Ab initio study of the dissociative recombination of Ne$_2^+$

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Abstract. We report extensive calculations of energy positions and autoionization widths for the doubly excited states of Ne$_2^+$ between the first and second ionization thresholds obtained from electron scattering calculations using the complex Kohn variational method. The dynamics of the dissociative recombination process was investigated using multichannel quantum defect theory. For these preliminary calculations, only the direct mechanism of the dissociative recombination reaction was studied and only the $^1\Sigma^+_g$ dissociative states, which lie closest in energy to the ion at its internuclear separation were included. These states should dominate the low-energy dissociative recombination.

1. Introduction

The molecular ion Ne$_2^+$ plays an important role in gaseous lasers, plasma processing, neon lamps and plasma displays. It has been predicted to have a very fast dissociative recombination rate, similar to other noble-gas diatomic molecular ions [1] with the exception of He$_2^+$ [2]. An afterglow measurement has confirmed this prediction and the fact that the rate for dissociative recombination of this ion decreases as $T^{-3/2}$ contrary to the $T^{-1/2}$ law generally assumed for atmospheric and interstellar molecular ions [3]. However, no calculation of the cross section has been reported. In order to understand the nature of the DR process in this system, we have begun a theoretical study with a Multi-Channel Quantum Defect treatment of the dissociation dynamics using resonance energies and autoionization widths determined from electron-scattering calculations from the molecular ion using the Complex Kohn Variational method [5]. Our preliminary results will be reported here and compared to the available experiment.

2. Calculations of molecular data

The ground state configuration of the ion is

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 1\pi_g^4 3\sigma_u^2 3\sigma_g,$$

corresponding to an overall $^2\Sigma_u^+$ symmetry. The first excited state, $^2\Sigma_u^+$, is

$$[\text{core}] 3\sigma_g^2 3\pi_u^2.$$

These two states go to the same asymptotic limit for large internuclear separation. We carried out an SCF (self consistent field) calculation on the ion. These orbitals were then used in a multi-reference CI (configuration interaction) calculation, where the lowest eight orbitals were frozen, and all single and double excitations were performed from a reference space generated by a full CI for three electrons in
the \(\sigma_g, \sigma_u\) occupied orbitals and the two lowest unoccupied orbitals, \(\pi_{ux}\) and \(\pi_{uy}\). This was necessary to generate a good description of the higher lying \(\Pi\) states and virtual \(\pi\) orbitals. In order to produce a balanced treatment we took natural orbitals from averaging the density matrices for the lowest four states of the ion, \(^2\Sigma_u, ^2\Sigma_g, \) and \(^2\Pi_u\). Four natural orbitals (4\(\sigma_g, 4\sigma_u, 2\pi_{ux}, 2\pi_{uy}\)) were included as well as the occupied orbitals. The basis set was expanded to include additional diffuse orbitals. The eight lowest orbitals were frozen and the target states were determined from a full CI in the natural orbital space (of six orbitals). The resulting ion curves are shown in figure 1. Our calculations are in good agreement with the potential energy curves of Ne\(^+\) ion recently computed by Naumkin and Wales [4].

We carried out electron scattering calculations for low-energy electrons from the ion using the Complex Kohn Variational method. The method has been described earlier in the volume (see the article by Orel) and we will only highlight the specifics for this calculation.

The trial wave function for the \((N+1)\)-electron system is expanded as

\[
\Psi_{I_o} = \sum A_i \Phi_i(r_1, r_N) F_{I_o} (r_{N+1}) + \sum_\mu d^{I_o}_\mu \Theta_\mu (r_1, r_{N+1}),
\]  

(1)

where the first sum (\(P\)-space) usually runs over open electronic \(N\)-electron target states \(\Phi_i\). A antisymmetrizes the coordinates of the incident electron with those of the target electrons. The second sum (\(Q\)-space) contains \(\Theta_\mu\) which are square-integrable \((N+1)\)-electron configuration state functions (CSFs). The \((N+1)\)-electron CSFs describe short-range correlations and the effects of closed channels, and contain the information about the resonance portion of the scattering wave function. In the case of Ne\(^+\), since the resonances are converging to the excited states of the ion, and because the two ion curves go to the same asymptotic limit, it was important to treat both channels equivalently. Therefore the calculation included the first excited state of the ion in the \(P\)-space sum. For low scattering energies this is a closed channel. Note that as the internuclear separation is increased (see figure 1), the channel becomes open at much lower electron scattering energies.

This also changes the \(Q\)-space. Two classes of terms were included in the correlation part of the wave function. The first class is the set of all \((N+1)\)-electron CSFs that can be formed from the active space of target orbitals. These are generally referred to as “penetration terms” [5], which relax any orthogonality restraints. However, in addition to the penetration terms, we included a second class of “CI relaxation terms” [5], which are the complement \((1-P)\) of the \(P\)-space portion of the wave function.
This complement, combined with the penetration terms, constitute the correlation part of the trial wave function. These CI relaxation terms included the resonances which are a Rydberg series converging to the first excited state of the ion.

Addition of one electron to the $^2\Sigma_u^+$ system yields both singlet and triplet spin couplings and all symmetries, $\Sigma_{g,u}$, $\Pi_{g,u}$ and $\Delta_{g,u}$. We performed calculations for singlet and triplet spin couplings in all symmetries at the equilibrium internuclear separation. Below the threshold for the first excited state, resonances occurred in the $\Sigma$ and $\Pi$ symmetries, but not in $\Delta$. Therefore calculations were performed over a range of internuclear distances for only the $^1\Sigma_{g,u}^+$ and $^1\Sigma_{g,u}^+$ symmetries. The resonance parameters were then extracted by fitting the eigenphase sums to a Breit-Wigner form. It was found that there were only small differences in the resonance energies and autoionization widths between singlet and triplet spin couplings.

The resonance curves compared to the ion ground state and the corresponding autoionization widths are shown in figures 2 and 3 for the singlet $\Sigma$ and for the singlet $\Pi$ symmetries, respectively. In almost all symmetries, the largest autoionization width corresponds to the lowest excited state. We also noticed that the singlet state widths are slightly smaller than those of the corresponding triplet states. As can be seen from the figures, scattering in $^2\Sigma_{g,u}^+$ symmetry yields a resonance that lies only about 1eV above the ground state of the ion. The interactions of the lowest states pertaining to this symmetry with the ionization continuum, represented in the figures by the autoionization widths, are also stronger than that of the other symmetries.

3. Dynamics

The dissociation dynamics was calculated by using the multichannel quantum defect theory (MQDT) [6]. In these preliminary calculations with a second order $K$-matrix [9], we did not include the Rydberg bound states responsible for the “indirect” DR process. Only the lowest $^1\Sigma_{g,u}^+$ resonances, which should dominate the low-energy recombination cross section with a strong direct contribution, were included in the calculation.

In contrast to the case of dissociative attachment [8], previous studies of DR [7] have shown that the local model, where the coupling is a function only of internuclear separation, well-describes the DR process. This is due to the strong Coulomb field which dominates the interaction of the electron near the ion core and allows the additional dependence of the coupling on the incident energy of the electron to be ignored.

The absolute cross sections of the direct DR of the $v = 0$ and $v = 1$ initial states of the ion are
displayed in figure 4. The drops observed in the direct cross section are due to the opening of new ionization channels. The absolute rate coefficient obtained for the initial vibrational state $v = 0$ at 300 K is $1.18 \times 10^{-7} \text{cm}^3\text{s}^{-1}$. This value is lower by a factor of 1.5 than the experimental value of Chang and coworkers [3]. For a better comparison, we plan to include all resonant states obtained in various symmetries and the Rydberg states, responsible for the temporary electron capture and the indirect DR process. It is also important to note that the initial vibrational level of the ion is not well-defined in the above mentioned experiments. The rate coefficients measured may thus be an average over numerous initial vibrational levels. As shown in figure 4 the cross section for the $v = 1$ initial vibrational state is almost twice that for the ground vibrational state. The more excited vibrational states could recombine with higher rate coefficients.

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\[ \text{cross section (cm}^2\text{)} \]

\[ \text{Collision energy (eV)} \]
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