Ab initio study of resonant dissociative recombination of He$_2^+$

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Abstract. Resonant dissociative recombination of the He$_2^+$ molecular ion is an important process in the ionosphere as well as in laboratory plasmas. Recently, rate coefficients have been measured for the dissociative recombination of He$_2^+$ using the ion storage ring TSR in Heidelberg, Germany. Previously, calculations have been reported for the cross section in the low energy region. We will report results in the 0 to 15 eV energy region, where the cross section is dominated by a series of resonances converging to the first excited state of the molecular ion. We will also discuss the resonances converging to the next series of excited states. The resonance parameters for this system are obtained from electron scattering calculations using the Complex Kohn variational method. These resonance parameters are used as input to a time-dependent wave packet calculation of the dissociation dynamics. The calculated cross sections and rates will be reported and compared to available experiment.

1. Introduction

In the study of dissociative recombination (DR), the He$_2^+$ molecular ion holds a special place. Bates [1] suggested that this process, which had been previously proposed for the ionosphere, was important in laboratory plasmas as well. This could explain the fast recombination rates observed in a helium discharge. However, He$_2^+$ was later recognized [2] as one of the few molecular ions with a small recombination rate (i.e., much smaller than 10$^{-7}$ cm$^3$s$^{-1}$ at 300 K). Because of the interest in helium discharges and helium afterglows, this molecule has been studied many times both theoretically and experimentally [3, 4]. Due to the complexity of this process in such media, only controversial results could be obtained. Not only is it difficult to form He$_2$ molecules, but it has also been shown [4] that due to various collisional processes in plasma afterglows most of the He$_2^+$ ions relax rapidly to their ground vibrational level. This vibrational level has a very low probability of recombination due to the lack of favorable routes for DR near the bottom of the He$_2^+$ ground-state potential well [5]. This low energy region has been previously studied [5]. It has been suggested that ion storage rings might provide a promising alternative to the plasma afterglow measurements. Experiments have been done on the storage ring ASTRID in Denmark [6]. More recently, rate coefficients have been measured for dissociative recombination of He$_2^+$ using the ion storage ring TSR in Heidelberg, Germany [7].

The present work focuses on the determination and explanation of the total dissociative recombination cross section in the energy range of 0 to 30 eV. In the current calculations, we will be using the mixed isotope, $^3$He$^4$He$^+$, which is what has been used in recent experiments [7]. We will give the total cross section for the incident electron energy region between 0 and 15 eV, and discuss the peaks found in the cross section at higher energies.
2. Theory

2.1. Potential energy curves

For small internuclear separations (<1.5 a.u.), the resonance parameters, which include the resonance energy and the autoionization width, can be obtained from electron scattering calculations. In this set of calculations, the Complex Kohn variational method is used as described in [8]. As the internuclear separation is increased, the resonance state becomes bound and is determined through the use of standard quantum chemistry techniques. To obtain the target state, a set of molecular orbitals were generated from a self-consistent-field calculation generated from the basis described in [3]. To obtain a more compact representation for the scattering, a configuration interaction calculation on the ion was carried out consisting of all singles and doubles from an active space of two orbitals, $1\sigma_u$ and $1\sigma_g$. To better represent the resonance states of both $\Sigma$ and $\Pi$ symmetries, the natural orbitals obtained were then averaged over the four lowest roots, $2\Sigma_u$, $2\Sigma_g$, and the doubly degenerate $2\Pi_u$. The target basis then consisted of 8 natural orbitals with the highest occupation numbers, two $\sigma_u$, two $\sigma_g$, and the degenerate $\pi_u$ and $\pi_g$ orbitals. The target wave functions used in the scattering calculation were obtained by a full CI in the smaller natural orbital space of eight orbitals. The target basis was augmented with five Gaussian functions, one diffuse s (exponent 0.001), three diffuse p’s (exponents 0.05, 0.01, 0.005) and one diffuse d (exponent 0.5). The variational calculations included basis functions up to $l = |m| = 4$. Because the range of scattering energies desired lies above the first excited state of the ion, two channels were treated in the $P$-space, the ground $2\Sigma_u$ and $2\Sigma_g$, however, only one channel may be open.

The calculations were performed in all symmetries, $1^3\Sigma_g$, $1^3\Sigma_u$, $1^3\Pi_g$, $1^3\Pi_u$, $1^3\Delta_g$ and $1^3\Delta_u$, and over a range of energies around each expected resonance. In each case, a cross section and an eigenphase sum was obtained from the scattering calculation, which was then fit to the Breit-Wigner form to obtain the resonance energy and autoionization width. A total of 30 resonances were obtained in the region between 0 and 10 eV. The resonances in this system are Feshbach resonances corresponding to a Rydberg series converging to excited states of the ion. In the 0 to 10 eV region, the Rydberg series is converging to the first excited state of the ion, $2\Sigma_g$.

In the energy range 10 to 30 eV, where fewer resonances were found, the Rydberg series are converging to higher excited states of the ion with various configurations.

The calculated resonance states were then used as an input into a wave packet treatment of the dissociation dynamics.

2.2. Dissociation dynamics

The dissociation dynamics are determined by solving the time dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi = \mathcal{H} \Psi$$

(1)

where $\Psi$ is a column vector representing the amplitude on each of the resonance states. Using wave packet methods [9], the initial wave packet at $t = 0$ is given by

$$\Psi_i(R, t = 0) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{\nu=0}(R),$$

(2)

where $\chi_{\nu=0}(R)$ is the initial vibrational wave function of the molecule and $i$ labels the various electronic states. The vibrational wave function for the $\nu = 0$ vibrational level of the $2\Sigma_u$ ground state is calculated using a finite difference method to solve the time-independent Schrödinger equation for the $2\Sigma_u$ ground state potential. The Hamiltonian for this system becomes

$$\mathcal{H}_i = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + V_{res}(R)$$

(3)
where the wave packets are propagated on local complex potential curves given by

$$V_{\text{res}}(R) = V_0(R) - i\frac{\Gamma_i(R)}{2}$$

(4)

where \(V_0(R)\) is the real part of the resonance potential curve, and \(\Gamma_i(R)\) is again the autoionization width.

After the wave packets have been propagated out to the asymptotic region, the partial cross sections are calculated by projecting the final wave functions onto energy normalized eigenfunctions

$$\phi_k(R) = \left(\frac{\mu}{2\pi\hbar^2}\right)^{1/2} e^{ikR}$$

(5)

where the wave number \(k\) is given by the kinetic energy of the dissociating fragments. The DR cross section corresponding to a single resonance, \(i\), for different collision energies is given by

$$\sigma_i(E) = \frac{2\pi^3}{E} |\langle \phi_i(R) | \psi_i(R, t_f) \rangle|^2.$$  

(6)

The total cross section is then determined by summing over the partial cross sections.

### 3. Results

We now present the results from the previously described calculations. Figure 1 shows the resonance potential energy curves for the various symmetries resulting from the Complex Kohn and quantum chemistry calculations. Only the triplet states are shown in the figures because the singlet states lie similar in energy and shape to the triplet states. In each of the symmetries, the solid curves represent the ground, \(2\Sigma_u\), and first excited state, \(2\Sigma_g\), which the resonances are converging to. Each of the resonance curves included in this calculation are dissociating to one of the He + He(3S), He + He(1S), He + He(3P), He + He(1P), He + He(3D) and He + He(1D) limits. Upon examination of the potential energy curves, one would expect that the resulting cross section should have a peak around 7 eV.

Using the calculated potential energy curves, the dynamics are determined and a cross section is obtained. Figure 2 shows the resulting total dissociative recombination cross section for the energy region 0 to 15 eV, obtained by summing over each of the partial cross sections. All the resonances contributing to this cross section are those which are converging to the first excited state, which lies about 10 eV higher in energy at equilibrium internuclear separation. Upon inspection of the partial cross sections, it is clear that the total cross section is dominated by only some of the symmetries. \(3\Sigma_g\), \(1\Sigma_u\), \(3\Pi_u\) and \(3\Pi_d\) have the largest contributions to the cross section, while \(1\Sigma_g\), \(1\Pi_g\), \(3\Pi_g\), \(1\Delta_g\) and \(3\Delta_g\) contribute much less. For the majority of the states, as the energy above the ground state increases, the contribution of that states decreases. However, we have not yet been able to observe this behavior in the \(1\Pi_g\), \(3\Pi_u\) and \(1\Sigma_g\) states. Therefore, because there is an infinite number of these resonance states converging to the first excited state of the ion, the inclusion of more states may increase the magnitude of the total cross section. Figure 3 shows the rate coefficient for this cross section compared to the available experiment [7]. The magnitude of the calculated cross section differs from the experiment by a factor of 2.8. However, the peak position and shape are in good agreement.

Scattering calculations also show bound resonance states converging to higher excited states of the ion. Preliminary results indicate the presence of one or more steeply repulsive resonance states which cross the bound resonance states. Coupling between these states would lead to dissociation, and therefore cause peaks in the total cross section between 18 and 35 eV.
Figure 1. The potential energy curves for the system. In each case, the two solid curves represent the $\text{He}_2^+$ ground state, $^2\Sigma_u$, and the first excited state, $^2\Sigma_g$, respectively. The dotted curves represent the various neutral resonance states included in the calculation. Note that only the triplet states are shown in each of the symmetries.

4. Conclusions
We have calculated the dissociative recombination cross section for $\text{He}_2^+$ in the energy region of 0 to 15 eV. For small internuclear separations, the potential energy curves and autoionization widths were obtained by using the Complex Kohn variational method. For regions of the potential energy curves bound with respect to autoionization, standard quantum chemistry techniques were used. The dissociation dynamics were calculated by solving the time-dependent Schrödinger equation. These calculations produce a total cross section which is in agreement with experiment with respect to position and shape, however, lacks the experimental magnitude. The contribution of more resonance states would increase the magnitude of the cross section by a small amount, but would probably not increase it enough to match the experimental results.
Figure 2. The resulting total dissociative recombination cross section for the energy region 0 to 15 eV.

Figure 3. The resulting total dissociative recombination rate coefficient compared to available experiment.

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