

Channel Mixing Effects in the Dissociative Recombination of H_3^+ with Slow Electrons

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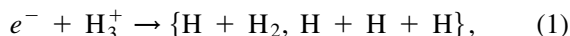
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We discuss the low-energy dissociative recombination of H_3^+ , which strongly influences the abundance of this ion in diffuse interstellar molecular clouds. The kinetic couplings between the ionization continuum and the dissociative ground state of H_3 have been used as input to a two-dimensional wave packet calculation of dissociation dynamics. The cross section obtained for *direct* dissociative recombination is much smaller than the latest experimental results. However, a multichannel quantum defect treatment shows that an *indirect* mechanism via bound Rydberg states of H_3 prevails for this process.

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The chemistry of the H_3^+ molecular ion, a generous proton donor, is of central interest for the kinetics and the composition of many ionized media, in particular, the cold interstellar clouds of molecules [1,2]. The reaction of dissociative recombination (DR),



is the dominant destruction process for this ion in diffuse interstellar clouds with high electron densities [2]. Most experiments using either electron-ion merged beam [3,4] or flowing afterglow [5,6] techniques agree within 1 order of magnitude on a relatively fast process at low electron energy.

The lowest dissociative excited states of H_3 [7,8] occur at about 9 eV above the ground state of the ion at the equilibrium geometry. Their contribution to DR has been evaluated [8,9] and found in good agreement with the experimental values for electron incident energies in the range 5–12 eV, both for H_3^+ and D_3^+ [4]. However, these states dissociate at 0.974 eV above the lowest vibrational level of the ion ground state. Consequently, they cannot play the role of dissociation paths in the low-energy DR of fully relaxed ions, which can dissociate only through the ground surface of H_3 . However, contrary to the high-energy region, the H_3 ground state is *not* coupled to the ionization continuum by *Rydberg-valence* interactions. Therefore, the relatively high DR thermal rates measured in the majority of experiments have been considered as an enigma.

Some years ago, the study of HeH^+ DR [10,11] clearly proved that *nonadiabatic* interactions can also induce reasonably high thermal DR rates. Since then, considerable effort has been made to estimate the strength of such interactions in the case of H_3^+ DR. The main part of the nonadiabatic coupling between the ground state of H_3 and an ionization continuum ($\text{H}_3^+ + e^-$) is expressed by the operator

$$\begin{aligned} \mathbf{V}(r, R, \theta) = & -\frac{\hbar^2}{m_r} \langle \Psi_c | \frac{\partial}{\partial r} | \Psi_{gd} \rangle \frac{\partial}{\partial r} \\ & -\frac{\hbar^2}{m_R} \langle \Psi_c | \frac{\partial}{\partial R} | \Psi_{gd} \rangle \frac{\partial}{\partial R} \\ & -\frac{\hbar^2}{I} \langle \Psi_c | \frac{\partial}{\partial \theta} | \Psi_{gd} \rangle \frac{\partial}{\partial \theta}, \quad (2) \end{aligned}$$

where Jacobi coordinates (r, R, θ) are used, with r being the distance between two H atoms and R the distance between the third H and the midpoint of the line connecting the other two. The wave functions Ψ_c and Ψ_{gd} correspond to $(\text{H}_3^+ + e^-)$ and H_3 electronic states, respectively, m_r and m_R are the reduced masses associated with the internuclear motion along r and R , respectively, I is the momentum of inertia, and the matrix elements represent integration over electronic coordinates only. The nonadiabatic “bound-free” matrix elements—i.e., the bra-kets in Eq. (2)—are (almost) independent of the energy of the incident electron and can be related to their “bound-bound” precursors, using the scaling law (in a.u.) [12]:

$$\begin{aligned} \langle \Psi_c | \frac{\partial}{\partial X} | \Psi_{gd} \rangle = & \langle \Psi_{Ry}^n | \frac{\partial}{\partial X} | \Psi_{gd} \rangle \\ & \times [n - \mu(r, R, \theta)]^{3/2}, \quad (3) \end{aligned}$$

where X stands for r , R , or θ , Ψ_{Ry}^n is the electronic wave function of an H_3 Rydberg state of principal quantum number n , and $\mu(r, R, \theta)$ is the quantum defect of the corresponding Rydberg series. We have evaluated the nonadiabatic matrix elements appearing on the right-hand side of Eq. (3) for $2s$, $3s$, $4s^2A'_1$, and $3p^2E'$ states and estimated their predissociation rates using a time-dependent wave-packet approach [13]. In spite of severe approximations—first order treatment, restriction to C_{2v} geometry ($\theta = 90^\circ$), and harmonic oscillator modeling of the H_3^+ vibration—the results were in satisfactory agreement with the spectroscopic measurements [14]. On the other hand, the use of the scaling law (3) in Eq. (2)

allowed us to estimate the strength of the bound-free nonadiabatic interactions, necessary for the quantitative study of the H_3^+ DR.

Indeed, these couplings are responsible for the so-called *direct* DR process, which consists in the capture of the incident electron into the dissociative state, leading to dissociation in competition with autoionization. Our preliminary calculation was restricted to this direct mechanism, and, in addition, autoionization was neglected. We have used a time-dependent wave-packet approach [13], which relies on the direct integration of the time-dependent Schrödinger equation associated to the dissociative surface $U_d(r, R)$ of interest:

$$i\hbar \frac{\partial}{\partial t} \Psi(r, R; t) = [\mathbf{T}(r, R) + U_d(r, R)]\Psi(r, R; t) \quad (4)$$

with the initial condition

$$\Psi(r, R; t = 0) = V(r, R)\chi_{v_1 v_2}(r, R). \quad (5)$$

Here $\mathbf{T}(r, R)$ is the nuclear kinetic energy operator, and the initial wave packet is given by the action of the nonadiabatic coupling operator [Eq. (2), with θ dependence omitted] on the vibrational eigenfunction of the target ion in the symmetric stretch v_1 and bending normal v_2 modes, $\chi_{v_1 v_2}$.

The cross section for the DR of an H_3^+ ion in the $(v_1 v_2)$ level of energy $E_{v_1 v_2}^+$, with an electron of energy ε is given (in a.u.) by

$$\sigma_{v_1 v_2} = \frac{\pi^3}{\varepsilon} g S_{v_1 v_2}(E), \quad (6)$$

where g is the multiplicity ratio of the neutral and ion states, $E = E_{v_1 v_2}^+ + \varepsilon$ is the total energy of the H_3 system, and $S_{v_1 v_2}(E)$ is the Fourier transform of the overlap between the propagated and initial wave function [15]:

$$S_{v_1 v_2}(E) = \int_{-\infty}^{\infty} e^{iEt/\hbar} \langle \Psi(r, R; t = 0) | \Psi(r, R; t) \rangle dt. \quad (7)$$

Using the technique described above, we have evaluated [9] the contribution of three ionization continua (s^2A_1 , $p_z^2A_1$, and p^2B_2) to the DR cross section of H_3^+ and D_3^+ in their ground state [$(v_1, v_2) = (0, 0)$]. Although, within the same wave-packet approach, our predissociation rates estimated for some Rydberg states agree well with the measurements [13,14], the DR computed cross sections are 4–5 orders of magnitude below the experimental data measured in storage rings [4].

This result, concerning exclusively the *direct* mechanism, is not surprising: the position of the neutral dissociative state with respect to the molecular ion surface [7] corresponds to a very low Franck-Condon factor with the ground vibrational state of the ion. However, if H_3^+ is vibrationally excited, the spread of the wave function results in much larger Franck-Condon factors. For example, the

cross section increases by almost 2 orders of magnitude when the ion is in its fourth vibrational level in the symmetric stretch mode, $(v_1, v_2) = (3, 0)$.

The excited levels are certainly not populated, neither in cold interstellar clouds nor in storage rings, but they can play a very important role in the DR process via the *indirect* mechanism [9,10]. This mechanism consists in temporary capture into bound Rydberg states, subsequently predissociated, and is possible if some of the excited vibrational levels of the molecular ion are situated *above* the total energy of the recombining system: with respect to these levels, the incident electron is “bound,” although it is “free” with respect to the initial level of the target. Our time-dependent method proceeds presently by the propagation of the wave packet on a *single* dissociative surface. We can add one or more surfaces, corresponding to bound Rydberg states, and simultaneously propagate on them our wave packet, but the number of such Rydberg states necessary to achieve convergence could be prohibitively large. So far, another method [16], based on the multichannel quantum defect theory (MQDT), can handle the indirect process, but applying it to the dissociation of polyatomic systems is a difficult task. Indeed, the basic element of the MQDT approach is the strength of the coupling $\zeta_{v_1 v_2}(E)$ of the channel ($e^- + \text{H}_3^+[v_1 v_2]$) with the dissociative continuum, given by

$$\zeta_{v_1 v_2}^2(E) = \sum_{\beta} |\langle \chi_{v_1 v_2}(r, R) | V(r, R) | F_{d\beta}(E; r, R) \rangle|^2 \quad (8)$$

where $F_{d\beta}(E; r, R)$ is the scattering function associated with the potential surface $U_d(r, R)$ and the asymptotic limit β . This latter index labels the dissociation products in their different levels of internal energy. Whereas for the recombination of a diatomic ion only one asymptotic condition is available for the nuclear wave function—and the sum in Eq. (8) reduces to one single term—the DR of H_3^+ can result either in an H atom and an H_2 molecule in different vibrational levels or in $\text{H} + \text{H} + \text{H}$, which can be regarded as an H atom and an H_2 molecule in its vibrational continuum. For each asymptotic limit β , one has to solve the two-dimensional Schrödinger equation for the nuclear motion. Hence, the MQDT procedure would require an enormous computational effort.

To solve this methodological dilemma, we have elaborated a “hybrid” method, which combines the advantages of each of the two treatments. The MQDT-type approach can be linked to the wave-packet one by equating the right-hand side of Eq. (6) with the MQDT formula of the *direct* DR cross section [16], which when autoionization is neglected, is proportional to the square of the coupling strength involved in Eq. (8). We then get

$$\zeta_{v_1 v_2}(E) = [S_{v_1 v_2}(E)]^{1/2} \quad (9)$$

which allows us to estimate $\zeta_{v_1 v_2}(E)$ using the result of a wave-packet propagation, rather than dealing with the difficult evaluation of the numerous terms involving the

scattering functions $F_{d\beta}$ from Eq. (8). In fact, in the case of the direct DR, $\zeta_{v_1 v_2}(E)$ expresses the strength of the coupling between the “effective” dissociative state of electronic energy $U_d(r, R)$ —disregarding the different possible dissociation limits—and the entrance channel.

When an H_3^+ ion in its ground vibrational level recombines with an electron of energy less than the first vibrational excitation energy, all the ionization channels, except the entrance one, are *closed*. The direct DR cross section (neglecting autoionization) can be evaluated within the wave-packet method, with $(v_1, v_2) = (0, 0)$ in Eq. (5) and performing the procedure described by Eqs. (4)–(7). As a by-product of this procedure, we can estimate the strength of the coupling between the entrance ionization channel $(v_1, v_2) = (0, 0)$ and the effective dissociative one by calculating $\zeta_{00}(E)$ from Eq. (8).

We can also perform another wave-packet propagation, choosing as the source term in Eq. (5) the vibrational wave function corresponding to an excited state $(v'_1, v'_2) \neq (0, 0)$, and we can calculate the function $S_{v'_1 v'_2}(E)$ from Eqs. (7) and (8) at the *same* total energy E as before. This describes the predissociation of a fictitious Rydberg state, in an initial excited level (v'_1, v'_2) which would have the same energy as the ion ground level. Since the coupling operator $\mathbf{V}(r, R)$ is energy independent, the corresponding $\zeta_{v'_1 v'_2}(E)$ given by Eq. (8) is exactly the strength of the coupling between the effective dissociation channel and the *closed* ionization channel (v'_1, v'_2) . By such simulations corresponding to successive excited vibrational states, we are able to evaluate the couplings of all the closed ionization channels to the effective dissociative one. We did this evaluation for the particular case where the Rydberg manifold describing the $(H_3^+ + e^-)$

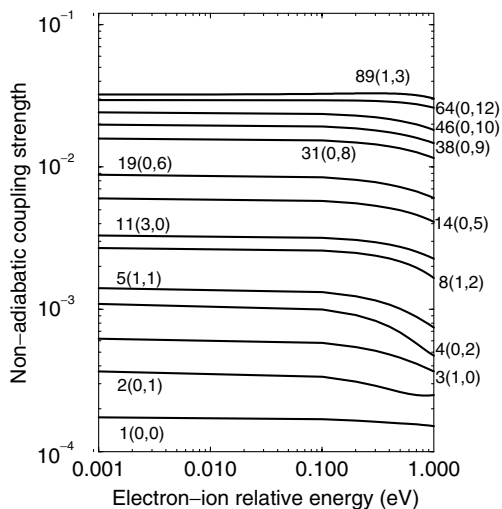


FIG. 1. The strengths of the nonadiabatic couplings of the “effective” dissociation channel associated to the 2B_2 electronic ground state of H_3 , with the different $H_3^+ + e^-$ channels. The curves are labeled by the rank of the threshold in energy followed by its vibrational quantum numbers (v_1, v_2) .

system has the symmetry p^2B_2 and the dissociation channel is the upper sheet of the ground state, converging asymptotically to the $H + H + H$ limit. Some of the couplings are plotted in Fig. 1, which shows an important feature: the corresponding values are spread over almost 3 orders of magnitude, the values corresponding to the entrance channel being *at the bottom* of the range. Note from the curves in Fig. 1, which are labeled by their order in energy, that the nonadiabatic coupling simply increases with the energy. Indeed, since the ion potential surface lies so far above the dissociative surface, the dominant factor is the Franck-Condon overlap which scales with energy. The relatively strong couplings of most of the *closed* ionization channels to the dissociative one is an indication of their possible role in the H_3^+ DR process.

The representation relying on the effective dissociation channel allows us to perform an MQDT-type modeling of the DR process, including all the important mechanisms, i.e., direct and indirect capture and autoionization. The ionization channels, besides being coupled to the dissociative state—as shown in Fig. 1—are also mutually coupled by vibrational interaction, which is described by the channel mixing coefficients $\langle \chi_{v_1 v_2} | \cos[\pi\mu(r, R, \theta = 90^\circ)] | \chi_{v_1' v_2'} \rangle$ and $\langle \chi_{v_1 v_2} | \sin[\pi\mu(r, R, \theta = 90^\circ)] | \chi_{v_1' v_2'} \rangle$. We have evaluated these quantities for the 2B_2 symmetry, starting from the quantum defect previously computed [13]. We could thus estimate the contribution of this symmetry to the H_3^+ DR cross section, both direct and total. The result is shown in Fig. 2. Although the initial discrepancy between theory and experiment is not yet removed, the computed cross section increases by 2 orders of magnitude on the average when the *indirect* process is included. This clearly demonstrates the decisive *constructive* role of this mechanism in the case of the low-energy DR of H_3^+ . Qualitatively, a similar effect was also observed in low-energy DR of HeH^+ [10], but the relative importance of the indirect process is by far more significant in the H_3^+ case.

A strong vibrational interaction between the ionization channels is a necessary condition for the spectacular effect illustrated by Fig. 2. In fact, it is this interaction that allows a contamination of the genuine weak coupling between the entrance and the dissociative exit channel by the much stronger couplings involving the closed channels. To get better insight into this phenomenon, we have artificially canceled the vibrational couplings, choosing a constant value for the quantum defect. The result, displayed in Fig. 3(a), shows a dramatic change in the role of the indirect mechanism: its contribution to the total process consists in narrow destructive resonances, without any quantitative effect with respect to the direct one.

On the other hand, we are able now to check the validity of an ingenious scenario proposed by Bates in his very last DR study [17]. It is based on the so-called “propensity rule,” stating that vibrational couplings are most effective between consecutive— $\Delta v = \pm 1$ —vibrational levels.

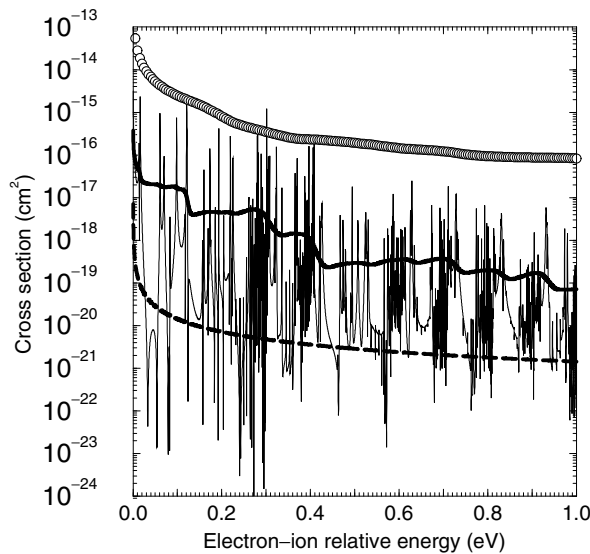


FIG. 2. Dissociative recombination of H_3^+ at low energy, modeled within a combined MQDT/wave-packet approach (restriction to the 2B_2 symmetry). Dashed line: *Direct* cross section. Solid narrow line: *Total* cross section. Circles: CRYRING measurements [4]. Solid broad line: Total cross section, convoluted according to the anisotropic Maxwell distribution in the storage ring [4].

According to this ansatz, the fast H_3^+ DR should occur by a sequence of $(\Delta v_1 = 1, \Delta v_2 = 0)$ or $(\Delta v_1 = 0, \Delta v_2 = 1)$ transitions. By canceling artificially all the vibrational coupling terms except those obeying the propensity rule, we have obtained the results shown in Fig. 3(b). Clearly, such a multistep scenario does make sense, but comparison with Fig. 2 also demonstrates the important role of the vibrational couplings between ionization channels corresponding to more distant $(|\Delta v_1| + |\Delta v_2| > 1)$ vibrational levels.

The increase of the theoretical cross section caused by the inclusion of the indirect process into the modeling is an important step towards reconciling experiment and theory. However, Fig. 2 still shows a gap of more than 2 orders of magnitude between them. A partial explanation is that our present calculation is restricted to the contribution of the p^2B_2 symmetry to the cross section, whereas at least two further symmetries— s^2A_1 and $p_z^2A_1$ —should be accounted for. Still, the main source of the persisting disagreement is probably the restriction in our calculation to two dimensions— $\theta = 90^\circ$, i.e., C_{2v} symmetry. The Franck-Condon overlaps could change considerably when passing from two to three dimensions (C_s symmetry) and the corresponding change of couplings would alter the computed DR cross section—direct and total. Moreover, the actual vibrational structure in three dimensions is much more dense than in the present calculations, where only two vibrational modes were available, within a crude harmonic oscillator approximation. Additional mechanisms, such as the actual opening of the doubly excited states for

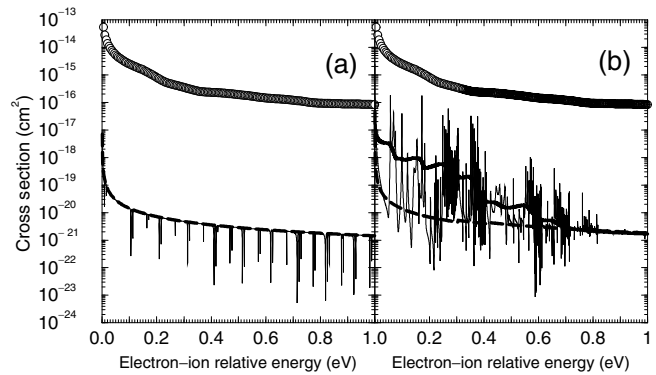


FIG. 3. Same as Fig. 2, with vibrational coupling artificially canceled (a) or restricted to $\Delta v = \pm 1$ (b) (see text). The convoluted results are missing in (a), since irrelevant.

low-energy DR through an efficient coupling to the ground state, should also be carefully examined.

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