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Scattering matrix approach to the dissociative recombination of HCO^+ and N_2H^+

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We present a theoretical study of the indirect dissociative recombination of linear polyatomic ions at low collisional energies. The approach is based on the computation of the scattering matrix just above the ionization threshold and enables the explicit determination of all diabatic electronic couplings responsible for dissociative recombination. In addition, we use the multi-channel quantum-defect theory to demonstrate the precision of the scattering matrix by reproducing accurately *ab initio* Rydberg state energies of the neutral molecule. We consider the molecular ions N_2H^+ and HCO^+ as benchmark systems of astrophysical interest and improve former theoretical studies, which had repeatedly produced smaller cross sections than experimentally measured. Specifically, we demonstrate the crucial role of the previously overlooked stretching modes for linear polyatomic ions with large permanent dipole moment. The theoretical cross sections for both ions agree well with experimental data over a wide energy range. Finally, we consider the potential role of the HOC^+ isomer in the experimental cross sections of HCO^+ at energies below 10 meV. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4871982>]

I. INTRODUCTION

Dissociative electron-ion recombination (DR) is an important deionization process in many plasma media, such as cometary gas, interstellar clouds, protoplanetary disks, planetary atmospheres, technological plasmas, and combustion flames. Despite significant experimental and theoretical progress over the last three decades in the understanding of the main DR mechanisms at low collision energies, there still remains many open questions, specifically in the case of polyatomic molecular ions. Indeed, the theoretical treatment of DR in polyatomic ions is especially difficult because several degrees of freedom are involved and strong non-Born-Oppenheimer couplings need to be considered. In the present study, we develop an improved theoretical approach to obtain the cross section for dissociative recombination of small polyatomic ions at low collision energies and treat the example of the two linear molecular ions HCO^+ and N_2H^+ .

Both HCO^+ and N_2H^+ ions have been detected in a number of regions in the interstellar medium (ISM)^{1–4} and serve as probe to the innermost dense regions of dark clouds due to their large dipole moment. Moreover, HCO^+ is the second most abundant polyatomic ion in the Universe and represents an important constituent of the Martian ionosphere.⁵ The main process of formation of HCO^+ and N_2H^+ in dense interstellar clouds is proton transfer from H_3^+ to either CO or N_2 neutral molecules. Both ions are mainly destroyed by recombination with low energy electrons. The dominant dissociation channels at low collision energies are

The experimental measurements by Geppert *et al.*⁶ determined that the branching ratio for CO production is about 93%, whereas the experiments by Molek *et al.*⁷ and Vignen *et al.*⁸ demonstrated that the branching ratio for the N_2 product channel represents about 95% of the observed products. Note that we only listed the energetics for fragments in their ground electronic states, but the electronically excited $\text{N}_2(B^3\Pi_g)$, $\text{N}_2(A^3\Sigma_u^+)$, and the long-lived $\text{CO}(a^3\Pi)$ triplet-states can also be formed through the DR of these ions and have been experimentally detected.^{9–11}

The data from flowing afterglow,^{12,13} storage ring⁸ or merged-beam¹⁴ experiments have revealed that the low-energy DR rate coefficient for both ions is large. On the other hand, theoretical calculations indicate that a direct DR process via dissociative Feshbach resonances is only possible at high energy for both ions. Recently, Larson *et al.*¹⁵ calculated the direct DR cross section of HCO^+ on a wide energy range and concluded that the contribution of the direct mechanism is negligible below 0.1 eV. For N_2H^+ , Hickman *et al.*¹⁶ and Talbi *et al.*¹⁷ studied the linear dissociation path of this ion and suggested that the DR of N_2H^+ should involve a direct mechanism through the second dissociative state. Nevertheless, they found that the crossing between ionic and dissociative potential energy surfaces occurs near the classical turning point of the ground vibrational state of N_2H^+ , so that the direct DR is an inefficient process in a medium where N_2H^+ is not vibrationally excited. We have recently carried out three-dimensional calculations of the direct DR mechanism in N_2H^+ and our preliminary results confirm their findings. Therefore, it seems unlikely that the direct DR process at low collision energies could explain the relatively large DR cross section observed experimentally.

On the other hand, the study of the non-Born-Oppenheimer Jahn-Teller effect in the DR of H_3^+ ^{18–20} revealed the efficiency of the indirect mechanism in molecules with degenerate vibrational modes. A similar treatment including the Renner-Teller effect was applied to HCO^+ ²¹ and it was found that the indirect mechanism, which is mainly mediated by the coupling between electronic and bending nuclear motion, is also efficient for this ion. Although the inclusion of the Renner-Teller coupling produced a theoretical cross section of the same order of magnitude as experimentally measured, the results remained lower than the lowest experimental data by a factor of 3–4. The theoretical approach was later improved with the inclusion of the CO vibration²² and permanent dipole moment of HCO^+ .²³ As a result, a better agreement with the experimental DR cross section was obtained, however, there still remains some discrepancies with the experimental data.

Meanwhile, Pratt and Jungen have simplified the treatment of the indirect DR mechanism in polyatomic ions, by considering electronic capture to the first excited degenerate vibrational states as the rate limiting process.²⁴ Their treatment was applied to H_3^+ ²⁴ and their structureless cross section agrees well with the fully quantum calculations by Fonseca dos Santos *et al.*²⁵ The same treatment was also employed for the DR of HCO^+ ²⁶ for which spectroscopic data was used in the model (contrary to the first principles approach of Refs. 19, 20, and 25) and the cross section obtained was only slightly lower than the theoretical treatment of Refs. 21–23, which is about a factor two lower than the experimental data by Le Padellec *et al.*¹⁴ Concerning the DR of N_2H^+ , different experimental studies^{8,12,13} have been carried out, but no theoretical calculation of the indirect DR cross section has been reported. Because of the longstanding disagreement between theory and experiment for HCO^+ and the lack of theoretical data for N_2H^+ , we have investigated the indirect DR mechanism of these two systems using the improved approach developed in this study.

The treatment presented below goes beyond a restricted Renner-Teller coupling scheme and considers several types of vibronic couplings through all vibrational modes of the molecular ions. In this way, we demonstrate that the stretching modes also play a crucial role in the DR of linear molecular ions possessing a large permanent dipole moment and we show that this fact is largely supported by the experimental measurements. More generally, we believe that the main source of the remaining disagreement between theory and experiment lies in an accurate description of the non-adiabatic couplings. An example showing how an important non-adiabatic coupling can be overlooked is the study of H_3O^+ dissociative recombination, for which a first theoretical study only accounted for the Jahn-Teller effect²⁷ (linear with respect to the distortion normal modes) and led to a theoretical cross section about two times lower than experimentally measured. It was later realized, that in addition to the $p\pi$ Jahn-Teller energy coupling, exists a strong non-degenerate coupling originating from an interaction with the nearby $\sigma\sigma$ state. Once this additional coupling was taken into account, the new calculated DR cross section reproduced well the experimental data.²⁸ In the case of HCO^+ , former studies^{21–23} used Rydberg parameters extrapolated from low-lying valence states and

used Koopman's theorem to approximate the electron affinity by the energy of virtual molecular orbitals. It is clear that this level of calculation can be critically improved. In addition, the electronic couplings in linear polyatomic molecules are difficult to extract from bound state energy calculations, mainly because the Renner-Teller coupling is a quadratic effect for degenerate states and cannot be distinguished from couplings induced by other states. In a general case of linear molecules, the procedure of fitting the results obtained from *ab initio* calculations to the model is ambiguous since the complete model of diabatic electronic Hamiltonian has more parameters than the number of bound state energies. In this study we overcome this difficulty by performing electron-ion scattering calculations just above the ionization threshold, such that all electronic couplings are obtained directly from the *S*-matrix calculated via the variational complex Kohn method.^{29,30} Using multi-channel quantum-defect theory (MQDT), we verify that the *S*-matrix obtained in the ionization continuum reproduces quantum defects extracted from accurate bound state calculations performed in the discrete spectrum. Therefore, we enlarge the previous models, which only considered a three-state electronic Hamiltonian. Finally, additional improvements were made in the study of the DR of HCO^+ by (i) adding the direct cross section,¹⁵ which is important at energies above 0.1 eV, and (ii) by calculating the cross section for the DR of the HOC^+ isomer, which might be present in DR experiments of HCO^+ .

The article is organized as follows. In Sec. II, we present the theoretical approach, discuss the DR cross section formula and the relevant parameters calculated either from bound states *ab initio* calculations or through the scattering variational complex Kohn technique. In Sec. III, the computational details are discussed and the results are compared with available data. We present and discuss the obtained cross sections for both ions in Sec. IV. Finally, Sec. V is devoted to our conclusions.

II. THEORETICAL APPROACH

A. DR cross section formula

We present the basic formalism underlying the theoretical model. More details can be found in Refs. 24 and 27, for example. The theoretical model starts from the following assumptions.

- (i) The rotation of the molecular target is neglected. This approximation results in a structureless cross section without rotational resonances. This assumption is justified considering that the target ions are rotationally excited in the experiments, such that these resonances are averaged out in the experimental cross sections.
- (ii) The cross section is averaged over autoionizing resonances. This leads to a constant probability of electronic capture since the density of resonances in a Rydberg series is inversely proportional to their width in the quasi-continuum. It represents a reasonable simplification, considering that in the experiment these resonances are not individually resolved.
- (iii) The autoionization lifetime is assumed to be much longer than the predissociation lifetime. Once the

electron is captured into a Rydberg resonant state, its energy is quickly converted into vibrational motion.

- (iv) The harmonic approximation is used to describe the vibrational states of the core ion.

Using (i)-(iii) and applying the vibrational frame transformation, the total DR cross section is expressed as

$$\langle\sigma\rangle = \frac{\pi\hbar^2}{2m\epsilon} \sum_v \sum_{\gamma\gamma'} \left| \int \chi_v(q) S_{\gamma\gamma'}(q) \chi_{v'}(q) dq \right|^2. \quad (1)$$

In the above expression, the brackets indicate averaging of the cross section over Rydberg resonances, ϵ represents the asymptotic electronic energy, m is the electron mass, $\chi_{v'}(q)$ and $\chi_v(q)$ are the initial and final vibrational states of the ionic core, respectively, and q denotes collectively the coordinates of all nuclei. The coefficients $S_{\gamma\gamma'}(q) = \langle\gamma|\hat{S}(q)|\gamma'\rangle$ represent the elements of the smooth scattering matrix, where $|\gamma'\rangle$ and $|\gamma\rangle$ denote, respectively, initial and final electronic states that diagonalize the scattering matrix at the linear equilibrium of the molecule. Therefore, these states are characterized by the projection λ of their angular momentum on the molecular axis. Finally, note that each contribution in the cross section from capture into excited vibrational states χ_v , with corresponding energy E_v , vanishes identically when $\epsilon + E_v' > E_v$.

The electronic basis states $|\gamma\rangle$ form eigenchannels of the scattering matrix at the linear equilibrium of the molecule and thus serve as a diabatic basis whose elements are coupled through molecular distortion. The latter non-adiabatic electronic couplings are represented by the perturbation potential V to form the total electronic Hamiltonian $H = H_0 + V$, in which H_0 is the electronic Hamiltonian at the equilibrium geometry. The approach is similar to the two-step treatment developed by Giusti-Suzor and Lefebvre-Brion³¹ in which most of the electronic interactions are accounted for in a first step by using eigenchannel states $|\gamma\rangle$ with respective quantum defects $\mu_\gamma^{(0)}$, whereas Renner-Teller and other residual interactions are treated in a perturbative approach. The direct effect of the perturbation potential V is to induce an additional phase shift $\mu_\alpha^{(V)}$ with respect to regular functions defined in the $|\gamma\rangle$ basis (see details in Ref. 31–33 for a comprehensive discussion), and where $|\alpha\rangle$ represent the eigenchannels of the total Hamiltonian H . Considering a given electronic channel basis, whose elements are denoted by the index i , it can be shown³² that the total scattering matrix in this electronic representation has elements

$$S_{ii'} = \sum_{\alpha\gamma\gamma'} \langle i|\gamma\rangle e^{i\pi\mu_\gamma^{(0)}} \langle\gamma|\alpha\rangle e^{2i\pi\mu_\alpha^{(V)}} \langle\alpha|\gamma'\rangle e^{i\pi\mu_{\gamma'}^{(0)}} \langle\gamma'|i'\rangle. \quad (2)$$

Note that only elements $\langle\gamma|\alpha\rangle$ and $\mu_\alpha^{(V)}$ are q -dependent parameters in Eq. (2). Using the latter formula, we can express $S_{\gamma\gamma'}$ in terms of quantum defect parameters

$$S_{\gamma\gamma'} = \sum_\alpha e^{i\pi\mu_\gamma^{(0)}} \langle\gamma|\alpha\rangle e^{2i\pi\mu_\alpha^{(V)}} \langle\alpha|\gamma'\rangle e^{i\pi\mu_{\gamma'}^{(0)}}. \quad (3)$$

Because the terms $\mu_\alpha^{(V)}$ are small around the equilibrium q_0 of the molecular ion, one can develop the expression above to first order in $\mu_\alpha^{(V)}$ and obtain

$$S_{\gamma\gamma'} = e^{2i\pi\mu_\gamma^{(0)}} \delta_{\gamma\gamma'} + 2i\pi e^{i\pi(\mu_\gamma^{(0)} + \mu_{\gamma'}^{(0)})} \mu_{\gamma\gamma'}^{(V)}, \quad (4)$$

where $\mu_{\gamma\gamma'}^{(V)} = \sum_\alpha \langle\gamma|\alpha\rangle \mu_\alpha^{(V)} \langle\alpha|\gamma'\rangle$ are the elements of the quantum defect matrix $\mu^{(V)}$ expressed in the $|\gamma\rangle$ basis. The expression (4) suggests that $\mu^{(V)}$ represents the first order perturbation to the quantum defect matrix $\mu^{(0)}$ (diagonal in the γ representation with elements $\mu_\gamma^{(0)}$), to form the total quantum defect matrix μ (diagonal in the α representation with elements μ_α). This statement can be readily verified by using the Maclaurin series expansion of the matrix $\exp[2i\pi(\mu^{(0)} + \mu^{(V)})]$, namely,

$$\exp[2i\pi(\mu^{(0)} + \mu^{(V)})] = \sum_{n=0}^{\infty} \frac{[2i\pi(\mu^{(0)} + \mu^{(V)})]^n}{n!}. \quad (5)$$

To first order in $\mu^{(V)}$, it is straightforward to show that the elements of the above expansion in the $|\gamma\rangle$ basis set are identical to the elements of Eq. (4), thus $S = \exp[2i\pi(\mu^{(0)} + \mu^{(V)})]$. This relation is noteworthy since it equivalently means that $\mu = \mu^{(0)} + \mu^{(V)}$ and the electronic coupling can be abstracted from diagonal quantum defects μ_α obtained through *ab initio* methods.

Following Pratt and Jungen,²⁴ we now introduce the $3N - 5$ normal coordinates q_i , where N is the number of atoms, and use approximation (iv)

$$\chi_v(q) = \prod_{i=1}^{3N-5} \eta_{v_i}(q_i) \text{ and } \chi_{v'}(q) = \prod_{i=1}^{3N-5} \eta_{v'_i}(q_i), \quad (6)$$

where $\eta_{v_i}(q_i)$ represents the harmonic vibrational function with v_i quanta and corresponding vibrational frequency ω_i , reduced mass μ_i and dimensionless normal coordinates q_i . Next, we apply the Taylor expansion in terms of q_i

$$\mu_{\gamma\gamma'}^{(V)} = \sum_{i=1}^{3N-5} \left(\frac{\partial \mu_{\gamma\gamma'}}{\partial q_i} \right) q_i, \quad (7)$$

where the derivative, as well as all derivatives below, are taken at the equilibrium q_0 of the ion and where we used the fact that $\partial \mu_{\gamma\gamma'}^{(V)} / \partial q_i = \partial \mu_{\gamma\gamma'} / \partial q_i$. Substituting (7) in (4), the cross section (1) can be evaluated in analytical form if we use the harmonic vibrational wave functions (6) and bear in mind the following identities

$$\int \eta_{v_i}(q_i) q_i \eta_{v'_i}(q_i) dq_i = \sqrt{\frac{v_i}{2}} \delta_{v_i, v'_i+1}, \quad (8)$$

$$\int \eta_{v_i}(q_i) \eta_{v'_i}(q_i) dq_i = \delta_{v_i, v'_i}. \quad (9)$$

Assuming that the ion is initially in its vibrational ground state ($\forall i, v'_i=0$), we conclude that the electron can only be captured in the first excited vibrational state of each mode. Strictly speaking, this statement is only valid in the harmonic approximation picture while, in general, capture into higher vibrational states is also possible, although expected to be small. Finally the cross section is expressed as

$$\langle\sigma\rangle = \frac{\pi^3 \hbar^2}{m\epsilon} \sum_{i=1}^{3N-5} \sum_{\gamma\gamma'} \left(\frac{\partial \mu_{\gamma\gamma'}}{\partial q_i} \right)^2. \quad (10)$$

The above equation gives a simple analytical formula for indirect dissociative recombination cross section. The quantum

defect matrix elements are extracted from *ab initio* calculations of excited Rydberg states energies. This procedure is not well adapted in the present case for reasons discussed in detail in Sec. IV B.

Alternatively, the cross section can be obtained directly via the low-energy scattering matrix calculated in our case using the variational complex Kohn method (Sec. II B). In this approach, the scattering matrix is expressed in the spherical harmonic channel basis, namely as $S_{l\lambda, l'\lambda'}(q) = \langle l\lambda | \hat{S}(q) | l'\lambda' \rangle$, where $Y_{l\lambda}(\theta, \phi) = \langle \theta\phi | l\lambda \rangle$ are centered at a fixed origin in the molecular frame and (θ, ϕ) denote polar angles. In order to calculate the cross section in Eq. (1), one can either transform the S -matrix to the γ representation, or simply use the fact that the expression for the cross section would be the same if we use the $l\lambda$ representation. First, recall that both sets of electronic functions are eigenvectors of the operator $\mathbf{L}_z$, projection of the electronic angular momentum along the molecular axis, such that the unitary transformation $\langle \gamma | l\lambda \rangle$ only transforms states with a same value of λ . This transformation is independent of the nuclei coordinates. To simplify the notations, we introduce the matrix elements

$$S_{l\lambda, l'\lambda'}^{vv'} = \int \chi_v(q) S_{l\lambda, l'\lambda'}(q) \chi_{v'}(q) dq, \quad (11a)$$

$$S_{\gamma\gamma'}^{vv'} = \int \chi_v(q) S_{\gamma\gamma'}(q) \chi_{v'}(q) dq. \quad (11b)$$

Because of the unitarity transformation $|l\lambda\rangle \rightarrow |\gamma\rangle$, we have

$$\sum_{l'l'} |S_{l\lambda, l'\lambda'}^{vv'}|^2 = \sum_{\gamma\gamma'} |S_{\gamma\gamma'}^{vv'}|^2. \quad (12)$$

Using again the harmonic approximation and expanding the scattering matrix elements to first order in the normal coordinates, we obtain the following equivalent form for the cross section

$$\langle \sigma \rangle = \frac{\pi \hbar^2}{4m\epsilon} \sum_{i=1}^{3N-5} \sum_{l'l'\lambda\lambda'} \left| \frac{\partial S_{l\lambda, l'\lambda'}}{\partial q_i} \right|^2. \quad (13)$$

The form of the first-order electronic coupling elements in the cross section formulas (10) and (13) can be deduced from symmetry considerations. Both triatomic ions possess four internal degrees of freedom: two stretching modes ν_1 and ν_3 , with respective frequencies ω_1 and ω_3 , and corresponding coordinates q_1 and q_3 , and a doubly degenerate transverse mode ν_2 with a lower frequency ω_2 and coordinates (q_{2x}, q_{2y}) . The vibrational states are denoted in the usual convention (v_1, v_2^l, v_3) , where v_i is the number of quanta of the i th mode and l_2 denotes the projection of the degenerate vibrational angular momentum on the molecular axis. Because the stretching modes are totally symmetric, the only allowed couplings are between electronic states of the same irreducible representation in the $C_{\infty v}$ symmetry group ($\Sigma, \Pi, \Delta, \dots$). Note that it includes as well additional diagonal couplings. On the other hand, once the Renner-Teller splitting between degenerate Π states has been accounted for, each component of the transverse degenerate mode can only couple states belonging to the same irreducible representation of the C_s group (a' or a'') and with the additional condition $\Delta\lambda = \pm 1$ for first-order terms.

Comprehensive discussions of symmetry in polyatomic linear molecules can be found in Refs. 34 and 35.

B. Complex Kohn variational method

We use the complex Kohn variational method^{29,30} to describe the scattering of an electron from a target ion. In the Kohn method, the wave function representing the electron-ion scattering is expressed as

$$\Psi_{\Gamma_o l' \lambda'}^+ = \hat{A}(\chi_{\Gamma_o} F_{l' \lambda'}^+) + \sum_i d_i \Theta_i, \quad (14)$$

where χ_{Γ_o} represents the $(N-1)$ -electron ground state wave function of the target and the second sum runs over N -electron configuration-state functions Θ_i representing penetration and correlation terms. The operator $\hat{A}$ antisymmetrizes the wave function. The functions $F_{l' \lambda'}^+$ are expanded as

$$F_{l' \lambda'}^+(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r}) + \sum_{l\lambda} [f_l(kr) \delta_{ll'} \delta_{\lambda\lambda'} + T_{l\lambda, l' \lambda'} f_l^+(kr)] Y_{l\lambda}(\hat{r})/r, \quad (15)$$

where $\mathbf{r} = r\hat{r}$ is the electron position vector and k is its asymptotic wavenumber. The partial wave continuum radial functions f_l and f_l^+ behave asymptotically as regular and outgoing Coulomb functions, respectively, and ϕ_i are square integrable functions. Upon applying the variational Kohn principle, the coefficients d_i , c_i , and the elements of the T -matrix can be determined. In terms of the scattering matrix, $S = I - 2iT$, the asymptotic behavior of the electronic functions at $r \rightarrow \infty$ is

$$F_{l' \lambda'}^+(\mathbf{r}) \rightarrow \frac{i}{2} \sum_{l\lambda} [f_l^-(kr) \delta_{ll'} \delta_{\lambda\lambda'} - S_{l\lambda, l' \lambda'} f_l^+(kr)] Y_{l\lambda}(\hat{r})/r. \quad (16)$$

The incoming and outgoing functions have the asymptotic form $f_l^\pm(kr) \rightarrow \frac{1}{\sqrt{k}} \exp[\pm i(kr + \frac{1}{k} \ln(2kr) - \frac{l\pi}{2} + \eta_l)]$ where $\eta_l = \arg[\Gamma(l+1-i/k)]$ is the Coulomb phase shift.

Using the eigenchannel version of MQDT introduced by Fano,³⁶ one can diagonalize the scattering matrix

$$S_{l\lambda, l' \lambda'} = \sum_{\alpha} \langle l\lambda | \alpha \rangle e^{2i\delta_{\alpha}} \langle \alpha | l' \lambda' \rangle, \quad (17)$$

and express the asymptotic form of the independent eigenchannel solutions as superpositions of functions (16), namely,

$$F_{\alpha}(\mathbf{r}) \rightarrow \frac{i}{2} \sum_{l\lambda} \langle l\lambda | \alpha \rangle [f_l^-(kr) - e^{2i\delta_{\alpha}} f_l^+(kr)] Y_{l\lambda}(\hat{r})/r, \quad (18)$$

which have a common phase shift δ_{α} in each partial wave channel. The unitary transformation $\langle l\lambda | \alpha \rangle$ brings S to a diagonal form, such that $F_{\alpha}(\mathbf{r}) = \langle \mathbf{r} | \alpha \rangle$. Due to the strong Coulomb attraction at small r , the phase shifts δ_{α} are nearly energy-independent close to the ionization threshold and are extrapolated as quantum defects into the discrete part of the spectrum. This is usually expressed as the Seaton's theorem

$$\lim_{\epsilon \rightarrow 0} \delta_{\alpha}(\epsilon) = \lim_{n \rightarrow \infty} \pi \mu_{n, \alpha}, \quad (19)$$

where $\mu_{n,\alpha}$ is the quantum defect associated with the principal quantum number n . The relation (19) implies that the low-energy eigenphases obtained through the complex Kohn variational technique should reproduce quantum defects calculated from bound state calculations.

III. COMPUTATIONAL DETAILS

A. Molecular ions calculations

In this study, we use the cc-pVTZ basis set centered on each atom and include all s , p , and d orbitals. The target ion is described by a complete active space configuration interaction (CAS-CI) calculation performed in a sizable reference space. This procedure is required in order to describe consistently the Rydberg states energies, i.e., including all configurations that describe the target ion with the additional electron in the CAS or excited Rydberg molecular orbitals (MOs). This approach should produce accurate energy difference between ionic and neutral molecule electronic states, as it ensures that the N -electron wave function is not over-correlated with respect to the $(N - 1)$ -electron wave function.

Although the highest level of description for the target ion is *a priori* not required to obtain accurate eigenphases and quantum defects, we verify that the main characteristics of the ions are well reproduced in our calculation, specifically properties related to the vibrational dynamics, because an accurate determination of the geometry-dependent parameters is crucial for the DR treatment. We have used two main criteria to check the accuracy of our calculations: (1) the value of the permanent dipole moment and (2) the value of the vibrational frequencies.

The main electronic ground state configuration $X^1\Sigma$ of the isoelectronic ions N_2H^+ and HCO^+ is $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^4$. At first, the MOs are optimized by performing a multi-reference-configuration-interaction (MRCI) calculation to obtain natural orbitals for both ions. These orbitals form the active space in which our CAS-CI calculations will be carried out. We achieved accurate descriptions of the ionic ground states while using a large active space of eleven molecular orbitals. Unfortunately, this level of description of the ions leads to intractable scattering calculations. Moreover, a smaller size of the active space results in overestimated bending frequencies and underestimated permanent dipole moments. We overcome these difficulties by freezing, in addition to the core orbitals, the inner-shell 3σ bonding orbital as well. The occupation number of this doubly occupied natural orbital is basically two, because this orbital represents partially the strong N–N (or C–O) bondings, such that the vibrational frequencies and dipole moments were only negligibly modified by freezing this orbital. On the other hand, note that the bound states calculations can be performed freezing only core orbitals and we have checked that the value of the quantum defects are almost identical by freezing the first two or three MOs, which also confirms the validity of this procedure.

Permanent dipole moments and vibrational frequencies obtained from the CAS-CI calculations are presented in Table I and are compared with different *ab initio* studies and experimental measurements available in the literature. Fi-

TABLE I. Characteristics of the molecular ions HCO^+ and N_2H^+ obtained in this study and compared with other theoretical and experimental results. Frequencies are given in cm^{-1} and permanent dipole moments μ_e in debye.

Ion	ω_1	ω_2	ω_3	μ_e	Method	Taken from
HCO^+	3229	790	2186	...	CEPA	This work
	3224	863	2212	3.843	CAS-CI	This work
	3231	845	2215	...	CCSD(T)	Ref. 37
	3224	840	2203	3.888	CCSD(T)	Ref. 38
	...	830	2184	...	Exp.	Ref. 39
	...	...	...	3.922	Exp.	Ref. 40
N_2H^+	3413	675	2290	...	CEPA	This work
	3383	641	2252	3.381	CAS-CI	This work
	3403	695	2140	...	MP2	Ref. 41
	3398	695	2297	...	MRCI	Ref. 42
	3400	693	2269	...	Exp.	Ref. 43
	...	...	...	3.400	Exp.	Ref. 1

nally, we have also performed a separate coupled electron pair approximation (CEPA) calculation using the MOLPRO suite of codes⁴⁴ to have another basis for comparison. As can be seen from the table, our CAS-CI results, which are further used in both Rydberg bound states and continuum scattering calculations, agree well with other studies. Thus, it confirms that a good description of the core-ion is achieved, such that the interaction potential and exchange with the Rydberg or continuum electron should be correctly represented.

B. Rydberg states and scattering calculations

In order to calculate Rydberg energies, the initial gaussian basis set is augmented with the diffuse universal gaussian basis set $[8s, 7p, 6d]$ optimized by Kaufmann *et al.*⁴⁵ to represent accurately Rydberg wave functions. The energies of Rydberg states were obtained up to $n = 5$ through a MRCI calculation in the active space of eleven MOs (see Sec. III A) with all single excitations. Note that it leads to a rather demanding calculation of about 1×10^6 configurations and required to calculate eighteen energy roots in a' symmetry at non-linear geometries. From the calculated energies, we deduce geometry-dependent quantum defects using the Rydberg formula

$$E_{n,\alpha}(q) = V^+(q) - \frac{me^4}{2\hbar^2} \frac{1}{(n - \mu_{n,\alpha}(q))^2}, \quad (20)$$

where e is the charge of the electron, $V^+(q)$ is the ion energy, and $E_{n,\alpha}(q)$ represents the energy of the electronic state $|\alpha\rangle$ with corresponding principal quantum number n . The quantum defects between principal quantum numbers $n = 4$ and $n = 5$ have converged to an accuracy better than 0.01 and, more importantly, the values of the quantum defects as a function of the molecular geometry have converged to about 5%–10%. This means that the quantum defects for $n = 5$ are close to their asymptotic values.

In the complex Kohn variational method calculations (see Sec. II B), the initial gaussian basis set is augmented with a small set of diffuse orbitals $[2s, 2p, 1d]$ to improve the description of the intermediate range region. The phase shift are extracted at energy just above the ionization threshold,

approximately at 30 meV and were found to be almost energy-independent below 200 meV. Furthermore, from the scattering matrix elements, we can label each eigenchannel with the dominating spherical harmonics in the expansion (18). Let us stress that the incoming and outgoing Coulomb function $f_l^\pm(r)$ and corresponding spherical harmonics have to be defined with respect to the origin of a chosen reference frame. The usual way is to choose the origin at the center of mass of the molecular ion. Nevertheless, in the present case for which rotation of the molecular ion is neglected, the cross section for vibrational capture is independent of the choice of origin as long as a complete basis set is used. Because of the large dipole moments of both ions, choosing the origin as the center of charge of the molecular ion (where the permanent dipole moment vanishes) leads to better convergence of the calculations and a simplification in the analysis of the results. First, recall that the quantum defects are defined with respect to a set of reference functions centered at a chosen origin. Neglecting the influence of quadrupole and higher multipole interactions, the Rydberg formula in (20) is only exact if the permanent dipole moment of the ion is zero. With the origin of the coordinate system chosen such that the permanent dipole moment is large (e.g., the center of mass of HCO^+ or N_2H^+), the relation between energies and quantum defects becomes more complicated, as described by the generalized quantum-defect theory.⁴⁶ In addition, the S -matrix computed in the Kohn method is defined with respect to pure Coulomb functions (no dipole; l is an integer), such that the calculated phase shift is directly related to the quantum defect through Eq. (19) only if the origin is at the center of charge of the target ion. Finally, due to the large permanent dipole moment of HCO^+ and N_2H^+ at their center of mass, partial waves centered at the latter point would be strongly coupled asymptotically through the long-range anisotropic dipole potential, which would complicate the scattering calculation and result in poor accuracy. However, the choice of the center of charge in our study is merely a matter of convenience: The final results remain independent of the choice of origin as long as a sufficient number of partial waves is included.

IV. RESULTS AND COMPARISON WITH PREVIOUS STUDIES

A. Quantum defects and eigenphaseshifts

The results of the bound state and scattering calculations for both molecular ions are presented separately in Tables II and III. The tables show the agreement between the two different calculations for the equilibrium parameters, according to Eq. (19). The remaining small discrepancies could be explained, in part, by the limited accuracy of the calculations, but also because the quantum defects extracted from the $n = 5$ Rydberg series have not completely converged with respect to n . Even more remarkable is the agreement between the quadratic shifts of these parameters as the linear geometry of the ion is distorted through the degenerate normal mode. The extremely small changes of the parameters at small distortion are identical in both calculations within accuracy 10^{-3} in the dimensionless quadratic coefficients. In terms of energy for the $n = 5$ state, it represents an agreement within less

TABLE II. Calculated equilibrium effective quantum numbers $\nu^{(0)}$, quantum defects $\mu^{(0)}$, and eigenphaseshifts $\delta^{(0)}$ divided by π , for all s , p , and d electronic states of HCO^* . Also shown in the table, the calculated dimensionless quadratic coefficients of μ_α and δ_α/π with respect to HCO^+ bending. Prime and double-prime signs refer, respectively, to the irreducible representations a' and a'' in the C_s group. The $d\delta$ states only split to fourth order with respect to q_{2x} .

State	$\nu^{(0)}$	$\mu^{(0)}$	$\delta^{(0)}/\pi$	$\frac{1}{\pi} \frac{\partial^2 \delta_\alpha}{\partial q_{2x}^2}$	$\frac{\partial^2 \mu_\alpha}{\partial q_{2x}^2}$
$s\sigma$	4.957	0.043	0.046	4.5×10^{-3}	3.8×10^{-3}
$p\pi'$	4.395	0.605	0.598	2.3×10^{-3}	2.8×10^{-3}
$p\pi''$	...	...	...	-0.0×10^{-3}	-0.2×10^{-3}
$p\sigma$	4.683	0.317	0.314	-9.1×10^{-3}	-9.9×10^{-3}
$d\sigma$	4.142	-0.142	-0.173	-4.8×10^{-3}	-4.2×10^{-3}
$d\pi'$	4.057	-0.057	-0.066	0.8×10^{-3}	0.1×10^{-3}
$d\pi''$	...	...	...	-0.2×10^{-3}	-0.2×10^{-3}
$d\delta$	3.999	0.001	0.014	-0.2×10^{-3}	-0.2×10^{-3}

than 1 meV in the energy change along the nuclei coordinates. The good agreement is also demonstrated in Fig. 1, where we plotted the quadratic shift of the $p\sigma$ state of HCO^* and the quadratic splitting of the $p\pi$ states in N_2H^* as a function of q_{2x} .

Numerous experimental studies have been conducted by Mayer and co-workers,^{39,47–49} and Brownbill and Softley⁵⁰ on double-resonance spectroscopy of rovibrationally excited Rydberg states of HCO . Although a detailed theoretical attempt to reproduce their experimental spectra is out of scope of the present study, we briefly discuss the consistency of our results with the parameters extracted from the experimental measurements.

In Ref. 49, a first photon prepares HCO in the $3p\pi^2\Pi(010)$ state (the quantum number l_2 is not specified) and a second photon allows transition to vibronically autoionizing high Rydberg states converging to the (010) states of HCO^+ . The spectra are then recorded for Rydberg series with principal quantum numbers $n = 13, 14$, and 15 , for several rotational states. By selecting individual resonances of the largest intensity, they identify states obeying the Rydberg formula. Their phenomenological quantum defects are then averaged over many states and are assigned to principal partial waves. In Table IV, our *ab initio* equilibrium quantum defects are compared with their averaged fitted quantum defects. In principle, one should not expect an excellent agreement because the quantum defects in Ref. 49 correspond to excited

TABLE III. Same as Table II for N_2H^+ .

State	$\nu^{(0)}$	$\mu^{(0)}$	$\delta^{(0)}/\pi$	$\frac{1}{\pi} \frac{\partial^2 \delta_\alpha}{\partial q_{2x}^2}$	$\frac{\partial^2 \mu_\alpha}{\partial q_{2x}^2}$
$s\sigma$	4.889	0.111	0.098	1.8×10^{-3}	1.4×10^{-3}
$p\pi'$	4.314	0.686	0.684	2.9×10^{-3}	2.4×10^{-3}
$p\pi''$	...	...	...	1.6×10^{-3}	0.8×10^{-3}
$p\sigma$	4.668	0.332	0.312	0.2×10^{-3}	-0.4×10^{-3}
$d\sigma$	4.165	-0.165	-0.181	-7.1×10^{-3}	-6.0×10^{-3}
$d\pi'$	4.071	-0.071	-0.085	1.5×10^{-3}	0.2×10^{-3}
$d\pi''$	...	...	...	-1.5×10^{-3}	-2.0×10^{-3}
$d\delta$	4.011	-0.011	-0.000	2.3×10^{-3}	1.8×10^{-3}

FIG. 1. Example of agreement between the geometry-dependent quantum defects and phase shift divided by π , as a function of the q_{2x} dimensionless component of the transverse mode. Left and right panels show, respectively, the quadratic dependence of the $p\sigma$ state of HCO* and the splitting of the $p\pi$ states of N2H*.

rovibrational states of HCO and are averaged over many Rydberg states, whereas we only compare here with equilibrium values of the quantum defects. Nevertheless, there is an overall agreement in the quantum defects, both in the assignment of the states and in the numerical values. The maximum discrepancy ~ 0.06 is observed for $p\sigma$ and $d\sigma$ states. Let us mention that an unassigned quantum defect of 0.29 was obtained in a similar study³⁹ on the (020) vibrational excited states and could represent the quantum defects of the $p\sigma$ state, thus situated closer to our calculated value.

Brownbill and Softley⁵⁰ considered the experimental spectra of Mayer *et al.*,⁴⁷ as well as their own spectra converging to excited (020) and (030) vibrational states of HCO⁺, and used MQDT to simulate the Rydberg autoionization spectra. In their approach, the quantum defect parameters are not calculated explicitly, such that certain approximations must be employed to avoid the use of an unmanageable number of variable quantum defect parameters. The first approximation used was that the diagonal vibrational quantum defect are not calculated from the integration of fixed-nuclei quantum defects, but are given directly as input parameters for each vibronic state. The second main approximation was to consider that the value of off-diagonal quantum defects allowed by symmetry is independent of the values of l and λ . The initial estimates for the diagonal quantum defects were obtained from Song and Cool⁵¹ and from the quantum defects of Grant and co-workers,^{39,47–49} whereas the initial off-diagonal quantum defects were set initially to an arbitrary but small value. The optimization was then performed by manual adjustment

of parameters to give the best visual fit to the experimental spectra. Their results are presented as well in Table IV and show an overall agreement, except that some differences exist for (010) compared to Ref. 49, especially the surprisingly large quantum defect values for $d\pi$ and $d\delta$ states. Considering the higher vibrational states, non-negligible variations are observed for s and p states, as well as a sudden drop for the quantum defects $d\pi$ and $d\delta$. Thus, it was concluded in Ref. 50 that the electronic quantum defect matrix should vary significantly with the bending angle, which is in agreement with our calculations. To ensure the accuracy of our results, we have increased the level of our bound state calculations by including all single excitations for the ion and all single and double excitations to describe the Rydberg states of HCO and observed only negligible change (<0.01) in the quantum defects.

We do not have a clear explanation for the non-negligible difference in the values of $\mu_{d\sigma, d\sigma}$ between our results and the results of Refs. 49 and 50. This could indeed come from complex vibronic coupling or the difficulty of describing this state by quantum chemistry codes. However, note that independent bound state calculations performed in Ref. 52 found as well the $d\sigma$ state to have a quantum defect of about -0.15 . On the other hand, we believe that there is a simple explanation for the value and behavior of the $p\sigma$ quantum defect as a function of bending coordinate obtained in Ref. 50. Our calculations show that this state is only very weakly coupled to other electronic states through bending and that its strong quadratic shift (see Table II and Fig. 1) mainly comes from its diagonal matrix element. Indeed, our scattering calculation reveals that this diabatic quadratic coefficient is ≈ -0.01 . Therefore, using the simple formula $\langle v_2 | q^2 | v_2 \rangle = (v_2 + 1/2)$ and considering one quantum of excitation along a component of the degenerate mode and no quantum in the other normal modes, we obtain for $v = (010)$ a reduced quantum defect $\mu_{vp\sigma, vp\sigma} = 0.297$, which is close to the value given by Brownbill and Softley.⁵⁰ More importantly, this suggests that changing v_2 by one quantum $\Delta v_2 = 1$ modifies the quantum defect by $\Delta \mu_{vp\sigma, vp\sigma} \approx -0.01$, which is exactly what Brownbill and Softley⁵⁰ have found (see Table IV).

Finally, we have performed the same calculations considering variations along the stretching normal coordinates of

TABLE IV. *Ab initio* quantum defects for HCO at its equilibrium geometry compared with fitted averaged quantum defects of Refs. 49 and 50 used to reproduce double-resonance spectrum of Rydberg autoionizing states converging to excited vibrational states ($0v_2^1 0$) of HCO.

μ	$s\sigma$	$p\sigma$	$p\pi$	$d\sigma$	$d\pi$	$d\delta$	Taken from
q_0	0.043	0.317	0.605	-0.142	-0.057	0.001	This work
(010)	0.062	0.253	0.606	-0.076	-0.027	0.002	Ref. 49
(010)	0.062	0.280	0.670	-0.070	-0.120	-0.140	Ref. 50
(020)	0.112	0.270	0.670	0.050	-0.057	0.015	Ref. 50
(030)	0.057	0.260	0.670	-0.060	-0.010	0.015	Ref. 50

FIG. 2. Comparison between the geometry-dependent quantum defects obtained via the bound state calculations and the complex Kohn method as a function of the dimensionless normal coordinate q_1 ($\omega_1 = 3383 \text{ cm}^{-1}$) of N_2H^+ . Upper and lower panels show, respectively, the $p\sigma$ and $s\sigma$ state.

both ions. Because the $C_{\infty v}$ symmetry is conserved through such distortions, the adiabatic quantum defects can also exhibit a linear dependence with respect to stretching around the equilibrium geometry. Again, we have compared the results of the bound state and scattering calculations as a test of the computational accuracy. The agreement is even more striking in this case, because one can verify that the linear shift (resulting from diagonal diabatic perturbation) and the quadratic shift (resulting from off-diagonal diabatic perturbation) are almost identical in both calculations. As an example, Fig. 2 shows the variations along the q_1 normal coordinate of N_2H^+ for the $p\sigma$ and $s\sigma$ quantum defects obtained by both methods. As can be seen from both calculations, the $p\sigma$ quantum defect exhibits a large linear variation and curves down for larger values of q_1 due to strong couplings with the $s\sigma$ and $d\sigma$ states.

B. Interpretation of the vibronic interactions

The values of the diabatic electronic couplings can be deduced either from the bound state calculations or directly through the results of the complex Kohn method. Nevertheless, the former procedure of inverting the potential energy surface in order to extract the parameters of the quantum defect matrix is ambiguous in linear molecules. This procedure has given reliable quantum defect matrices in past studies on molecules with C_{3v} or T_d symmetries,^{28,53} because the degenerate normal modes only break the symmetry to the C_{2v} point group. On the other hand, the molecular bend in linear molecules lowers the symmetry to the C_s point group, such that numerous electronic couplings become allowed and the quantum defect matrix parameters cannot be sorted out with certainty from the *ab initio* data. In fact, the previous considerations already account for the assumption, used for instance in Refs. 26, 28, 35, and 53, that all diagonal elements of the quantum defect matrix are constant with respect to variation of a degenerate coordinate. However, our scattering and bound state calculations revealed that it represents a poor approximation for linear molecules, whereas it has shown to

TABLE V. Partial derivatives with respect to the normal coordinates of the largest quantum defect couplings for HCO^+ and N_2H^+ molecular ions.

Mode	HCO^+		N_2H^+	
	Coupling	Value	Coupling	Value
q_1	$\partial\mu_{p\sigma, p\sigma}$	0.034	$\partial\mu_{p\sigma, p\sigma}$	0.045
	$\partial\mu_{s\sigma, p\sigma}$	0.031	$\partial\mu_{p\sigma, d\sigma}$	0.030
	$\partial\mu_{p\sigma, d\sigma}$	0.020	$\partial\mu_{s\sigma, p\sigma}$	0.025
	$\partial\mu_{s\sigma, d\sigma}$	0.019	$\partial\mu_{s\sigma, d\sigma}$	0.018
	$\partial\mu_{p\pi, d\pi}$	0.004	$\partial\mu_{p\pi, d\pi}$	0.008
q_2	$\partial\mu_{s\sigma, p\pi}$	0.019	$\partial\mu_{s\sigma, p\pi}$	0.029
	$\partial\mu_{p\pi, d\delta}$	0.011	$\partial\mu_{p\sigma, p\pi}$	0.023
	$\partial\mu_{d\pi, d\delta}$	0.010	$\partial\mu_{p\pi, d\delta}$	0.017
	$\partial\mu_{s\sigma, d\pi}$	0.010	$\partial\mu_{s\sigma, d\pi}$	0.012
	$\partial\mu_{p\sigma, d\pi}$	0.006	$\partial\mu_{d\pi, d\delta}$	0.010
q_3	$\partial\mu_{p\sigma, d\sigma}$	0.015	$\partial\mu_{p\sigma, p\sigma}$	0.016
	$\partial\mu_{s\sigma, p\sigma}$	0.011	$\partial\mu_{s\sigma, s\sigma}$	0.010
	$\partial\mu_{p\sigma, p\sigma}$	0.011	$\partial\mu_{p\pi, d\pi}$	0.010
	$\partial\mu_{p\pi, d\pi}$	0.009	$\partial\mu_{s\sigma, p\sigma}$	0.009
	$\partial\mu_{d\sigma, d\sigma}$	0.009	$\partial\mu_{p\sigma, d\sigma}$	0.008

be a good approximation in our previous studies.^{28,53} Another weakness of this procedure, as explained by Pratt and Jungen,³⁵ is that the model considers dominant interactions between pairs of levels belonging to the same Rydberg series. For two states with quantum defects that differ by a significant amount, which is the case in both molecular ions, the spacing between the states of the n and $n + 1$ Rydberg series can be approximately equal. Therefore, a better treatment should be used. Because of these numerous limitations, all the electronic couplings used to calculate the DR rates and cross sections were extracted directly from the S -matrix, which is calculated by the complex Kohn variational technique. This technique enables to overcome the approximations and uncertainties mentioned above.

Table V presents the main vibronic interactions in both molecules and along each normal coordinate. The couplings are given in the form of partial derivative, with respect to the normal coordinates, of the quantum defect matrix elements obtained from the S -matrix, using Eq. (4). The quantum defect elements are expressed in the γ basis of adiabatic states at the equilibrium geometry of the ion (see Sec. II A), such that they represent the additional couplings induced by molecular distortions. There are several observations that can be made from the values and form of the couplings. It is evident that the indirect DR cross section of N_2H^+ will be the largest. However, the most interesting point is certainly the unexpected high values of the vibronic couplings induced by the stretching mode of largest frequency in both ions. Indeed, it has been believed that vibronic interactions mediated by the molecular bending should be the main factor responsible for the indirect DR mechanism in linear polyatomic ions (e.g., Renner-Teller effect). However, the present results demonstrate that the contribution from the vibronic interactions induced by bending does not represent the major part of all the vibronic interactions. On the other hand, the second stretching mode of lowest frequencies clearly exhibits the smallest contributions in both ions.

Considering in closer detail the vibronic interactions, it is possible to give some qualitative explanations for the previous observations and also concerning the general form of the major couplings. Because molecular distortions modify the charge distribution of the polyatomic ion, they induce an additional dipole moment μ_e that should play an important role in the vibronic interactions. This induced dipole couples partial waves for which $\Delta l = \pm 1$ and with the additional rule that $\Delta \lambda = 0$ if the dipole is directed along the molecular axis and $\Delta \lambda = \pm 1$ if the dipole is perpendicular to the molecular axis. Recall that stretching distortions induce a dipole moment along the molecular axis, whereas to first order in the coordinates, transverse distortions induce a dipole moment perpendicular to the molecular axis. Hence, the results of Table V appears to confirm the important role of the induced dipole, since $s\sigma - p\sigma$ and $p\sigma - d\sigma$ are among the largest couplings through q_1 distortion, while $s\sigma - p\pi$ and $p\pi - d\delta$ are among the largest couplings through q_2 distortion. Nevertheless, all the main couplings cannot be explained by this simple picture. For instance, the large values of the couplings $p\sigma - p\sigma$ and $s\sigma - d\sigma$ through q_1 , or $p\sigma - p\pi$ and $s\sigma - d\pi$ through q_2 , do not take their origin from the induced dipole in N_2H^+ . One could argue that the dipole couples these states due to strong l -mixing, however, a direct analysis of the S -matrix in the partial-wave basis contradicts this argument, as these strong dipole-forbidden partial-wave couplings survive. Nevertheless, the induced dipole moment can provide a rough idea of the strength of the vibronic couplings. For this purpose we have plotted their values for both ions in Fig. 3 as a function of each normal coordinate. First of all, the main induced dipole moments are larger for N_2H^+ , which explains partially the strongest vibronic couplings observed for this ion in Table V. Second, the mode ν_1 induces large dipole moments that are close in value for both ions, which explains the large and similar values for the $s\sigma - p\sigma$ and $p\sigma - d\sigma$ couplings in both molecules. The induced dipole through bending ν_2 in HCO^+ is rather small, but because it is doubly degenerate and all the corresponding vibronic couplings are off-diagonal, it still gives an important contribution to the total cross section. The ν_3 mode also has a relatively small induced dipole for HCO^+

FIG. 3. Induced dipole moment for the HCO^+ and N_2H^+ ions as a function of the dimensionless normal coordinates. The dipole moments are along the molecular axis for ν_1 and ν_3 , perpendicular to the molecular axis for ν_2 .

FIG. 4. The theoretical DR cross section (solid red line) obtained in this study compared with the experimental results (blue circles) from the CRYRING storage ring⁸ for N_2H^+ . The dashed line represents a numerical fit $\sigma = aE^{-b}$ to the experimental data of Ref. 8. The first vibrational thresholds of each normal mode are indicated by arrows. Error bars correspond to the uncertainty in the experiment.⁸

and a negligible one for N_2H^+ . The latter fact is simply understood as these modes mediate distortions of the molecular ions more symmetric than the mode ν_1 and also have the largest reduced mass. Finally, it is clear that one cannot give a quantitative one-to-one correspondence between the relative values of the induced dipole moments and the relative values of the dipole-allowed couplings, meaning that short range, exchange or quadrupole interactions might play an important role as well.

C. DR cross sections and rate coefficients

The theoretical DR cross section and rate coefficient for N_2H^+ are given in Figs. 4 and 5, respectively, and are compared with available data from storage ring and flowing afterglow plasma experiments. As can be seen from both figures, the rate coefficients measured in the different experimental studies do not agree well with each other, however, the DR

FIG. 5. The figure compares the N_2H^+ DR rate coefficient obtained in this study (red solid line) with three different experiments.^{8,12,13} We also introduce error bars associated with the uncertainty in the experiment.⁸

cross section of N_2H^+ measured in a recent CRYRING storage ring experiment⁸ clearly gives very similar values with the present theoretical results at energies above 0.05 eV. In this energy range, an apparent experimental noise hinders an accurate comparison with the theoretical cross section at the different vibrational thresholds. Nevertheless, it is clear that the cross section does not exhibit an observable drop at the first degenerate vibrational threshold, thus confirming our theoretical predictions that other modes contribute significantly in the DR reaction.

On the other hand, the experimental results disagree rather strongly with the theoretical calculations at very low energy, because the cross section exhibits an energy dependence $\sigma(E) \sim E^{-1.42}$, whereas the theoretical cross section behaves as $\sigma(E) \sim E^{-1}$ in agreement with the Wigner threshold law. The reason for departure of the experimental cross section from the Wigner law at low collision energies is unclear. One speculative possibility is that the rotational states of the N_2H^+ ion could be relatively strongly coupled to vibration, in a way that a temporary electron captured into such rotational states may lead to relatively quick predissociation. It is known that the probability of the rotational capture of the incident electron during an electron-ion collision is large for many molecular ions. The probability is also large for N_2H^+ , simply because the quantum defects for $s\sigma$, $p\sigma$, and $p\pi$ states are very different. But such a large probability should in principle not enhance significantly the DR cross section because for other studied molecular ions, the rotation is not strongly coupled to vibration compared to the coupling between electronic and rotational motion. Therefore, for many molecular ions, rotationally excited resonances formed during a collision would likely autoionize rather than predissociate. Nevertheless, it is not excluded that for the N_2H^+ ion, the coupling between rotation and vibration is not as weak as expected but it is not included in present theory. If this coupling is indeed strong, rotational resonances should be present in the DR spectrum, although they would not be resolved in the experiment, and could produce a low-energy dependence in the cross section significantly different than predicted by the Wigner threshold law. Finally, we would like to mention here that according to Eq. (8), the DR cross section scales as $(v_i' + 1)$ for the ion initially excited vibrationally with v_i' quanta (and assuming that the direct DR mechanism can be neglected). Therefore, if the ions were vibrationally excited the DR cross section would be larger. However, in the experiment the ions are in the ground electronic and vibrational state.

The theoretical cross section and rate coefficient obtained for the HCO^+ ion are shown respectively in Figs. 6 and 7. Note that our calculated indirect DR cross section is now summed incoherently with the direct DR cross section calculated by Larson *et al.*,¹⁵ whose contribution is only significant at energy above ~ 0.1 eV. A comparison with several theoretical and experimental results is given in the figures as well, and discrepancies between the different experimental data also exist in this case. In particular, the cross sections measured in a merged beam experiment by Le Padellec *et al.*¹⁴ and in a recent CRYRING storage ring experiment by Hamberg *et al.*⁵⁴ can disagree up to a factor 2-3 in some energy regions. In

FIG. 6. The theoretical DR cross section obtained in this study for pure HCO^+ (red solid line) and for a mixture (red dashed-dotted line) of the HCO^+ (90%) and HOC^+ (10%) isomers. For comparison, we also plotted results of two experiments, merged beam (purple dots)¹⁴ and CRYRING storage ring (blue dots),⁵⁴ and previous theoretical calculations (green solid and black dashed lines)^{21,22} based on a quantum defect approach. The first vibrational thresholds of each normal mode of HCO^+ and of the degenerate mode of HOC^+ are indicated by arrows. Error bars correspond to the uncertainty in the CRYRING experiment.⁵⁴

Fig. 6, the theoretical DR cross section of HCO^+ agrees well with the CRYRING experimental data on a wide energy range within 10%–20% for the major part of the energies above 0.02 eV. More precisely, the values of the relative drops in the experimental cross section at the vibrational thresholds are well reproduced. Previously, it was questioned why such sudden decreases are absent in both experimental cross sections^{14,54} at the first excited degenerate vibrational level. Indeed, it was estimated that second-order Renner-Teller couplings are too weak to explain the very mild drop in the cross section. On the other hand, in their analytic three-channel model, Schneider *et al.*⁵⁵ speculated that a low-energy direct DR mechanism

FIG. 7. The figure compares the DR rate coefficient obtained in this study for pure HCO^+ (red solid line) and for a mixture (red dashed-dotted line) of HCO^+ (90%) and HOC^+ (10%) with results of several experiments.^{12–14,56–61} In the experiments, the ratio of densities of HCO^+ and HOC^+ is unknown. Also shown, the experimental error bars as given in Ref. 54.

could potentially explain this experimental feature. The present results actually demonstrate that the mild drop observed in the cross section should mainly be due to the fact that the ν_2 mode only accounts for a part of the total cross section at low energy. Another indication to support this interpretation is the fact that the theoretical cross section calculated in a past study by Douguet *et al.*,²² which also considered all internal degrees of freedom for the molecular ion, produces a similar smooth behavior at the first vibrational threshold, whereas the calculation by Mikhailov *et al.*,²¹ which did not include CO stretching, gave a very sharp decrease of the cross section in that region. On the other hand, the calculated DR cross sections in Refs. 21 and 22 are too low compared to the experimental results. The disagreement is partially attributed to the poor precision in the vibronic couplings obtained by fitting the PES, but more importantly, to the fact that the $s - p$ and $p - d$ couplings were neglected in Refs. 21 and 22. It is now clear that these couplings are very important for the electron recombination with molecular ions having strong dipole moments.

We do not have a clear explanation for the apparent lack of sharp drop in both experimental cross sections at the ω_1 threshold. This phenomenon could be due to simultaneous direct and indirect processes described in the three-channel model.⁵⁵ Especially, in the case of N_2H^+ , we did not add the direct DR cross section, which should contribute at larger energies. It is also possible that the lack of sharp drop comes from the contribution of capture with $\Delta v = 2$, which could occur through first order couplings if the harmonic approximation is relaxed, or directly through second order couplings.

In both experimental cross sections plotted in Fig. 6, one notices a strong change in slope appearing far below 0.01 eV, which disagrees with the theoretical calculations. One potential explanation for this unexpected behavior could be the presence of the stable isomer HOC^+ in the experiments. This possibility is supported by the fact that the first excited degenerate vibrational level of HOC^+ has a very low value $\hbar\omega_2 \approx 150 \text{ cm}^{-1}$ located exactly in the region of change in slope and which implies a large cross section for the ion. Recall that once expressed in length-unit coordinates, the cross section in Eq. (10) is inversely proportional to the vibrational frequency. For these reasons, we investigate the DR cross section of this isomer as well. However, because the precise calculation of the DR cross section of this isomer is out of scope of the present study, we only give an estimation of its value by fitting the quantum defects obtained through *ab initio* bound state energy calculations and considering that the coupling scheme should be similar to the one obtained more precisely for HCO^+ . One complication, already mentioned by Martin *et al.*,³⁷ is the need for large scale calculations to reproduce the lowest vibrational frequency of HOC^+ , which we found to be 180 cm^{-1} , in good agreement with the value of 153 cm^{-1} calculated in Ref. 37. The partial cross sections for the stretching modes are slightly smaller than for HCO^+ . On the other hand, the partial cross section for bending in HOC^+ is more than an order of magnitude larger than the one of HCO^+ . The ratio of density is unknown in these experiments and we have chosen a reasonable mixture with 90% of HCO^+ and 10% of HOC^+ and plotted the cross section in Fig. 6 as

TABLE VI. Contribution and relative weight at low energies of each vibrational mode into the total DR cross sections for the HCO^+ and N_2H^+ ions. The contributions are given as products $E\sigma$ that are energy-independent (see Eq. (13)). Contribution from a particular vibrational mode should be set to zero if the electron energy exceeds the vibrational energy of one quantum of the mode.

Ion	Mode	$E\sigma \text{ (cm}^2 \text{ eV)}$
HCO^+	q_1	$10.779 \times 10^{-17} \text{ (46.6\%)}$
	q_2	$9.354 \times 10^{-17} \text{ (40.4\%)}$
	q_3	$3.019 \times 10^{-17} \text{ (13.0\%)}$
N_2H^+	q_1	$14.153 \times 10^{-17} \text{ (35.8\%)}$
	q_2	$22.348 \times 10^{-17} \text{ (56.6\%)}$
	q_3	$2.994 \times 10^{-17} \text{ (7.6\%)}$

well. The resulting cross section appears to reproduce qualitatively the change of behavior observed in both experimental data, even though it remains lower than the results of the CRYRING experiment. There could be different reasons for the remaining disagreement as, for example, a larger fraction of HOC^+ in the experiment than what we have assumed, the fact that there is a larger uncertainty in our calculation of the HOC^+ cross section or the presence of excited electronic or vibrational states of the HOC^+ ion in the experiments. Notice that in the case of HCO^+ , the data from both experiments are in agreement with the Wigner threshold law. Despite the fact that the main ingredients of the indirect mechanism in HCO^+ appear to be better understood, recall that the cross section calculated in this model should represent an upper bound to the exact cross section. Therefore, further improvements in the theory (e.g., accounting for autoionization) or experimental refinements could always be addressed in the future. Finally, we give in Table VI the values of the calculated partial cross section for each normal mode.

V. CONCLUSIONS

We have improved the theoretical approach for studying the dissociative recombination of linear polyatomic ions. In previous theoretical studies^{21–24,26,28,35,53,62} employing a similar approach, the DR cross section was obtained from quantum defects calculated using energies of excited bound electronic states, which in turn are obtained from *ab initio*^{21–23,28,53} or experimental data.^{24,26,35,62} The quantum defect approach, which was well adapted for molecules with C_{3v} , D_{3h} , or T_d symmetry, such as H_3^+ , H_3O^+ , CH_3^+ , and NH_4^+ ,^{24,27,28,53} does not apply as well in the case of linear polyatomic ions as HCO^+ ,^{21–23,26,35,62} because the fitting of the quantum defect is not unique and the approximations, which must be used, are not appropriate. In this study, instead of using the quantum defect approach, we use the electron-ion scattering matrix calculated directly from the first principles. This powerful technique allows us to avoid the main difficulties by removing the inherent uncertainties and approximations. Furthermore, using MQDT, we have verified that one can reproduce, to striking accuracy, Rydberg states energies using the scattering matrix calculated by the complex Kohn variational method.

The results obtained in the present theoretical approach have improved substantially the agreement with experimental measurements and produced a larger cross section for the DR of HCO^+ compared to the previous theoretical studies,^{21–23,26,35,62} as well as demonstrating that the DR of N_2H^+ also occurs through an indirect mechanism at low energy. The main results are that the scattering matrix approach allows one to account precisely for all couplings between various electronic states, whereas couplings originating from the induced dipole moment through nuclei distortion were previously neglected. Moreover, we have found that the stretching modes can play an important role in the electronic capture by linear polyatomic ions with a large dipole moment, thus explaining why the experimental cross sections decrease only relatively weakly above the lowest excited vibrational threshold for both studied molecular ions. At very low energy, both experimental cross sections disagree with our theoretical results. In the case of HCO^+ , we explain and correct this disagreement by considering a contamination from the HOC^+ isomer, whereas for N_2H^+ we suggest possible reasons explaining why the experimental cross section does not follow the Wigner threshold law. For both ions, experimental results from different studies are somewhat not in agreement with each other. Therefore, more experimental studies are needed to clarify precisely the possible reasons for remaining disagreements.

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