Effects of Open Inelastic Channels in the Resonant Dissociative Recombination of HeH^+

A. E. Orel,[1] K. C. Kulander,[2] and T. N. Rescigno[2]

[1]*Department of Applied Science, University of California at Davis, Livermore, California 95616*

[2]*Physics and Space Technology Directorate, Lawrence Limvermore National Laboratory, Livermore, California 94550*

(Received 9 January 1995)

We show that *ab initio* theory provides a quantitative description of resonant dissociative recombination. Using a variational method for the electronic scattering problem and a wave packet treatment of the dissociation dynamics, we obtain excellent agreement with recent absolute cross sections for dissociative recombination of $^3HeH^+$ in the 10–30 eV region. The cross section contains significant contributions from several resonance states, some of which autoionize into electronically excited states. A proper multichannel treatment of the resonances is needed to achieve quantitative agreement with experiment.

PACS numbers: 34.80.Gs, 34.80.Ht

Molecular ions can be converted to neutral fragments by the process of dissociative recombination (DR). In direct DR [1], a free electron is resonantly captured by a molecular ion into an electronically excited state that dissociates, thereby converting the initial free-electron energy into translational and/or internal energy of the neutral fragments. The resonance may also re-emit an electron (autoionization), leaving the ion either in its original state or, if enough energy is available, in an excited electronic state. The branching ratio to either charged or neutral products is determined by the shape of the resonance electronic state(s) and its (their) R-dependent lifetime (or inverse width $1/\Gamma$) against autoionization. If the resonance curve is repulsive enough that the neutral fragments can separate before autoionization is complete, direct DR will be observed, generally enhancing the cross section at the resonance energy. Formal resonance theory [2] provides an elegant and potentially exact framework for describing this process and has been the basis for many semiempirical treatments of DR. In these treatments the required resonance parameters are varied to achieve a best fit to experimental data. However, with the development of increasingly accurate numerical methods for solving the fixed-nuclei electron-molecule scattering problem, *ab initio* theory can supply resonance parameters of sufficient accuracy to provide a reliable, nonempirical approach to the calculation of DR cross sections.

Current models of star evolution predict observable abundances of HeH^+ in the interstellar medium. However, a recent search of the bright planetary nebula NGC 7027 failed to detect it [3]. One possibility is that the formation rates for HeH^+ (radiative association of $He^+ + H$ and associative ionization of $He^* + H$) have been overestimated. Another possibility is that low-energy electrons can increase the destruction rate of HeH^+ through dissociative recombination. Not surprisingly, DR of HeH^+ has been the subject of considerable experimental and theoretical interest. The focus has been primarily on the low-energy region following the original observation [4] of an unexpectedly high recombination rate at thermal electron energies (10^{-8} cm^3/s at 300 K) even though there exists no suitable neutral curve that crosses the ionic ground state near its equilibrium position [5]. The behavior in this energy regime is still the subject of considerable uncertainty and controversy. Several mechanisms have been proposed to explain how large recombination rates can occur in the absence of curve crossings [6–8]. However, Youssif *et al.* [9] recently proposed that most of the observed low-energy DR can be attributed to the presence of metastables ($a^3\Sigma^+$) in the ion beam, although no credible theoretical calculation has been performed to support this claim. Their explanation appears to be at variance with the recent result of Sundström *et al.* [10] who observed no decrease in the DR rate when a large background (up to 30%) of oxygen, which rapidly quenches the triplet ions [9], was introduced into the ion source.

Less attention has been given to the prominent high-energy structure in the DR cross section between 10 and 40 eV. Sundström *et al.* [10] reported absolute measurements of the cross section for the ground vibrational state of $^3HeH^+$ in the region from 0.01 to 40 eV. In support of a mechanism proposed by Tanabe *et al.* [11], they were able to fit the high-energy peak in their using a simple model that consists of evaluating the bound-free Franck-Condon overlaps between the initial state and five repulsive doubly excited neutral states, then empirically adjusting their weights to achieve best agreement with experiment. An independent verification of the absolute cross section in this regime is desirable, since it would also validate the measured low-energy DR rate which is relevant to the astrophysical models. Here we report the results of calculations of direct DR of $^3HeH^+$ carried out entirely from first principles. In addition to accurately reproducing the measured resonance structures, our results demonstrate the critical importance of properly accounting for all energetically accessible excited states of the molecular ion.

0031-9007/95/74(24)/4807(4)$06.00

We begin by discussing the electronic states relevant to the present study. The ground state of HeH^+ has an equilibrium internuclear separation (R_e) of 0.77 Å, is bound by ~2.0 eV, and dissociates to ground-state helium plus a proton. Near R_e, HeH^+ is nominally described by a wave function of the form $1\sigma^2$. (Although we denote the various electronic states by their dominant configurations, our calculations were carried out with multiterm, configuration-interaction wave functions.) The first two excited states are the $(1\sigma 2\sigma)$, $a^3\Sigma^+$ and $(1\sigma 2\sigma)$, $A^1\Sigma^+$ states, which both dissociate to He^+ plus H and have vertical excitation energies of ~21.5 and ~26 eV, respectively. Note that these energies are substantially larger than the excitation energy at $R = \infty$ (10.98 eV), which means that vertical tansitions from the ground-state ion excite the repulsive walls of the upper states. The next manifold of excited ion states dissociate to excited helium plus a proton. The lowest of these states, $(1\sigma 3\sigma)$, $^3\Sigma^+$, correlates with He (2^3S) + H^+.

The excited states of the ion can serve as parents for series of doubly excited resonances of the neutral system which are formed by adding an electron in a Ryberg orbital to the excited ion core. The autoionization width of these states, and hence the probability of their formation, decreases as we move up a Rydberg manifold; the width of each state also goes to zero at large R where the atomic fragments become stable against autoionization. Since the resonance states, like their parent ion states, are all steeply repulsive in the Franck-Condon region of the ground-state ion, we expect that once excited the resonance states will be more likely to dissociate than to autoionize. For this reason, the direct DR cross section is dominated by those resonances that have substantial capture probabilities.

To track the dynamics of dissociation for each resonance state, we solve a time-dependent Schrödinger equation for a wave packet $\Psi_i(t)$ that sees the complex, one-dimensional potential $V(R) = E_{\rm res}(R) - i\Gamma(R)/2$ [12]. The real part of the potential is the R-dependent resonance energy and $\Gamma(R)$ is its *total* width, which is responsible for any loss of flux to autoionization that occurs as the excited neutral molecule dissociates. The propagation continues until the wave packet is in the region where the autoionization has ceased and the survival probability for the neutral fragments can be determined. The DR cross section corresponding to a single resonance is given by [13] $\sigma_i = 4\pi^2/E|P_i(E)|^2$, where the transition matrix element P is given by $P_i(E) = \lim_{t\to\infty}\langle\phi \mid \Psi_i\rangle$ and ϕ is an energy normalized, asymptotic scattering wave function for the separated atoms. The total DR cross section is obtained by summing the contributions from the individual resonances. We ignored any nonadiabatic couplings between the dissociating resonance states that might lead to a small redistribution among final channels. This approximation should not significantly alter the magnitude of the total DR cross section.

The initial condition for solving the time-dependent Schrödinger equation is given by

$$\Psi_i(t = 0) = \frac{|\gamma_i(R)|}{\sqrt{2\pi}}\,\chi_i(R), \tag{1}$$

where $\chi_i(R)$ is the initial vibrational wave function of the ion and $|\gamma_i(R)|^2$ is the *partial* resonance width with respect to decay into the initial electronic state. When there is only one electronic ion channel into which the resonance can decay, which is typically the case with low-energy DR, $|\gamma_i(R)|^2 = \Gamma(R)$. However, as we will see below, some of the resonances we deal with can decay into more than one ion channel, so for these states one needs the partial widths to evaluate the proper entry amplitudes defined by Eq. (1).

The electronic resonance parameters required to determine the DR cross sections were obtained by analyzing the S matrices obtained from electron-HeH^+ scattering calculations carried out at a series of fixed nuclear geometries. These calculations were performed using the complex Kohn variational method [14] with a trial function that explicitly included the $X^1\Sigma^+$, $a^3\Sigma^+$, and $A^1\Sigma^+$ target states. These are the only open electronic channels over most of the energy range we considered. Closed-channel and polarization effects were included by partitioning the $(N + 1)$-electron space into P- and Q-space parts and constructing an optical potential from the terms included in Q space (see Ref. [14] for further details). The resonance positions and autoionization widths were obtained from the eigenphase sum, which, for an isolated resonance, behaves like the phase shift in a potential scattering problem (increasing through π for each isolated narrow resonance) and which can be fit to a background plus a resonant (Breit-Wigner) term [15]. For large values of R where the splitting between the $a^3\Sigma^+$ and $A^1\Sigma^+$ states becomes small, the resonances begin to overlap and the eigenphase sum had to be fit using a sum of Breit-Wigner terms. For example, Fig. 1 shows the $^2\Pi$ eigenphase sum for $R = 4.0a_0$ in the vicinity of the $(1\sigma 2\sigma)^3 1\pi$ and $(1\sigma 2\sigma)^1 1\pi$ resonances, whose positions we determined to be 0.2733 and 0.2761 hartree, respectively, and whose widths are 0.000 59 and 0.000 16 hartree. We note that our results agree well with the earlier, but more limited, calculations of the resonance widths and positions reported by Sarpal, Tennyson, and Morgan [6] and the ion curves of Green *et al.* [16].

Several of these resonances can decay into more than one continuum and, consequently, we needed to develop a procedure to determine their partial widths. Since one cannot get information about the partial widths from a consideration of the eigenphase sum alone, we had to extend our analysis to the individual T-matrix elements. Near an isolated resonance, the T matrix can be partitioned into a slowly varying background term plus a resonance contribution that can be symmetrically

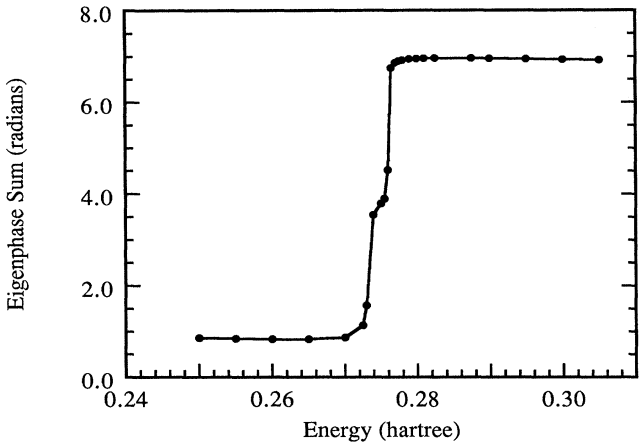

FIG. 1. Eigenphase sum at $R = 4.0a_0$ for $e^- + HeH^+$ in $^2\Pi$ symmetry in the vicinity of two overlapping $[(1\sigma 2\sigma)^3 1\pi$ and $(1\sigma 2\sigma)^1 1\pi]$ resonances.

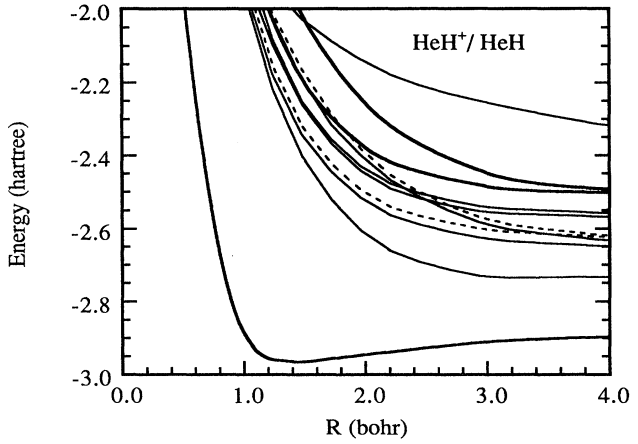

FIG. 2. Potential energy curves of HeH^+ and HeH relevant to the present study. The $X^1\Sigma^+$, $a^3\Sigma^+$, and $A^1\Sigma^+$ ion curves are the heavy solid curves. The thin solid curves are the $^2\Sigma$ neutral resonance states and the dashed curves are the $^2\Pi$ states.

factorized as [17,18]

$$(T^{\Omega\Omega'}_{\ell m \ell' m'})_{\rm res} = -\frac{\gamma^{\Omega}_{\ell m}\gamma^{\Omega'}_{\ell' m'}}{(E - E_{\rm res} + i\Gamma/2)}, \qquad (2)$$

where Ω refers to the electronic states of the target ion and ℓ, m label the angular momentum quantum numbers of the electron. Equation (2) shows that it is necessary to analyze only the diagonal elements of $\mathbf{T}$ to obtaine the partial widths. Having first obtained $E_{\rm res}$ and Γ from the eigenphase sum, we determined the individual $\gamma^{\Omega}_{\ell m}$ by using Eq. (2) to fit the diagonal T-matrix elements, with $E_{\rm res}$ and Γ fixed. The physical partial width $|\gamma_i(R)|^2$ is obtained by summing the partial widths associated with a specific electronic channel over angular momentum quantum numbers $|\gamma_i|^2 = \sum_{\ell m} |\gamma^{\Omega_i}_{\ell m}|^2$. The partial widths so determined were found to sum to the total autoionization width $\Gamma(R)$ to within a few percent, which we take as a measure of the accuracy with which partial widths can be extracted from the computed T-matrix elements.

Eight resonance states were included in calculating the DR cross sections. These were four $^2\Sigma$ and one $^2\Pi$ states $[(1\sigma 2\sigma^2)$, $(1\sigma 2\sigma)^3 3\sigma$, $(1\sigma 2\sigma)^3 4\sigma$, $(1\sigma 2\sigma)^3 5\sigma$, and $(1\sigma 2\sigma)^3 1\pi]$, whose parent ion state is $a^3\Sigma^+$, as well as the two lowest states $[(1\sigma 2\sigma)^1 3\sigma$ and $(1\sigma 2\sigma)^1 1\pi]$ associated with the $A^1\Sigma^+$ ion state. Higher resonance states in these series were found to be too narrow to contribute significantly to the DR cross section. We also included the $(1\sigma 3\sigma^2)$ state, which is the lowest state in a series that dissociates to $He(2^3S)$, plus an excited hydrogen atom. The potential energy curves of these states, and their parent ion states, are shown in Fig. 2. The $(1\sigma 2\sigma)^1 3\sigma$ and $(1\sigma 2\sigma)^1 1\pi$ states can decay into either the $X^1\Sigma^+$ or the $a^3\Sigma^+$ ion states for values of $R < 1.8a_0$, while the $(1\sigma 3\sigma^2)$ state has two decay channels for $R < 1.5a_0$ and three decay channels for large R.

In Fig. 3 we show the calculated total DR cross section, as well as the individual resonance contributions. We also show the experimental results recently measured by Sundström *et al.* [10] with their reported 10% error bars. The relative contributions from the various resonance states are quite different from those inferred by Sundström *et al.* [10] in fitting their data empirically. For example, while the two lowest $^2\Sigma$ resonances are dominant contributors to the main peak, we also find significant contributions from the $(1\sigma 2\sigma)^3 1\pi$ and $(1\sigma 2\sigma)^1 1\pi$ states, which were ignored previously. The experimental data also show a high-energy shoulder near 26 eV which correlates well with our $1\sigma 3\sigma^2$ resonance. However, there are clearly other resonances, presumably correlated with

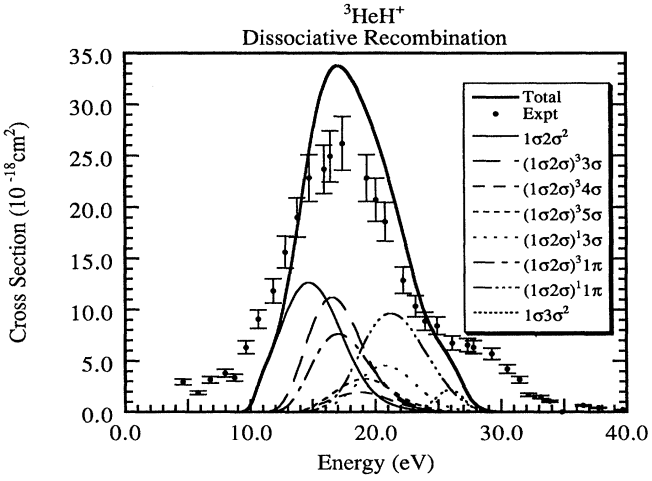

FIG. 3. Total (heavy solid curve) and partial DR cross sections for ground-state $^3HeH^+$ as a function of incident electron energy. The experimental points are those of Sundström *et al.* (Ref. [10]).

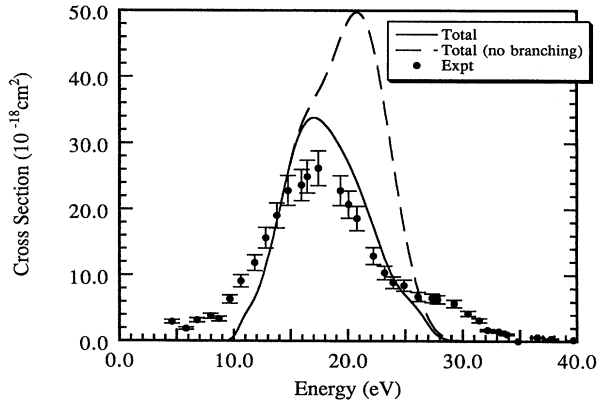

FIG. 4. Sensitivity of computed DR cross section to the neglect of partial widths to excited ion channels. The dashed curve is obtained by using the total widths to compute the entry amplitudes.

even more highly excited states of the ion, that are needed to properly describe this energy region.

Finally, we emphasize the importance of properly accounting for the existence of additional open channels in high-energy DR. Analysis of the eigenphase sum yields a total autoionization width that, in order to obtain the correct entry amplitude, must be scaled by an R-dependent branching ratio if the resonance energy lies above any excited states of the ion. This alters the shape and the overall norm of the wave packet that propagates on the complex resonance potential. To illustrate the significance of this point, we carried out an additional set of calculations where the real *partial* widths were replaced by the *total* widths in the entry amplitudes [the prefactor in Eq. (3)] for the $(1\sigma 2\sigma)^1 3\sigma$ and $(1\sigma 2\sigma)^1 1\pi$ states. As shown in Fig. 4, the resulting DR cross section is clearly distorted and overestimated. This effect has not been encountered in most DR studies to date, as the focus has generally been on lower energies where no excited channels are accessible. When excited channels become open, the analysis presented here is required.

We obtained quantitative agreement with measurements of Sundström *et al.* [10] with no adjustment of the resonance parameters. Our resonance peak agrees in both shape and magnitude with the storage ring measurements but is about an order of magnitude smaller than the merged beam results of Youssif *et al.* [9]. The latter experiments were done with $^4HeH^+$. To see if the mass effect is significant, we repeated the calculations for the heavier ion and found the DR cross sections *decreased* by ~20% (with the heavier ion, the fragment velocities are smaller and the branching to autoionization is larger). We restricted our calculations to the excitation from the ground vibrational state since the storage time in the ring is reported to be long compared to the vibrational relaxation time [10]. The only approximations we made were to consider only the three lowest excited states of HeH^+, which is adequate for scattering energies below 30 eV, and to limit the resonance states to those with significant capture widths. This is evidently sufficient to describe the DR cross section in the 10–25 eV energy range, but to faithfully reproduce the high-energy structure near 30 eV, one would have to include higher parent ion states.

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48. A. E. Orel acknowledges support from the National Science Foundation, Grant No. PHY-93-22067. Computer time was supplied by the National Energy Research Supercomputer Center.

[1] D. R. Bates and A. Dalgarno, in *Atomic and Molecular Processes,* edited by D. R. Bates (Academic, New York, 1962); J. N. Bardsley, J. Phys. B **1**, 365 (1968).
[2] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).
[3] J. M. moorhead, *et al.,* Astrophys. J. **326**, 899 (1988).
[4] F. B. Youssif and J. B. A. Mitchell, Phys. Rev. A **40**, 4318 (1989).
[5] H. H. Michels, in *Dissociative Recombination: Theory, Experiment and Applications,* edited by J. B. A. Mitchell and S. L. Guberman (World Scientific, Singapore, 1989), p. 97.
[6] B. K. Sarpal, J. Tennyson, and L. A. Morgan, in *dissociative Recombination: Theory, Experiment and Applications,* edited by B. R. Rowe, J. B. A. Mitchell, and A. Canosa (Plenum, New York, 1993), p. 163 .
[7] S. L. Guberman, Phys. Rev. A **49**, R4277 (1994).
[8] D. R. Bates, Comments At. Mol. Phys. **29**, 53 (1993).
[9] F. B. Youssif *et al.,* Phys. Rev. A **49**, 4610 (1994).
[10] G. Sundström *et al.,* Phys. Rev. A **50**, R2806 (1993).
[11] T. Tanabe *et al.,* Phys. Rev. Lett. **70**, 422 (1993).
[12] A. E. Orel and K. C. Kulander, Phys. Rev. Lett. **71**, 4315 (1993).
[13] C. W. McCurdy and J. L. Turner, J. Chem. Phys. **78**, 6773 (1983).
[14] A. E. Orel, T. N. Rescigno, and B. H. Lengsfield III, Phys. Rev. A **44**, 4328 (1991).
[15] A. U. Hazi, Phys. Rev. A **19**, 920 (1979).
[16] T. A. Green *et al.,* J. Chem. Phys. **61**, 5186 (1974); **69**, 101 (1978).
[17] W. Brenig and R. Haag, Fortschr. Phys. **7**, 183 (1959).
[18] J. Macek, Phys. Rev. A **2**, 1101 (1970).