross section observed by including the dipole moment of HCO$^+$ is due to the change in the asymptotic phase shifts of $p\sigma$ states induced by this dipole moment. The quantum defects of $p\sigma$ and $p\pi$ states split apart more than in the case of pure Coulomb field for HCO$^+$, which leads to larger Renner-Teller couplings. Still, it can not be asserted that this should be a general phenomenon, since the change in quantum defects could also decrease the couplings for another system under consideration.

8.1.2 Perspectives

We now describe possible reasons for the difference by a factor 2 between the presented theoretical approach and the experiment [89] at small incident electron energies. We also propose two ideas suggested by Johnsen to explain the discrepancies between the different experimental data. Finally, we consider the possible applications of our treatment to other molecular systems.

In our treatment, we still apply three main approximations: (1) we do not consider the rotation of the molecule as a whole, but treat relative rotation of H around CO, (2) we do not include Renner-Teller coupling for $d$-states and (3) we apply an adiabatic approximation for the $R_{GH}$ dissociative coordinate. Approximation (1) should be quite accurate considering the large difference of mass between CO and H. Furthermore, capture in rotational states does not usually lead to higher DR cross section, since rotation is not directly involved in the dissociation of the system, so that the captured electron in a rotational state of the ion will
very likely autoionize. Nevertheless, rovibronic couplings could possibly be not negligible, so that capture in rotational states could indeed have an effect. In any case, an increase of a factor 2 of the cross section by including the rotation of the ion is unlikely. Concerning approximation (2), the Renner-Teller effect of $d$-states is not expected to have a large impact on the cross section. These states have a high centrifugal barrier to overcome so that their quantum defects are weak. Nevertheless, future calculations on the Renner-Teller splitting for $d$-states could give a qualitative idea about its effect on the electron capturing process. The last approximation (3) could probably have an observable effect on the cross section.

When we solve the ionic Hamiltonian of $\text{HCO}^+$, we use $R_{GH}$ as an adiabatic coordinate, so that non-adiabatic vibrational couplings on $R_{GH}$ are not taken into account. In Chapter 3, we compared our vibrational energies with exact calculations. We found an overall agreement of 12% in energy, which translates in 25% in the vibrational wave functions. Therefore, the long-range scattering matrix obtained from the vibrational frame transformation could be slightly modified by solving exactly the vibrational ionic Hamiltonian. This should have a slight effect on the cross section, but probably not enhance the cross section by a factor 2 of low incident energy.

One other possible reason for the remaining disagreement could be related to the isomer $\text{HOC}^+$ of $\text{HCO}^+$ if (1) the isomer is present in the experiment of [89] in a non-negligible fraction and (2) the DR cross-section for the isomer is significantly larger than the cross section for $\text{HCO}^+$. Calculation by Larson et al. [56] suggested that the ground ionic potential of $\text{HOC}^+$ crosses the dissociative potential of $\text{HOC}$ in the Franck-Condon region. It means
that the DR cross section for HOC\(^+\) could indeed be larger. In fact, very recent unpublished full calculations by Larson \textit{et al.} reveals that the direct DR cross section for HOC\(^+\) at small energy is even lower than the cross section for HCO\(^+\). Furthermore, recent \textit{ab initio} energy calculations have been performed by Orel \textit{et al.} to get an estimation of the order of magnitude of the indirect DR process in HOC\(^+\). The obtained Renner-Teller splittings in HOC\(^+\) are extremely small, meaning that the indirect DR process is not possible. Hence, it seems that the presence of HOC\(^+\) in the experiment can not explain the large cross section observed experimentally.

Another suggestion was made recently by Johnsen. The buffer helium gas He presents in the experiment could enhance (catalyze) the DR reaction. Namely, the helium could serve as a third body in the collision and increase the electron capture probability. This could explain at once why the experimental cross section is different from the present theoretical study at low energies, and also why the experimental data from plasma experiments differ from each other, if the densities of buffer gas in the experiments are different.

The theoretical DR study of HCO\(^+\) including the CO vibration could serve as a benchmark for the DR of other linear triatomic ions, as for instance HCN\(^+\). The DR mechanism of HCN\(^+\) is similar in nature to the one of HCO\(^+\), since HCN\(^+\) is a closed shell ion dissociating as HCN\(^+\) + e\(^-\) \rightarrow \text{H}^+\text{CN}. From our results, it can be concluded that the approximation of frozen CN bond should be very good at energy significantly lower than the first quanta on CN vibration. More generally, if part of a molecular ion is not directly involved in the breaking of the molecule and its vibrational frequency is significantly higher than other relevant
vibrational frequencies for DR, then one can freeze this part of the ion at its equilibrium value with good accuracy in the results. The approximation should be accurate as long as the electron energy is too small to be captured in Rydberg states associated with excited quanta of vibration of this part of the ion.

Our treatment using the GMQDT formalism to model the large dipole moment of HCO\(^+\) can also be used for dissociative attachment and radiative attachment processes in neutral molecules with dipole moments. For instance, the model could be used in the radiative attachment of an electron to carbon chain molecules C\(_n\)H: C\(_n\)H\( + \)e\(^-\) \(\rightarrow\) C\(_n\)H\(^-\) + h\(\nu\), by using the GMQDT formalism for a pure dipole field. The study of such processes is important to model the formation of the observed negative ions in the interstellar medium (Subsection 1.1.2.1).

8.2 Dissociative recombination of H\(_3^+\) and H\(_3\)O\(^+\)

8.2.1 Results of the thesis

We applied a simplified treatment to study the DR of the highly symmetrical ions H\(_3\)O\(^+\) and H\(_3^+\). The general idea is to focus on the main factors of electron capturing process: the Jahn-Teller effect. In the model, we consider the ion as a set of harmonic oscillators and shows that the averaged cross section for electron capturing in first excited doubly degenerate normal modes takes a simple form. The calculated cross section is surprisingly in
good agreement with experimental data for both ions. For \( \text{H}_3^+ \), it also reproduces the results of two independent theoretical studies.

### 8.2.2 Perspectives

Our treatment relies on the harmonic approximation to describe the vibrational states. Actually, anharmonic terms in the electronic ionic potential of \( \text{H}_3\text{O}^+ \) exist and can be easily obtain via *ab initio* calculations. For instance, these anharmonicities in the potential could couple the second excited state of the degenerate normal modes (as well as other excited states) to their first excited states. This would probably not change the cross section at low energies in a noticeable way, but it has the advantage to allow the determination of the cross section at energies beyond the highest degenerate normal frequency, where the cross section is small, but still experimentally measurable.

This treatment could apply to other highly symmetric molecular ions. First, the \( \text{CH}_3^+ \) molecular ion is very important in interstellar clouds (see Fig. 1.7), since it forms numerous hydrocarbons by different types of reactions. \( \text{CH}_3^+ \) also has a closed shell so that it can be treated in a similar way as the \( \text{H}_3\text{O}^+ \) ion. The \( \text{NH}_4^+ \) ion could be studied in a same way. This ion is somewhat more complicated since \( \text{NH}_4^+ \) has triply degenerate normal modes, with the subsequent possibility of mixing different electronic angular momenta. Finally, we can also consider linear ions like \( \text{HCO}^+ \) and \( \text{HCN}^+ \) in this model, using the Renner-Teller model.
8.3 Symmetry in ultra-cold collisions of identical atoms

We found selection rules for rearrangements of three or four identical atoms with low energies. We study independently the symmetry of both spatial and spin wave functions and relate them to irreducible representations of the total symmetry group. When colliding at short distance, the conservation of the system symmetry should be given by the total symmetry group, which could connect different large distances symmetries. Thus, we found diagrams of correlations for different rearrangements. The main results of this study is the precise treatment of the dimer-dimer collisions. We separate the case of dimers in same and different electronic states and also in same rovibronic states by considering the consequences on the form of the approximate large distance Hamiltonian. It is shown that large distance symmetries for dimer-dimer can actually be mixed by the tetrahedron group.
LIST OF REFERENCES


