

Resonant Dissociative Recombination of H_3^+

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A recently reported peak near 9.5 eV in the cross section for electron impact dissociative recombination of vibrationally cold H_3^+ is due to four H_3 resonance states. Using a complex Kohn, electron scattering variational method to obtain resonance energies and widths and a time-dependent wave packet calculation of the dissociation dynamics in the presence of autoionization, we obtain excellent agreement with the position, shape, and magnitude of the reported feature. Vibrational excitation of H_3^+ is a dominant competing channel due to a high probability of autoionization during dissociation.

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Dissociative recombination (DR) of small molecular ions plays a significant role in the kinetics of low temperature plasmas. In this process an incident electron is captured by the ion into an excited electronic state of the neutral, causing the eventual dissociation of the molecule. Dissociation is highly likely because, following the capture, the internal energy is very high, approximately equal to the ionization potential of the molecular ground state plus the incident electron energy. The dissociation can be direct if the neutral state is itself dissociative or indirect if predissociation of a bound intermediate occurs. Modeling the kinetics of low temperature plasmas requires not only the knowledge of the DR rates but also the final product state distributions. Because of the very high internal energies involved, many molecular potential energy surfaces can play a role in the dissociation dynamics so that calculations of DR have been restricted almost exclusively to diatomics, or to triatomics treated with one-dimensional nuclear dynamics [1]. Here we report calculations of the total DR cross section through direct, resonant channels including the 2 nuclear degrees of freedom necessary to represent the dissociation properly.

Because of the difficulty of producing the ions in well defined initial vibrational-rotational states, most studies of DR have provided only rates for thermal, or hotter, internal state distributions. Recently measurements of the cross section for DR of the ground vibrational state of H_3^+ for incident electron energies from near threshold to almost 30 eV have been obtained using a storage ring [2]. In these experiments Larsson *et al.* observed a pronounced resonant enhancement in the cross section centered near 9.5 eV with a width of several volts. It is the purpose of this Letter to discuss the resonance states of H_3 which cause this enhancement and to present cross sections for this component of the DR.

In earlier studies [3] both neutral ($\text{H} + \text{H}_2$ or $\text{H} + \text{H} + \text{H}$) and ion-pair ($\text{H}^- + \text{H}_2^+$) fragment channels were found to be produced in the DR of H_3^+ . Previous electronic structure calculations of the core-excited or doubly excited states of the H_3 molecule predicted the existence of a resonant state within this region [4,5]. This particular state dissociates diabatically to the ion-pair channel

but only after crossing an entire Rydberg series of excited states. As pointed out in Ref. [4], both neutral and ionic product states are expected from this resonance state because of these crossings. In the work of Larsson *et al.* [2] only the neutral fragments were detected, but they believe, based on the earlier measurements [3], that the branching into the ion-pair channel is small, around 2% of the total DR cross section. In the calculations reported here we cannot distinguish between these two channels.

Resonant or direct DR can be considered to be a three step process. In the first step, the ion captures an incoming electron into a quasibound state of the neutral molecule which lies within the ionization continuum. Second, the excited, neutralized molecule begins to fragment, moving on the resonance surface. During this time the system can autoionize. The net effect of autoionization is to possibly transfer some of the incident electron energy to the internal degrees of freedom of the molecular ion, contributing to either the total elastic, or vibrationally or rotationally inelastic, scattering cross sections. At some point during the dissociation, the resonant state will fall below the continuum where it can no longer autoionize. Therefore the third step in DR is the final evolution to the asymptotic fragment states during which time the probability may be distributed among many electronic states via nonadiabatic transitions to other surfaces. Thus a complete calculation of DR requires (i) the determination of the resonant state surface and the excited electronic states to which it is coupled, (ii) evaluation of the autoionization width and the couplings between the excited surfaces, and (iii) the calculation of the coupled surface dynamics for the dissociation. Such a calculation combines electronic structure, electron-molecular ion scattering, and heavy particle dynamics on complex, coupled surfaces. For a triatomic system, this is beyond the state of the art, mainly due to the high dimensionality (number of degrees of freedom) and the number of electronic states involved. Therefore we have initially carried out a more modest study which incorporates the most important aspects of the dynamics in order to interpret these recent experimental results.

The DR cross section is given by

$$\sigma(E) = 8\pi^3/k_i^2 \sum_f |T_{fi}(E)|^2, \quad (1)$$

where $\hbar k_i$ is the momentum of the incident electron. In analogy to the time-dependent treatment of molecular photodissociation [6] we can evaluate the transition matrix element using

$$T_{fi}(E) = \lim_{t \rightarrow \infty} \langle \phi_f | \Psi_i(t) \rangle, \quad (2)$$

where ϕ_f is an asymptotic channel eigenfunction with energy E and $\Psi_i(t)$ is a wave packet which evolves on the resonance surface after the electron is captured. This wave packet satisfies the time-dependent Schrödinger equation

$$i\hbar(\partial/\partial t)\Psi_i(t) = H_{\text{res}}\Psi_i(t). \quad (3)$$

The potential in the resonance state Hamiltonian is a complex surface obtained from fixed-nuclei electron scattering calculations. The real part is the resonance position and the imaginary part, equal to half the resonance width, comes from the possibility of autoionization back to the ion and free electron. At nuclear geometries where the resonance state energy lies below the molecular ion ground state, the potential becomes real. The initial condition for Eq. (3) is given by $\Psi_i(t=0) = [\Gamma(\mathbf{R})/2\pi]^{1/2} \times \chi_i(\mathbf{R})$, where $\Gamma(\mathbf{R})$ is the autoionization width and $\chi_i(\mathbf{R})$ the initial vibrational wave function of the H_3^+ . Since we do the projections in Eq. (2) in the asymptotic region, the final state ϕ_f is simply a product of eigenstates of the separated fragments.

In the ground state H_3^+ is an equilateral triangle with bond lengths of $1.65a_0$ with electronic configuration $1a_1^2$. For purposes of simplicity we will discuss the electronic states in terms of their dominant configurations, but note that all results were obtained from multireference configuration interaction calculations [7-9]. The first excited orbital is the doubly degenerate $1e'$. As the symmetry is relaxed from the initial D_{3h} to C_{2v} by moving one of the nuclei to produce an isosceles geometry, the two components of $1e'$ become $2a_1$ and $1b_2$, meaning an orbital with a nodal plane either parallel with the in-plane molecular symmetry axis or perpendicular to it, respectively. As reported earlier [4] the configuration of the resonance state in this energy region is $1a_1^1 1e'^2$. The degeneracy of the excited orbital leads to four distinct states in C_{2v} , two of which are 2A_1 , $c_1 1a_1 2a_1^2 + c_2 1a_1 1b_2^2$, and two 2B_2 , $c_3 1a_1 2a_1 1b_2 + c_4 1a_1 2a_1 1b_2$, where the coefficients c_i depend on the nuclear geometry. Our calculations show that all four of these resonances contribute to the observed peak in the DR cross section.

The resonance energies and widths are obtained from electron- H_3^+ scattering calculations. Using the complex Kohn variational method [7] modified to include Coulomb scattering states [8] we carry out a series of elastic scattering calculations for fixed nuclear geometries, varying the incident electron energy. In C_{2v} symmetry we find two resonances in each calculation. We extract the

energy-dependent eigenphase sum which we fit by a sum of Breit-Wigner forms. In Fig. 1 we show a typical result for 2A_1 symmetry and the nuclei fixed at the equilibrium geometry of the H_3^+ ground state. Plotted are the calculated eigenphase sums along with our fit. We define the positions of the nuclei \mathbf{R} in terms of the usual scattering or Jacobi coordinates: r , the distance between two of the protons; R , the distance from the third proton to the center of mass of the first two; and θ , the angle between these two axes. In C_{2v} symmetry θ is 90° . From Fig. 1, we find the two resonance energies (widths) are 9.1 (0.64) and 10.3 (0.18) in eV at $r=1.65$ and $R=1.43a_0$. We repeated these calculations for a number (10-12) of nuclear geometries along two cuts on the C_{2v} surface, varying either R or r while holding the other fixed at its H_3^+ equilibrium value. We then fit the resonance surfaces and widths and tested our fit by performing additional calculations off these cuts and near the dissociation pathway. (See Ref. [9] for further details.) In Fig. 2 we show a cut through these surfaces along with the curve for the ion for r fixed at its equilibrium value, $1.65a_0$. All four resonances are strongly repulsive, leading to rapid dissociation following the capture step.

From these calculations we find the surprising result [9] that along the symmetric stretch *three* of these states are "crossing." For D_{3h} configurations, symmetry demands that $|c_1| = |c_2|$ and the two 2A_1 states have strong avoided crossings as can be seen in Fig. 2. The configuration with $c_1 = -c_2$ is lower in energy and becomes one of the degenerate components of an ${}^2E'$ state in D_{3h} . The second component is the lower energy 2B_2 state with $c_3 = -c_4$. This triple interaction between electronic states can be expected to be found also in alkali triatomics. Of course as the molecule is distorted so that all three bond lengths are different ($\theta \neq 90^\circ$), all three states

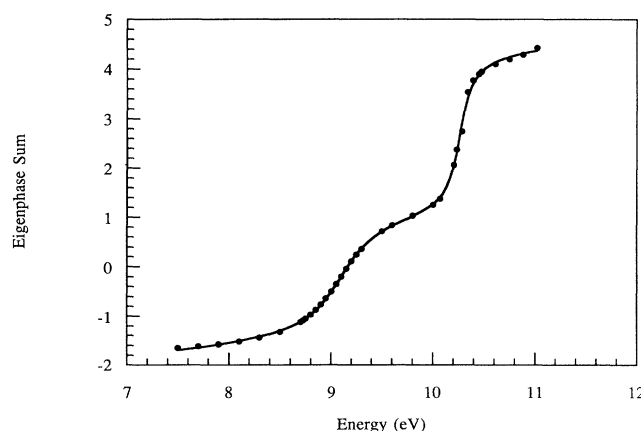


FIG. 1. Eigenphase sums for $e\text{-H}_3^+$ elastic scattering at the equilibrium geometry of the ion in 2A_1 symmetry. Solid circles are the calculated points and the line is the fit by a sum of two Breit-Wigner resonance line shapes. Rapid jumps by π in the eigenphase sum indicate resonances.

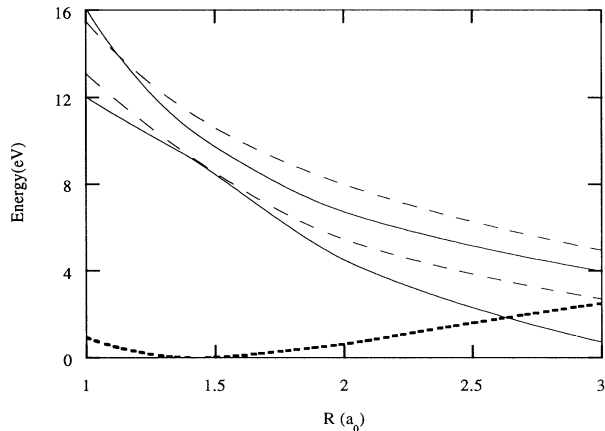


FIG. 2. Cuts through the H_3 resonant state surfaces as functions of R for fixed $r=1.65a_0$ and $\theta=90^\circ$. Shown are the 2A_1 (solid lines) and the 2B_2 (dashed lines) resonance states along with the 1A_1 ground state of the ion (heavy short-dashed line).

have the same symmetry, C_s . We performed a small number of calculations for these states for C_s geometries in the vicinity of the dissociation pathway and found the surface has a very small curvature in this dimension. Therefore we believe it is a reasonable approximation to ignore the small amount of spreading which takes place in this direction during the rapid dissociation in the two C_{2v} dimensions.

In these preliminary calculations we have also ignored the interaction between the different resonances. In a complete calculation the wave packet motion would occur on coupled surfaces. Since we are interested only in the total DR cross section and not in final state distributions in this work and because all surfaces are strongly repulsive, we do not believe this approximation will significantly affect our results. Also we find the wave packet moves quickly away from the symmetric stretch seam, so the effects of these couplings are minimized.

We propagate the wave packet [Eq. (3)] on the complex resonance surface until it has completely escaped from the autoionizing region using a finite difference grid representation for the wave packet and a Chebyshev expansion of the time evolution operator [10]. We then analyze the wave packet to obtain its amplitude as a function of total internal and fragmentation energy to calculate the survival probability and thus the DR cross section. In this system, once the wave packet reaches the region where autoionization no longer can occur, it undergoes a large number of avoided crossings with the Rydberg states of the molecule. Again, since we are not interested in the final state distributions, we ignore these crossings and have distorted the resonance surfaces in the asymptotic region to gradually become completely flat. Therefore we can examine its energy content of the surviving wave packet by simply projecting onto plane waves in the two-dimensional space. As expected, the faster

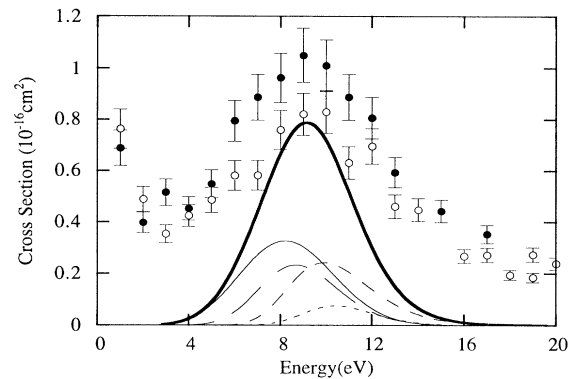


FIG. 3. Total (heavy solid line) and partial resonance DR cross sections as functions of the incident electron energy: 1^2A_1 (solid line), 1^2B_2 (long-dashed line), 2^2A_1 (medium-dashed line), and 2^2B_2 (short-dashed line). The open ($v_{rel} > 0$) and closed ($v_{rel} < 0$) symbols are the total cross sections of Larsson *et al.* (v_{rel} is the difference between the electron and ion velocities in the experiment; see Ref. [2].)

components have a higher survival probability because they spend less time subject to the imaginary part of the potential. We find by comparing the results with and without ionization that the system autoionizes up to 80% of the time, possibly leaving the molecular ion with a large amount of internal excitation, perhaps enough to cause dissociation. This means the capture cross section can be 5 times larger than the resulting DR cross section. Without considering the details of this transition back to the ion surface by, for example, using a boomerang model [11], we cannot predict the distribution of energy between the emitted electron and the vibrational modes of the molecule. However, our results indicate a strong probability for resonant enhanced vibrational excitation for electron impact energies in this regime.

In Fig. 3 we show the individual resonance contributions to the DR cross section along with their total as functions of the incident electron energy. All four resonances make significant contributions to the total. The position, magnitude, and the width of the calculated peak agree well with the observed feature, shown by the symbols in the figure with their reported 10% error bars [2]. We emphasize that the rise in the measured DR cross section as the energy decreases toward the threshold is due to an indirect mechanism not considered in this work. Although several approximations were necessary in order to make these calculations tractable, we believe none was so severe that the physical validity of the results has been compromised. It was very important to include both C_{2v} degrees of freedom in these calculations as the dissociation does not follow a single normal coordinate. The agreement with the experimental results indicates the use of storage rings [12] for electron-molecular ion scattering cross sections for well characterized (cold) initial states is very promising and will provide more rigorous tests of

theoretical studies. The agreement gives strong support for the expectation that the ion was in fact initially cold.

Finally, we note that there has been a long history of interest in the low energy (threshold) DR of H_3^+ with reported rates and cross sections differing by orders of magnitude. (See Ref. [2] for a recent list of relevant references.) In this paper we have found additional resonances not previously reported, but none which can directly affect DR near the threshold. All resonances we found have crossings with the ion surface which are well above the energy of the vibrational ground state. Therefore, there must be an efficient indirect channel involving the Rydberg states [4]. Experience has indicated that the indirect mechanism must lead to small cross sections. But this experience is mainly based on diatomic systems. The mechanism is to transfer electron kinetic energy through nonadiabatic coupling to vibrational motion. In a diatomic, this energy can be quite efficiently transferred back to the electron causing autoionization, and hence little DR. However, it may be the case that in a polyatomic, the vibrational excitation can be distributed in several modes so that the back transfer is substantially less efficient. Note at low incident energies all the energy transferred to vibrational motion must be recovered by the electron for autoionization to occur. If the distribution of energy in a system with several vibrational degrees of freedom can reduce the autoionization rate, predissociation of the Rydberg states can compete more successfully. Therefore indirect DR might be expected to be more efficient in polyatomic molecules. We are presently attempting to test this mechanism for this system.

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