

1-1-2011

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### Recommended Citation

Ayouz, M.; Lopes, R.; Raoult, M.; Dulieu, O.; and Kokoouline, Viatcheslav, "Formation of H-3(-) by radiative association of H-2 and H- in the interstellar medium" (2011). *Faculty Bibliography 2010s*. 7059.  
<https://stars.library.ucf.edu/facultybib2010/7059>

**Formation of  $\text{H}_3^-$  by radiative association of  $\text{H}_2$  and  $\text{H}^-$  in the interstellar medium**M. Ayouz,<sup>1</sup> R. Lopes,<sup>1</sup> M. Raoult,<sup>1</sup> O. Dulieu,<sup>1,\*</sup> and V. Kokoouline<sup>1,2</sup><sup>1</sup>Laboratoire Aimé Cotton, CNRS, Bât 505, Université Paris 11, F-91405 Orsay Cedex, France<sup>2</sup>Department of Physics, University of Central Florida, Orlando, Florida 32816, USA

(Received 24 February 2011; published 27 May 2011)

We develop the theory of radiative association of an atom and a diatomic molecule within a close-coupling framework. We apply it to the formation of  $\text{H}_3^-$  after the low-energy collision (below 0.5 eV) of  $\text{H}_2$  with  $\text{H}^-$ . Using recently obtained potential energy and permanent dipole moment surfaces of  $\text{H}_3^-$ , we calculate the lowest rovibrational levels of the  $\text{H}_3^-$  electronic ground state and the cross section for the formation of  $\text{H}_3^-$  by radiative association between  $\text{H}^-$  and ortho- and para- $\text{H}_2$ . We discuss the possibility for the  $\text{H}_3^-$  ion to be formed and observed in the cold and dense interstellar medium in an environment with a high ionization rate. Such an observation could be a probe for the presence of  $\text{H}^-$  in the interstellar medium.

DOI: [10.1103/PhysRevA.83.052712](https://doi.org/10.1103/PhysRevA.83.052712)

PACS number(s): 34.50.-s, 95.30.Ft

**I. INTRODUCTION**

Many chemical reactions in the interstellar medium (ISM) are powered by cosmic rays: atoms and molecules (mainly molecular hydrogen) are ionized by radiation, which provides sufficient energy to initiate a chain of chemical reactions in interstellar clouds leading to the synthesis of polyatomic molecules. About 14 positive ions have been observed and identified in the ISM, including the simplest triatomic one,  $\text{H}_3^+$ . This ion plays an important role in the chemistry and evolution of interstellar clouds [1,2], as its abundance is strongly related to the production of  $\text{H}_2^+$  in the ISM. In contrast, the existence of stable negative ions has long been thought to be impossible due to the presence of UV radiation in the ISM. In particular, the  $\text{H}^-$  ion, which has a single bound state, has not been directly detected yet, so its presence, though probable, is still controversial [3]. Although it was proposed some time ago [4], the surprise came with the detection of negative molecular ions in dense molecular clouds or carbon star envelopes. Several carbon chain ions have been detected so far:  $\text{C}_6\text{H}^-$  [5–7],  $\text{C}_4\text{H}^-$  [8],  $\text{C}_8\text{H}^-$  [9],  $\text{C}_3\text{N}^-$  [10],  $\text{C}_5\text{N}^-$  [6,7], and  $\text{CN}^-$  [11]. All these species are closed-shell systems with a quite high electron binding energy (3.8 eV for  $\text{C}_6\text{H}^-$ ) and the large permanent dipole moment of several debyes. Although it is generally accepted that in the ISM these ions are formed after radiative capture of an electron by the parent neutral molecules [12], no detailed quantum mechanical treatment has been developed yet for modeling the process.

As the negatively charged counterpart of  $\text{H}_3^+$ , the  $\text{H}_3^-$  ion is predicted to be stable by about 0.013 eV [13,14]. It has never been detected so far in the cold regions of the ISM, while Wang *et al.* [15] observed it by mass spectrometry of laboratory plasmas. The  $\text{H}_3^-$  ion cannot be formed by radiative attachment from the unstable  $\text{H}_3$  molecule, so one must consider alternative paths: three-body recombination (TBR),  $\text{H}_2 + \text{H}^- + X \rightarrow \text{H}_3^- + X$ , or radiative association (RA),  $\text{H}_2 + \text{H}^- \rightarrow \text{H}_3^- + \hbar\omega$ . The TBR mechanism must be the dominant process of  $\text{H}_3^-$  formation in laboratory plasma, but it is probably inefficient in the ISM because of low  $\text{H}_2$  densities. The goal of this study is to investigate the

possibility of forming  $\text{H}_3^-$  by RA of  $\text{H}_2$  and  $\text{H}^-$  in low-temperature (<150 K) environments. Note that RA between  $\text{H}_2$  and  $\text{He}^+$  was investigated recently in a similar energy range [16].

Collisions between  $\text{H}^-$  and  $\text{H}_2$  have been studied both theoretically [13,17] and experimentally [18,19], only for collision energies higher than 0.5 eV. In contrast, the structure of the  $\text{H}_3^-$  ion has rarely been explored in the past [13]. Recently, we calculated (see Ref. [14], hereafter referred to as paper I) a new accurate potential energy surface for the  $\text{H}_3^-$  electronic ground state, whose accuracy was improved compared to that of the previous *ab initio* calculations [13,17]. In addition, we have determined for the first time the  $\text{H}_3^-$  permanent dipole moment surface, which is needed for the RA calculations. The  $\text{H}_3^-$  ion is well represented as a loosely bound  $\text{H}_2 \cdots \text{H}^-$  complex with several rovibrational states, bound by, at most, about 70  $\text{cm}^{-1}$ . We have also found that there are a number of predissociation resonances, which can be described as excited rovibrational states ( $j, v$ ) of  $\text{H}_2$  perturbed by  $\text{H}^-$  coupled to the dissociation continuum  $\text{H}_2(j', v') + \text{H}^-$  with an energy of the dimer state  $E(j', v')$  lower than  $E(j, v)$ .

The paper is organized as follows. In the next section we discuss the geometry of the  $\text{H}_3^-$  molecule. In Sec. III we introduce the rovibrational wave functions of the molecule for bound and continuum states. The theory of RA of a dimer and an atom is developed in Sec. IV. Finally, in Sec. V we present results of numerical calculations of the RA cross section and of the rate coefficient for  $\text{H}_3^-$  formation, and we discuss the possibility of observing the  $\text{H}_3^-$  ion in the ISM.

**II. REPRESENTATION OF THE  $\text{H}_2 \cdots \text{H}^-$  COMPLEX AT LOW ENERGIES**

The  $\text{H}_3^-$  molecule is composed of three identical nuclei, described in principle within the CNPI (complete nuclear permutation inversion) group  $D_{3h}$  [20]. However, due to the loosely bound nature of the  $\text{H}_3^-$  ion in its electronic ground state [13,14], the probability of exchange of the  $\text{H}^-$  proton with the dimer protons is negligible. Moreover, the component of the permanent dipole moment of  $\text{H}_3^-$  along the axis separating  $\text{H}_2$  and  $\text{H}^-$  is 2 orders of magnitude

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larger than its transverse components (paper I). Therefore, low-energy collision between  $H_2$  and  $H^-$  can be studied as an inelastic collision of two structured particles. We first define two coordinate systems: The space-fixed (SF) frame, with axes  $(x, y, z)$ , and the body-fixed (BF) frame, with axes  $(X, Y, Z)$ , whose orientation in the SF frame is given by the Euler angles  $\alpha_e$ ,  $\beta_e$ , and  $\gamma_e$ . The  $Z$  axis connects the center of the  $H_2$  molecular axis with the nucleus of  $H^-$ , and its  $X$  axis is in the plane of the three nuclei. The orientation of the dimer with respect to  $Z$  is given by the azimuthal angle  $\theta$ . The natural coordinate system associated with the BF frame is the Jacobi coordinate system  $(R, r, \theta)$ , where  $R$  is the distance between  $H_2$  and  $H^-$  along the  $Z$  axis, and  $r$  the internuclear distance of  $H_2$ .

The quantum numbers resulting from the symmetry operations of the  $C_{\infty v}$  group are well adapted to this ‘‘superdimer’’ approximation. The quantum numbers of the  $H_2$  dimer are treated as good quantum numbers. The quantum states of the  $H_2 \cdots H^-$  complex at low energies are characterized by the quantum numbers  $(J, M, j, v, \Omega^\pm)$ :  $J$  and  $j$ , associated with the total angular momentum  $\hat{\mathbf{J}}$  of the complex and with the angular momentum  $\hat{\mathbf{j}}$  of the dimer, the vibrational state  $v$  of  $H_2$ , the absolute values  $M$  and  $\Omega$  of the projection of  $\hat{\mathbf{J}}$  on the SF  $z$  axis, and of  $\hat{\mathbf{j}}$  on the BF  $Z$  axis, and the intrinsic parity  $\pm$  of the wave function with respect to the reflection  $\sigma_v$  through the plane containing the  $Z$  axis. For  $\Omega \neq 0$  the  $\Omega^+$  and  $\Omega^-$  states are degenerate in this approximation. If the  $H_2 \cdots H^-$  complex is bound, an additional quantum number  $v_l$  characterizes the vibration along the  $Z$  axis. One defines the basis set  $|J, v, j, \Omega\rangle$

$$|J, v, j, \Omega\rangle = \sqrt{\frac{2J+1}{8\pi^2}} [D_{M\Omega}^J(\alpha_e, \beta_e, \gamma_e)]^* \Theta_j^\Omega(\cos\theta) \chi_{vj}(r), \quad (1)$$

where the normalized function  $\Theta_j^\Omega(\cos\theta) = P_j^\Omega(\cos\theta)/\sqrt{4\pi}$  [21] is proportional to the associated Legendre polynomial and describes the rotational state of the dimer, and  $\chi_{vj}(r)$  is the vibrational wave function of  $H_2$ . The Wigner function  $D_{M\Omega}^J(\alpha_e, \beta_e, \gamma_e)$  is associated with the rotation of the complex in the SF frame. The function above is not yet symmetrized with respect to  $\sigma_v$ , and correspondingly,  $\Omega$  can be positive or negative. Assuming that the potential energy surface  $V(R, r, \theta)$  is known (see paper I), one derives the interaction matrix  $\mathbf{V}$  (diagonal with respect to  $\Omega$ ) written in the above basis (after integration over  $r$  and  $\theta$ , denoted by the subscripts to the angle braces):

$$V_{vj\Omega, v'j'\Omega'}^J(R) = \langle Jvj\Omega | V(R, r, \theta) | Jv'j'\Omega' \rangle_{r,\theta} \delta_{\Omega\Omega'}. \quad (2)$$

As  $R \rightarrow \infty$ , the diagonal (in  $v$  and  $j$ ) elements of this matrix become equal to the energies  $\epsilon_{vj}$  of the rovibrational quantum states  $|vj\rangle$  of  $H_2$ . The diagonalization of the  $\mathbf{V}$  matrix at every  $R$  value yields a set of adiabatic potential energy curves, correlated, at large  $R$ , with the sum of  $\epsilon_{vj}$  and of the  $H^-$  ground state (Fig. 1). These curves can accommodate bound levels corresponding to the quantization of the vibrational motion along the  $R$  coordinate. The  $H_2$  nuclear spin  $i_d = 0$  (para- $H_2$ ) or  $i_d = 1$  (ortho- $H_2$ ) determines the possible values of  $j$ , namely, even in the former case, and odd in the latter

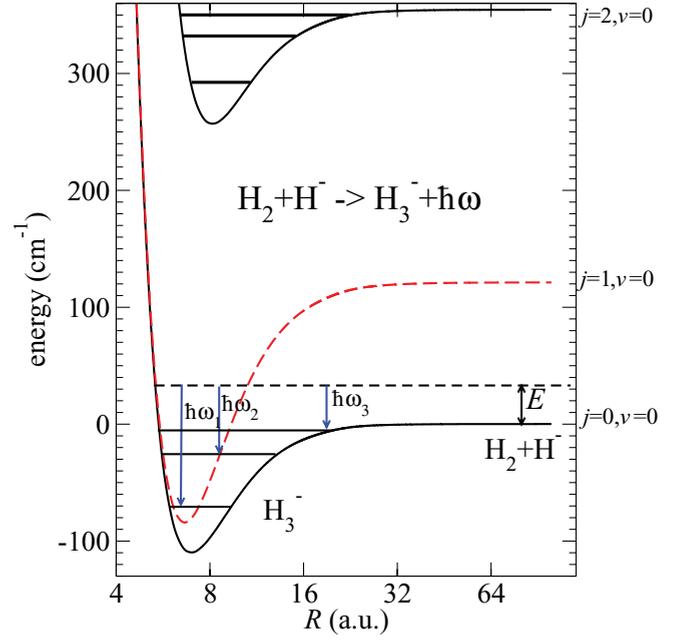


FIG. 1. (Color online) Adiabatic curves of  $H_3^-$  as functions of the Jacobi coordinate  $R$  (on a logarithmic scale), and the scheme for radiative association at a low collisional energy  $E$ . Horizontal lines indicate positions of several bound states (reported in Table I) and resonances.

case. The energy of the state does not depend on the quantum number  $M$ , which is omitted in the following.

The wave functions of Eq. (1) must be properly symmetrized with respect to  $\sigma_v$  and total inversion  $E^*$ , corresponding to the symmetry operators of the  $C_{\infty v}$  group relevant to the present approximation. The  $|J, v, j, \Omega\rangle$  functions obey the transformations

$$\begin{aligned} \sigma_v |J, v, j, \Omega\rangle &= |J, v, j, -\Omega\rangle \\ E^* |J, v, j, \Omega\rangle &= (-1)^J |J, v, j, -\Omega\rangle \end{aligned} \quad (3)$$

so we define the appropriate symmetrized combinations for  $\Omega > 0$ :

$$|J, v, j, \Omega^\pm\rangle = (|J, v, j, \Omega\rangle \pm |J, v, j, -\Omega\rangle) / \sqrt{2}. \quad (4)$$

From these equations, the total parity of the  $\Omega^+$  and  $\Omega^-$  states is given by the value of  $(-1)^J$  and  $(-1)^{J+1}$ , respectively. Permutation (12) of the two nuclei of  $H_2$  requires another symmetrization of the dimer wave functions,

$$(12) \quad |J, v, j, \Omega\rangle = (-1)^j |J, v, j, \Omega\rangle, \quad (5)$$

so that we can write the following four wave functions labeled by the irreducible representations (irreps) of the  $C_{2v}$  group  $\Gamma = A_1, A_2, B_1, B_2$  (see Eq. (94.18) of [21]) (with  $\Omega \geq 0$ ):

$$\begin{aligned} |A_1, J, v, j, \Omega\rangle &= \mathcal{N}(|J, v, j, \Omega\rangle + (-1)^j |J, v, j, \Omega\rangle \\ &\quad + (-1)^J |J, v, j, -\Omega\rangle \\ &\quad + (-1)^{J+j} |J, v, j, -\Omega\rangle), \end{aligned} \quad (6)$$

$$\begin{aligned} |A_2, J, v, j, \Omega\rangle &= \mathcal{N}(|J, v, j, \Omega\rangle + (-1)^j |J, v, j, \Omega\rangle \\ &\quad - (-1)^J |J, v, j, -\Omega\rangle \\ &\quad - (-1)^{J+j} |J, v, j, -\Omega\rangle), \end{aligned} \quad (7)$$

$$|B_1, J, v, j, \Omega\rangle = \mathcal{N}(|J, v, j, \Omega\rangle - (-1)^j |J, v, j, \Omega\rangle - (-1)^j |J, v, j, -\Omega\rangle + (-1)^{J+j} |J, v, j, -\Omega\rangle), \quad (8)$$

$$|B_2, J, v, j, \Omega\rangle = \mathcal{N}(|J, v, j, \Omega\rangle - (-1)^j |J, v, j, \Omega\rangle + (-1)^j |J, v, j, -\Omega\rangle - (-1)^{J+j} |J, v, j, -\Omega\rangle), \quad (9)$$

where the factor  $\mathcal{N}$  ensures normalization to unity. Some functions above are identically equal to 0 for certain combinations of  $J$ ,  $j$ , and  $\Omega$ , which means that the corresponding irreps are not allowed with these combinations.

### III. BOUND AND CONTINUUM WAVE FUNCTIONS OF THE H<sub>2</sub> · · · H<sup>-</sup> COMPLEX AT LOW ENERGIES

The superdimer approximation above is useful for defining basis functions with the appropriate symmetry. However, the quantum numbers of the H<sub>2</sub> internal state can be used at large separation, but not when H<sub>2</sub> approaches H<sup>-</sup>. An accurate description of the wave functions  $|\Gamma, J, E\rangle$  of the H<sub>2</sub> · · · H<sup>-</sup> complex with energy  $E$  ( $E$  being either the collision energy or the bound-state energy of the complex) is obtained within the close-coupling framework, for which we recall below the main steps. The close-coupled expansion on  $N_{\text{tot}}$  symmetrized channel functions  $|\Gamma, J, a\rangle$  is written as

$$|\Gamma, J, E\rangle = \sum_{a=1}^{N_{\text{tot}}} C_a(E) |\Gamma, J, a, E\rangle, \quad (10)$$

where  $a$  is the channel index. The channel functions  $|\Gamma, J, a, E\rangle$  are the independent solutions of the Schrödinger equation with appropriate boundary conditions. They are written as a linear combination of  $N_{\text{tot}}$  basis functions  $|\Gamma, J, v, j, \Omega^\pm\rangle$

$$|\Gamma, J, a, E\rangle = \sum_{k=1}^{N_{\text{tot}}} F_{k,a}(R; E) |\Gamma, J, v_k, j_k, \Omega_k\rangle. \quad (11)$$

In these expressions, the index  $a$  can be assigned to the asymptotic limit of the channel wave function in the BF frame at large distances, that is, ( $a \equiv v_a, j_a, \Omega_a$ ). The number of channels  $N_{\text{tot}}$  is determined by convergence check on the calculated physical property, namely, the binding energies or the RA cross sections.

The  $F_{k,a}$  expansion coefficients are solutions of the set of coupled differential equations written (in a matrix form) in the BF frame as

$$\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial R^2} \mathbf{I} + (\boldsymbol{\epsilon} - E\mathbf{I}) + \mathbf{W}(R) \right] \mathbf{F}(R) = \mathbf{0}, \quad (12)$$

where  $m$  is the reduced mass of the complex, and  $\boldsymbol{\epsilon}$  the diagonal matrix of the H<sub>2</sub> energies  $\epsilon_{vj}$ . The interaction matrix  $\mathbf{W}$  is the sum of the interaction potential matrix  $\mathbf{V}$  [Eq. (2)] and of matrix  $\mathbf{R}$  (diagonal in  $v$  and  $j$ ) describing the atom-diatom relative rotation with the orbital angular momentum operator  $\hat{\mathbf{l}} = \hat{\mathbf{J}} - \hat{\mathbf{j}}$ :

$$R_{vj\Omega, v'j'\Omega'}^{\Gamma J} = \langle \Gamma, J, v, j, \Omega | \hat{\mathbf{l}}^2 | \Gamma, J, v', j', \Omega' \rangle \frac{\delta_{vj, v'j'}}{2mR^2}. \quad (13)$$

A detailed expression of these matrix elements in the BF frame is given in Ref. [22]. The operator  $\hat{\mathbf{l}}^2$  couples channels

with different values of  $\Omega$ , through long-range terms that dominate the potential energy terms due to their  $R^{-2}$  character. Therefore to treat a scattering process conveniently, it is usual to choose the representation in the SF frame where the scattering channels are fully decoupled, and where the  $\hat{\mathbf{l}}^2$  operator is diagonal [with eigenvalues  $\ell(\ell+1)$ ]:

$$R_{vj\ell, v'j'\ell'}^{\Gamma J} = \frac{\ell(\ell+1)}{2mR^2} \delta_{vj\ell, v'j'\ell'}. \quad (14)$$

Similarly to Eq. (10), the total wave function  $|\Gamma, J, E\rangle$  in the SF frame is expressed as

$$|\Gamma, J, E\rangle = \sum_{\alpha=1}^{N_{\text{tot}}} C_\alpha(E) |\Gamma, J, \alpha, E\rangle, \quad (15)$$

where the channel wave functions  $|\Gamma, J, \alpha, E\rangle$  are expanded on the basis set  $|\Gamma, J, v, j, \ell\rangle$

$$|\Gamma, J, \alpha, E\rangle = \sum_{\kappa=1}^{N_{\text{tot}}} F_{\kappa,\alpha}(R; E) |\Gamma, J, v_\kappa, j_\kappa, \ell_\kappa\rangle. \quad (16)$$

Like the channel index  $a$  in the BF frame, the index  $\alpha$  can be assigned at large distances to the asymptotic channel, that is, ( $\alpha \equiv v_\alpha, j_\alpha, \ell_\alpha$ ). The  $F_{\kappa,\alpha}$  coefficients are solutions of Eq. (12) where the matrices are expressed in the SF basis set. The matrix elements of  $\mathbf{V}$  in the SF frame are related to those in the BF frame according to

$$V_{vj\ell, v'j'\ell'}^{\Gamma J}(R) = \sum_{\Omega=0}^J \langle \ell | \Omega \rangle^{\Gamma J} V_{vj\Omega, v'j'\Omega}^{\Gamma J}(R) \langle \Omega | \ell' \rangle^{\Gamma J}, \quad (17)$$

where  $\langle \ell | \Omega \rangle^{\Gamma J}$  is a matrix element of the transformation between BF and SF angular basis sets:

$$\langle \ell | \Omega \rangle^{\Gamma J} = (-1)^{J+\Omega} \sqrt{2\ell+1} \sqrt{2-\delta_{\Omega,0}} \begin{pmatrix} j & J & \ell \\ -\Omega & 0 & 0 \end{pmatrix}. \quad (18)$$

The total parity  $(-1)^J$  and  $(-1)^{J+1}$  for the  $\Omega^+$  and  $\Omega^-$  states imposes that the sum in Eq. (16) is restricted to  $j$  and  $\ell$  values satisfying  $(-1)^J = (-1)^{j+\ell}$  and  $(-1)^{J+1} = (-1)^{j+\ell}$ , respectively.

At this stage, the coefficients of channel superposition in Eq. (10) are still unspecified. They are determined by applying appropriate boundary conditions when the set of differential equations of Eq. (12) is solved. Bound states are characterized by imposing the standard boundary conditions for each channel  $\alpha$ :

$$F_{\kappa,\alpha}(0; E_t) = 0 \quad \forall \quad \kappa \in [1, N_{\text{tot}}], \quad (19)$$

$$F_{\kappa,\alpha}(R; E_t) \xrightarrow{R \rightarrow \infty} 0 \quad \forall \quad \kappa \in [1, N_{\text{tot}}].$$

These quantization conditions are fulfilled only for discrete energies  $E_t$ , corresponding to a discrete vibrational level  $v_t$  of H<sub>3</sub><sup>-</sup> characterizing the number of nodes (in the  $R$  coordinate) of the radial wave function in the dominant channel  $\alpha'_0$  for given  $\Gamma$  and  $J$ . We used the renormalized Numerov method [23] to solve the coupled Eq. (12) written in the SF frame, so the resulting superposition coefficients  $C_\alpha^{v_t}$  ensure that outward-propagated and inward-propagated wave functions are equal with identical derivatives at a well-chosen matching distance

TABLE I. Computed binding energies (in  $\text{cm}^{-1}$ ) of the vibrational levels  $v_t$  ordered as rotational progressions in  $J$ , of the para- $\text{H}_2\text{-H}^-$  complex with respect to the lowest dissociation limit  $\text{H}_2$  ( $v = 0, j = 0$ ) +  $\text{H}^-$ . Levels are labeled with the approximate quantum numbers  $v = 0, j = 0$ , and  $\ell \equiv J$ . Their total parity is given by  $(-1)^J$ .

$\Gamma, J, v, j, \ell, v_t$	Energy	$\Gamma, J, v, j, \ell, v_t$	Energy
$A_1, 0, 0, 0, 0, 0$	-71.2	$A_2, 1, 0, 0, 1, 1$	-23.8
$A_2, 1, 0, 0, 1, 0$	-68.2	$A_1, 2, 0, 0, 2, 1$	-20.2
$A_1, 2, 0, 0, 2, 0$	-62.4	$A_2, 3, 0, 0, 3, 1$	-15.0
$A_2, 3, 0, 0, 3, 0$	-53.8	$A_1, 4, 0, 0, 4, 1$	-8.6
$A_1, 4, 0, 0, 4, 0$	-42.8	$A_2, 5, 0, 0, 5, 1$	-1.7
$A_2, 5, 0, 0, 5, 0$	-29.7	$A_1, 0, 0, 0, 0, 2$	-5.4
$A_1, 6, 0, 0, 6, 0$	-15.3	$A_2, 1, 0, 0, 1, 2$	-4.5
$A_1, 0, 0, 0, 0, 1$	-25.7	$A_1, 2, 0, 0, 2, 2$	-2.7
		$A_2, 3, 0, 0, 3, 2$	-0.4

[23]. Equations (15) and (16) are recast for the wave function of an  $\text{H}_3^-$  bound level  $|\Gamma, J, v_t\rangle$  as

$$|\Gamma, J; \alpha'_0, v_t\rangle = \sum_{\kappa'=1}^{N_{\text{tot}}} \Phi_{\Gamma J \kappa'}^{\alpha'_0 v_t}(R) |\Gamma, J, v_{\kappa'}, j_{\kappa'}, \ell_{\kappa'}\rangle, \quad (20)$$

$$\Phi_{\Gamma J \kappa'}^{\alpha'_0 v_t}(R) = \sum_{\alpha'=1}^{N_{\text{tot}}} C_{\alpha'}^{\alpha'_0 v_t} F_{\kappa', \alpha'}(R; E_t). \quad (21)$$

As an illustration, the calculated energies of lowest  $\text{H}_3^-$  bound levels for  $J = 0$  to 6 corresponding to the binding of para- $\text{H}_2$  ( $v = 0, j = 0$ ) with  $\text{H}^-$  are reported in Table I, labeled with  $v_t$  and with the approximate quantum numbers  $v, j, \ell$  of the corresponding dissociation threshold. This is justified by the weak interaction of the lowest channel ( $v = 0, j = 0, \ell$ ) with the others, as already noted in paper I. There is a single dominant component in the expansion of Eq. (20). The present energies for  $J = 0$  are found to be in agreement within  $0.5 \text{ cm}^{-1}$  with those obtained in paper I using a different integration method. Beyond  $J = 6$  no bound level can exist below the dissociation threshold. Bound levels with energies below the ortho- $\text{H}_2$  ( $v = 0, j = 1$ ) +  $\text{H}^-$  threshold are reported in Table II. All other bound levels, which are found at energies below thresholds with nonzero even(odd) values of  $j$ , correspond to predissociation resonances, which will decay into the continua of the  $\text{H}_2$  ( $v = 0, j'$ ) +  $\text{H}^-$  thresholds with  $j'$  even(odd) and  $0(1) \leq j' < j$ . All these levels are included in the RA cross-section calculations below.

Note that these results, in addition to transition dipole moments obtained from the permanent dipole moment surface, could be used to model an absorption spectrum that could guide the search for  $\text{H}_3^-$  rotational transition lines in the ISM absorption spectra in the millimeter-wavelength range. Only  $P$  and  $R$  lines ( $\Delta J = \pm 1$ ) will be observed between levels within levels in the same part in Tables I ( $A_1$ - $A_2$  transitions) and II ( $B_1$ - $B_2$  transitions).  $Q$  transitions ( $\Delta J = 0$ ) will connect only levels from the upper part in Table II with levels from the lower part in this table ( $B_1$ - $B_2$  transitions).

In a scattering process with energy  $E$ , the number of energetically open channels  $N_o$  gives the number of physical solutions of Eq. (12). The remaining  $N_c = N_{\text{tot}} - N_o$  closed

TABLE II. Computed binding energies (in  $\text{cm}^{-1}$ ) of the vibrational levels  $v_t$  of the ortho- $\text{H}_2\text{-H}^-$  complex ordered as rotational progressions in  $J$ , with respect to the lowest dissociation limit  $\text{H}_2$  ( $v = 0, j = 1$ ) +  $\text{H}^-$ . Levels are labeled with the approximate quantum numbers  $v = 0, j = 1$ , and  $\ell$ . The total parity is  $(-1)^J$  for the levels in the upper part and  $(-1)^{J+1}$  for the levels in the lower part.

$\Gamma, J, v, j, \ell, v_t$	Energy	$\Gamma, J, v, j, \ell, v_t$	Energy
$B_2, 0, 0, 1, 1, 0$	-152.7	$B_2, 0, 0, 1, 1, 2$	-33.2
$B_1, 1, 0, 1, 0, 0$	-149.3	$B_1, 1, 0, 1, 0, 2$	-31.6
$B_2, 2, 0, 1, 1, 0$	-142.6	$B_2, 2, 0, 1, 1, 2$	-28.4
$B_1, 3, 0, 1, 2, 0$	-132.6	$B_1, 3, 0, 1, 2, 2$	-23.9
$B_2, 4, 0, 1, 3, 0$	-119.7	$B_2, 4, 0, 1, 3, 2$	-18.2
$B_1, 5, 0, 1, 4, 0$	-104.0	$B_1, 5, 0, 1, 4, 2$	-11.8
$B_2, 6, 0, 1, 5, 0$	-85.8	$B_2, 6, 0, 1, 5, 2$	-5.0
$B_1, 7, 0, 1, 6, 0$	-65.6	$B_1, 1, 0, 1, 2, 0$	-13.3
$B_2, 8, 0, 1, 7, 0$	-44.0	$B_2, 2, 0, 1, 3, 0$	-10.0
$B_1, 9, 0, 1, 8, 0$	-21.7	$B_1, 3, 0, 1, 4, 0$	-5.3
$B_2, 0, 0, 1, 1, 1$	-77.8	$B_2, 0, 0, 1, 1, 3$	-10.7
$B_1, 1, 0, 1, 0, 1$	-75.3	$B_1, 1, 0, 1, 0, 3$	-9.8
$B_2, 2, 0, 1, 1, 1$	-70.5	$B_2, 2, 0, 1, 1, 3$	-8.1
$B_1, 3, 0, 1, 2, 1$	-63.3	$B_1, 3, 0, 1, 2, 3$	-5.6
$B_2, 4, 0, 1, 3, 1$	-54.2	$B_2, 4, 0, 1, 3, 3$	-2.7
$B_1, 5, 0, 1, 4, 1$	-43.2	$B_2, 0, 0, 1, 1, 4$	-1.7
$B_2, 6, 0, 1, 5, 1$	-31.0	$B_1, 1, 0, 1, 0, 4$	-1.3
$B_1, 7, 0, 1, 6, 1$	-17.9	$B_2, 2, 0, 1, 1, 4$	-0.7
$B_2, 8, 0, 1, 7, 1$	-4.9	$B_1, 1, 0, 1, 0, 5$	-0.07
$B_2, 1, 0, 1, 1, 0$	-13.4	$B_1, 4, 0, 1, 4, 0$	-0.5
$B_1, 2, 0, 1, 2, 0$	-10.2	$B_2, 1, 0, 1, 1, 1$	-0.1
$B_2, 3, 0, 1, 3, 0$	-5.8		

channels should lead to nonphysical long-range behavior since the related wave functions diverge asymptotically. Accordingly, the sum in Eq. (15) is restricted to the  $N_o$  open channels

$$|\Gamma, J, \alpha; E\rangle = \sum_{\alpha=1}^{N_o} C_{\alpha}(E) \sum_{\kappa=1}^{N_{\text{tot}}} F_{\kappa, \alpha}(R; E) |\Gamma, J, v_{\kappa}, j_{\kappa}, \ell_{\kappa}\rangle, \quad (22)$$

and the usual boundary conditions are applied for each  $\alpha$  to the set of coupled equations

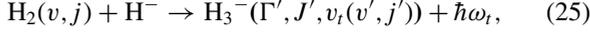
$$\begin{aligned} F_{\kappa, \alpha}(0; E) &= 0 \quad \forall \alpha \in [1, N_{\text{tot}}], \\ F_{\kappa, \alpha}(R; E) &\xrightarrow{R \rightarrow \infty} 0 \quad \forall \alpha \in [N_o + 1, N_{\text{tot}}], \\ F_{\kappa, \alpha}(R; E) &\xrightarrow{R \rightarrow \infty} j(R, k_{\kappa}) \delta_{\kappa, \alpha} - n(R, k_{\kappa}) K_{\kappa, \alpha}(E) \\ &\quad \forall \alpha \in [1, N_o]. \end{aligned} \quad (23)$$

The standard collision matrix  $\mathbf{K}(E)$  summarizes the channel interactions. The functions  $j(R, k_{\kappa})$  and  $n(R, k_{\kappa})$  are the regular and irregular spherical Bessel functions with momentum  $k_{\kappa}$  with respect to the  $\text{H}_2(v_{\kappa}, j_{\kappa}, \ell_{\kappa}) + \text{H}^-$  limit. To be fully determined, the total wave function  $|\Gamma, J, E\rangle$  must also specify the initial state of the scattering process, that is, the entrance channel  $\alpha_0$ , through standard outgoing wave normalization:

$$C_{\alpha}^{\alpha_0}(E) = [\mathbf{I} - i\mathbf{K}(E)]_{\alpha, \alpha_0}^{-1}. \quad (24)$$

#### IV. CROSS SECTION FOR DIMER-ATOM RADIATIVE ASSOCIATION

RA of H<sup>-</sup> with H<sub>2</sub> in an initial rovibrational level  $(v, j)$ , creating H<sub>3</sub><sup>-</sup> in a vibrational level  $v_t$ , with respect to a dissociation limit H<sup>-</sup> + H<sub>2</sub>( $v', j'$ ),



is shown schematically in Fig. 1 for  $v = 0, j = 0$ . A similar picture holds for H<sup>-</sup> and ortho-H<sub>2</sub>( $v = 0, j = 1$ ) association. We limit our study to these two states, which are the only ones populated in cold and dense molecular ISM (see, e.g., Ref. [24]). The two partners approach each other with a collision energy  $E$  above the threshold. A photon with energy  $\hbar\omega_t = E + E_{v_t}$  is emitted to stabilize H<sub>3</sub><sup>-</sup> in the vibrational level  $v_t$  with binding energy  $E_t$ , with respect to the H<sub>2</sub>( $v = 0, j = 0$ ) + H<sup>-</sup> or the H<sub>2</sub>( $v = 0, j = 1$ ) + H<sup>-</sup> limits.

To obtain the RA cross section and rate coefficient, we modify the theoretical approach developed by Herzberg [25], which was later used by several authors [26–28] for RA in diatomic molecules and for photoassociation of cold atoms [29,30]. This formalism is somewhat similar to the treatment one of us used previously for the photodissociation of van der Waals systems, which can be considered as the inverse process [31]. The initial and final states are specified in the SF frame by  $|\Gamma, J, E, \alpha_0\rangle$  and  $|\Gamma', J', v_t, \alpha'_0\rangle$ . The entrance channel index  $\alpha_0$  is correlated with the asymptotic quantum numbers  $v_0, j_0$  of the initial H<sub>2</sub> level, and  $\ell_0$  specifying the initial collisional state. The final state of the created bound H<sub>3</sub><sup>-</sup> molecule has a multichannel nature, but it is labeled, for convenience, with the vibrational index  $v_t$ , and the index  $\alpha'_0$  of the dominant channel in its expansion [Eq. (20)], also related to the asymptotic quantum numbers  $\alpha'_0 \equiv v'_0, j'_0, \ell'_0$  (as in Tables I and II).

The Einstein coefficient  $A_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t)$  for the process of Eq. (25) is written (in atomic units) [28]

$$A_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t) = \frac{4\omega_t^3}{3c^3} \sum_{\sigma=0, \pm 1} |\langle \Gamma' J' v_t \alpha'_0 | \mu^\sigma | \Gamma J E \alpha_0 \rangle|^2, \quad (26)$$

where  $\mu^\sigma = \mu^0, \mu^{\pm 1}$  are the three components of the permanent dipole moment operator  $\hat{\mu}$  in the SF frame. The  $\mu^\sigma$  components in the BF frame are related to those in the SF frame (determined in paper I) by the Wigner rotation functions  $D$  depending on the Euler angles  $\alpha_e$  and  $\beta_e$ :

$$\mu^\sigma = \sum_{\lambda=0, \pm 1} [D_{\sigma, \lambda}^1(\alpha_e, \beta_e, 0)]^* \mu^\lambda. \quad (27)$$

We obtain

$$\begin{aligned} A_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t) &= \frac{4\omega_t^3}{3c^3} (2J+1)(2J'+1) \\ &\times \sum_{\sigma=0, \pm 1} \begin{pmatrix} J & 1 & J' \\ M & \sigma & -M-\sigma \end{pmatrix}^2 \\ &\times \left| \sum_{\lambda=0, \pm 1} \langle \Gamma', J'; v_t, \alpha'_0 | \mu^\lambda | \Gamma, J; E, \alpha_0 \rangle \right|^2, \end{aligned} \quad (28)$$

which becomes, after averaging over the  $M$  values,

$$\begin{aligned} A_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t) &= \frac{4\omega_t^3}{3c^3} (2J'+1) \\ &\times \left| \sum_{\lambda=0, \pm 1} \langle \Gamma', J'; v_t, \alpha'_0 | \mu^\lambda | \Gamma, J; E, \alpha_0 \rangle \right|^2. \end{aligned} \quad (29)$$

We now introduce the expressions for the total wave functions [Eqs. (20) and (22)]:

$$\begin{aligned} A_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t) &= \frac{4\omega_t^3}{3c^3} (2J'+1) \\ &\times \left| \sum_{\lambda=0, \pm 1} \sum_{\alpha=1}^{N_o} C_\alpha^{\alpha_0}(E) d_{\lambda\alpha}^{\Gamma' J', \Gamma J}(E, v_t, \alpha'_0) \right|^2, \end{aligned} \quad (30)$$

with

$$\begin{aligned} d_{\lambda\alpha}^{\Gamma' J', \Gamma J}(E, v_t, \alpha'_0) &= \sum_{\kappa'=1}^{N'_o} \sum_{\kappa=1}^{N_{\text{tot}}} \langle \Phi_{\Gamma J \kappa'}^{\alpha'_0 v_t}(R) | \\ &\times \mu_{\kappa', \kappa}^\lambda(R) | F_{\kappa, \alpha}(R; E) \rangle_R. \end{aligned} \quad (31)$$

The subscript  $R$  to the angle braces denotes integration over the  $R$  coordinate.<sup>1</sup> The matrix elements of the  $R$ -dependent transition dipole moment in the SF basis are

$$\mu_{\kappa', \kappa}^\lambda(R) = \sum_{\Omega'=0}^{J'} \sum_{\Omega=0}^J \langle \ell' | \Omega' \rangle^{\Gamma' J'} \mu_{v' j' \Omega', v_j \Omega}^\lambda(R) \langle \Omega | \ell \rangle^{\Gamma J}, \quad (32)$$

related to the matrix elements in the BF basis

$$\begin{aligned} \mu_{v' j' \Omega', v_j \Omega}^\lambda(R) &= (-1)^{\Omega'} \begin{pmatrix} J & 1 & J' \\ \Omega & \lambda & -\Omega' \end{pmatrix} \langle \chi_{v' j'}(r) \Theta_{j'}^{\Omega'}(\theta) | \\ &\times \mu^\lambda(R, r, \theta) | \chi_{v_j}(r) \Theta_j^\Omega(\theta) \rangle_{r, \theta}. \end{aligned} \quad (33)$$

The subscripts  $r, \theta$  to the angle braces denote integration over the  $r$  and  $\theta$  variables. Note that the initial and final wave functions are not necessarily described by the same number of channels; that is,  $N_{\text{tot}}$  and  $N'_{\text{tot}}$  can be different because  $J \neq J'$  and  $\Gamma \neq \Gamma'$ . We use energy normalization for the initial continuum state.

The probability  $P_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t)$  of an RA event starting in the  $|\Gamma, J; E, \alpha_0\rangle$  state with momentum  $k = \sqrt{2mE}$  toward the final state  $|\Gamma', J'; v_t, \alpha'_0\rangle$  is given by the Einstein coefficient divided by the current density of incident particles, which is  $1/(2\pi)$  for the energy-normalized wave function [21]. The corresponding RA cross section is then expressed as

$$\sigma_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t) = \pi P_{\alpha'_0; \alpha_0}^{\Gamma' J', \Gamma J}(E, v_t) / k^2. \quad (34)$$

In the following, the indexes  $\alpha_0$  and  $\alpha'_0$  are assigned to their asymptotic labeling  $(v_0, j_0, \ell_0)$  and  $(v'_0, j'_0, \ell'_0)$ . Physically, the

<sup>1</sup>Note that in the numerical implementation, the initial (energy-normalized) and final (unity-normalized) wave functions are not directly computed with the renormalized Numerov method; the integral is progressively built during the integration process, as explained in the Appendix in Ref. [31].

entrance channel is determined asymptotically by the initial rovibrational  $\text{H}_2$  level  $(v'_0, j'_0)$ , so that a sum over  $\ell_0$  must be performed. Since nuclear spin is conserved during the RA process, there is no need to include the nuclear spin degeneracy factor. All possible final states should also be included for computation of the total RA cross section. For each initial  $J$  value, the contributions from each final value  $J' = J, J \pm 1$  must be added together. At a given collision energy  $E$ , the summation over all possible values of  $J$  must be performed as well. Finally, we are interested in the formation of  $\text{H}_3^-$  in any of its stable bound levels  $v_f$ , so that the total cross section is obtained as follows:

$$\sigma_{v_0 j_0}(E) = \sum_{\Gamma J \ell_0, \Gamma' J' \ell'_0} \sigma_{v'_0 j'_0 \ell'_0, v_0 j_0 \ell_0}^{\Gamma' J', \Gamma J}(E, v_f). \quad (35)$$

As reported in paper I, the component  $\mu^0(R, r, \theta)$  (along the  $Z$  axis) of the  $\text{H}_3^-$  dipole moment in Eq. (33) is larger by 2 orders of magnitude than the other two components  $\mu^{\pm 1}(R, r, \theta)$ . Therefore, the contribution from the transverse components is neglected. The total cross sections  $\sigma_{00}(E)$  and  $\sigma_{01}(E)$  for RA of  $\text{H}^-$  with para- $\text{H}_2$  ( $v = 0, j = 0$ ) and with ortho- $\text{H}_2$  ( $v = 0, j = 1$ ), respectively, are shown in Fig. 2. We have already mentioned that at low collision energies (below  $400 \text{ cm}^{-1}$ ), a single component dominates the multichannel expansion of the initial and final wave functions. Therefore, the approximate selection rules  $v_i \rightarrow v_f = v_i$ ,  $j_i \rightarrow j_f = j_i$ , and  $J \rightarrow J' = J \pm 1$  hold for the RA process (with the appropriate selection rule for the parity). As expected from Eq. (29), the cross section for RA with ortho- $\text{H}_2$  is larger than the one with para- $\text{H}_2$ , as the former species has a deeper potential well and has more bound states than the latter. The bumps near  $1.5 \text{ cm}^{-1}$  visible in both curves are due to the enhancement of the probability density at the top of the

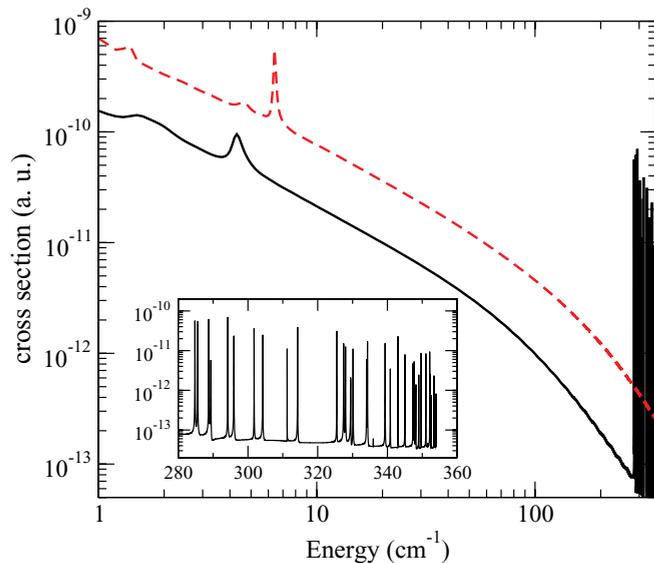


FIG. 2. (Color online) RA cross section (in atomic units) starting from para- $\text{H}_2$  ( $v_0 = 0, j_0 = 0$ ) (solid line) and from ortho- $\text{H}_2$  ( $v_0 = 0, j_0 = 1$ ) (dashed line) as a function of collision energy  $E$  above the corresponding thresholds. Inset: Enlargement of the region of Feshbach resonances induced by the bound states of the closed-channel para- $\text{H}_2$  ( $v = 0, j = 2$ ) +  $\text{H}^-$  (see Fig. 1).

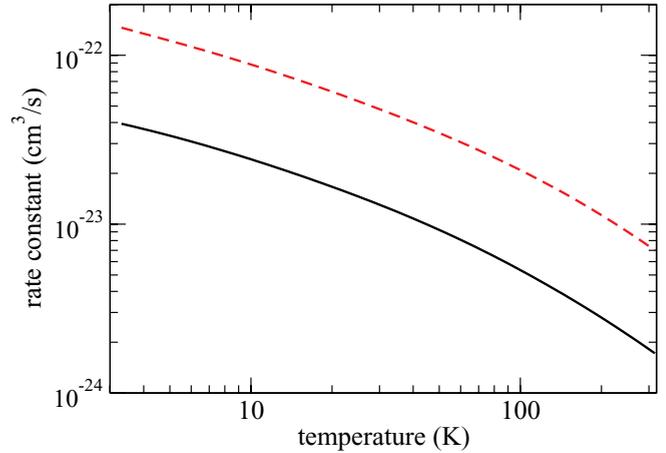


FIG. 3. (Color online) Rate coefficient  $k_{\text{RA}}$  as a function of temperature for RA of  $\text{H}^-$  with para- $\text{H}_2$  ( $v_0 = 0, j_0 = 0$ ) (solid line) and with ortho- $\text{H}_2$  ( $v_0 = 0, j_0 = 1$ ) (dashed line).

centrifugal barrier for low  $J$ . Moreover, one shape resonance is predicted near  $4.3 \text{ cm}^{-1}$  in  $\sigma_{00}(E)$  and near  $6.5 \text{ cm}^{-1}$  in  $\sigma_{01}(E)$  associated with nonzero  $J$  values. Once the collision energy reaches  $285 \text{ cm}^{-1}$ , at which the  $j = 2$  rotational state of para- $\text{H}_2$  can be populated, a series of Feshbach resonances induced by the bound states of the closed-channel para- $\text{H}_2$  ( $v = 0, j = 2$ ) +  $\text{H}^-$  appears in the cross section.

The RA rate coefficient  $k_{\text{RA}}(T)$  is obtained by a standard integration over the Maxwell-Boltzmann collision velocity distribution. Its variation with temperature is displayed in Fig. 3 for RA of  $\text{H}^-$  with para- $\text{H}_2$  ( $v_0 = 0, j_0 = 0$ ) and with ortho- $\text{H}_2$  ( $v_0 = 0, j_0 = 1$ ). As a follow-up to Fig. 2, the rate is found to be about 4 times larger in the ortho- $\text{H}_2$  case than in the para- $\text{H}_2$  case. Note that the resonances in the latter case are too narrow to influence the rate above 200 K. The relative abundances of ortho- $\text{H}_2$  and para- $\text{H}_2$  could be out of thermal equilibrium in the interstellar clouds [24]. The obtained RA rates suggest that the ratio of ortho- $\text{H}_2$ - $\text{H}^-$  to para- $\text{H}_2$ - $\text{H}^-$  is enhanced by a factor of 4 compared to the ratio of ortho- $\text{H}_2$  to para- $\text{H}_2$ .

## V. DISCUSSION: IS THE FORMATION OF $\text{H}_3^-$ IN THE ISM POSSIBLE?

The production rate of  $\text{H}_3^-$  in the ISM is directly related to the presence of  $\text{H}^-$ . Here, we propose a rough estimation of the abundance of  $\text{H}^-$  in the ISM assuming that it is formed only by dissociative attachment (DA) of an electron to  $\text{H}_2$ . Other possible mechanisms such as radiative attachment to H are neglected. The chemistry of interstellar clouds is initiated by ionization of molecular hydrogen by cosmic rays with a typical rate constant  $\zeta \sim 3 \times 10^{-17} \text{ s}^{-1}$  in diffuse interstellar clouds [2]. (Cloud densities are  $\sim 10^2 \text{ cm}^{-3}$  in diffuse clouds and  $\sim 10^4 \text{ cm}^{-3}$  in dense clouds.) The ionized molecular hydrogen  $\text{H}_2^+$  quickly forms  $\text{H}_3^+$  in collisions with  $\text{H}_2$ , with a rate constant  $\sim 2 \times 10^{-9} \text{ cm}^3/\text{s}$  [2]. The electron that escapes after ionization of  $\text{H}_2$  has a high kinetic energy and undergoes many elastic collisions with environmental  $\text{H}_2$  before it thermalizes. In each elastic collision with  $\text{H}_2$ , the electron loses a fraction (about  $4m_e/m_{\text{H}_2}$ ) of its incident energy. For example, the electron should experience about

6200 elastic collisions with  $\text{H}_2$  before its energy is decreased from 10 keV to 10 meV ( $T \sim 120$  K). Possible inelastic  $e^- + \text{H}_2$  collisions will lead to vibrational excitation of  $\text{H}_2$  and to DA,  $e^- + \text{H}_2 \rightarrow \text{H} + \text{H}^-$ . The DA reaction is allowed for collision energies above the threshold at 3.7 eV with a cross section of about  $\sigma_{\text{DA}} \sim 3 \times 10^{-21}$  cm<sup>2</sup> at 4 eV [32,33].

We can roughly estimate the fraction  $f_{\text{DA}}$  of escaped electrons that would form  $\text{H}^-$  rather than undergo the thermalization process. This gives us an estimate of the production rate of  $\text{H}^-$  in the ISM. The upper bound for the  $e^- + \text{H}_2$  elastic cross section  $\sigma_{\text{el}}$  is about  $1.7 \times 10^{-15}$  cm<sup>2</sup> [34]. If we take  $N_{\text{th}} = 1000$  elastic collisions corresponding to the thermalization down to the energy below which DA is impossible, we should compare  $\sigma_{\text{el}}/N_{\text{th}}$  with  $\sigma_{\text{DA}}$ . It gives approximately the value  $f_{\text{DA}} = \sigma_{\text{DA}}N_{\text{th}}/\sigma_{\text{el}} \sim 0.0018$  for the fraction of escaped electrons that form  $\text{H}^-$  by DA of  $\text{H}_2$ . Therefore, the rate of  $\text{H}^-$  production (in cm<sup>-3</sup>.s<sup>-1</sup>) in the ISM can be estimated as  $\zeta n(\text{H}_2)f_{\text{DA}} = \zeta n(\text{H}_2)\sigma_{\text{DA}}N_{\text{th}}/\sigma_{\text{el}}$ . The  $\text{H}^-$  ion has only one bound electronic state and cannot be detected directly. However, if it forms a molecular ion  $\text{AH}^-$  by an association with an atom or molecule A, its presence in the ISM can be proven indirectly by rovibrational absorption spectroscopy of  $\text{AH}^-$ .

One of the motivations for this study was to investigate whether  $\text{H}_3^-$  can be formed in the ISM and be detected by photoabsorption spectroscopy. The stability of  $\text{H}_3^-$  was confirmed in this study. Therefore,  $\text{H}_3^-$  can exist in the ISM in cold clouds ( $T < 100$  K). However, to be observed by far-infrared absorption spectroscopy,  $\text{H}_3^-$  should be present in the ISM in relatively large amounts. The  $\text{H}_3^-$  molecular ion and the  $\text{H}^-$  ion can be destroyed in the ISM by cosmic rays and by mutual neutralization with positive ions. These processes limit the absolute abundance of  $\text{H}_3^-$ . To determine the  $\text{H}_3^-$  abundance, one has to consider rate equations for all reactions involving formation and removal of  $\text{H}^-$  and  $\text{H}_3^-$  in the ISM. However, a rough estimation of  $\text{H}^-$  and  $\text{H}_3^-$  abundance in the ISM can be made using the available data.

First, we estimate the  $\text{H}^-$  abundance  $n(\text{H}^-)$ . According to our model the rate of  $\text{H}^-$  production is given by  $\zeta n(\text{H}_2)f_{\text{DA}}$ . The principal channel of destruction is due to the mutual neutralization with positive ions. Destruction by collisions with other negative species with higher electronic affinities is possible in principle, but their abundance is probably too low compared to those of positive ions to induce a significant loss channel. The number density  $n_+$  of positive ions can

be taken to be equal to the number density of electrons in the ISM. In diffuse clouds, the electron number density is about 0.1% of  $n(\text{H}_2)$ , that is,  $n_+ \sim 0.01$  cm<sup>-3</sup>. Therefore, the rate of removal of  $\text{H}^-$  from the ISM is  $k_{\pm}n(\text{H}^-)n_+$  where  $k_{\pm}$  is the rate constant for mutual neutralization. We take the value of  $k_{\pm} \sim 10^{-7}$  cm<sup>3</sup>/s for the  $\text{H}^- + \text{H}^+ \rightarrow \text{H} + \text{H}$  reaction [35–37] at 10 meV. Therefore, we derive the equilibrium abundance of  $\text{H}^-$ :  $n(\text{H}^-) = \zeta n(\text{H}_2)f_{\text{DA}}/(k_{\pm}n_+) \sim 5 \times 10^{-7}$  cm<sup>-3</sup>. If we take the size of a cloud to be 10 pc, the resulting column density is  $\sim 10^{13}$  cm<sup>-2</sup>, which is a reasonable value for observation.

The estimation of  $\text{H}_3^-$  abundance  $n(\text{H}_3^-)$  can be made in a similar way. The rate of  $\text{H}_3^-$  removal is determined by a similar formula:  $k_{\pm}n(\text{H}_3^-)n_+$ . The rate of  $\text{H}_3^-$  formation is  $k_{\text{RA}}n(\text{H}^-)n(\text{H}_2)$ . The equilibrium  $\text{H}_3^-$  abundance is then given by  $n(\text{H}_3^-) = k_{\text{RA}}n(\text{H}^-)n(\text{H}_2)/(k_{\pm}n_+) \sim 10^{-17}$  cm<sup>-3</sup>. This abundance would produce a column density that is low even for a large interstellar cloud.

If we combine the formulas for  $\text{H}^-$  and  $\text{H}_3^-$  abundances, we obtain

$$n(\text{H}_3^-) = \frac{k_{\text{RA}}\zeta f_{\text{DA}}}{(k_{\pm})^2} \left( \frac{n(\text{H}_2)}{n_+} \right)^2. \quad (36)$$

This formula suggests that the  $\text{H}_3^-$  abundance should be larger in an environment with a smaller degree of ionization (i.e., with a lower number density of positive ions). The environment should be cold enough ( $< 100$  K) for the  $\text{H}_3^-$  ion to be stable with respect to nonreactive collisions with other species (assuming, as above, that collisions with other negative species with high electronic affinities are negligible). Therefore, if  $\text{H}_3^-$  can be detected in the ISM, one has to search for it in cold, dense interstellar clouds. If  $\text{H}_3^-$  is detected, it would prove that  $\text{H}^-$  is also present in the ISM.

#### ACKNOWLEDGMENTS

We thank Roland Wester for motivating us to study  $\text{H}_3^-$  structure and dynamics. Stimulating discussions with Professor Jacques Robert are gratefully acknowledged. The study was supported by Triangle de la Physique as part of the project Quantum Control of Cold Molecules (Contract No. QCCM-2008-007T) and by the National Science Foundation under Grant No. PHY-0855622.

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