NeH$^+$ dissociative recombination

A I Florescu$^1$ and A E Orel$^2$

1 Laboratoire PALMS (UMR CNRS 6627), Bât. 11B, University of Rennes 1, 35042 Rennes Cedex, France
2 Department of Applied Science, University of California, Davis, Davis CA 95616, USA

Abstract. The rate coefficient for the NeH$^+$ dissociative recombination (DR) with electrons was recently measured at the ASTRID storage ring in Denmark. The rate coefficient, as a function of the electron energy, is non-negligible at near-zero energy and displays two broad peaks between 10 and 30 eV. Both peaks are due to DR via Rydberg states converging to different dissociation limits of the NeH$^+$ ion. The first one is due to the capture of the incoming electron by doubly excited Rydberg states dissociating in Ne($1s^22s^22p^53s$) + H($n \geq 2, s, p$). This series of Rydberg states converges to the core-excited ion state dissociating to Ne$^+(3s) + H^+$. The second peak is due to the electron capture by Rydberg states dissociating to Ne($1s^22s^22p^5$) + H(1s). This series converges to the second ionization limit Ne$^+(1s) + H(1s)$. We will report resonances found in the 10–30 eV energy range by electron scattering calculations using the Complex Kohn Variational method. The resonances, electronic couplings between resonances and the autoionization widths will be used in the time-dependent wave packet calculation describing the dissociation dynamics. The calculated cross sections and dissociation rates will be compared to the experimental ones measured by Mitchell et al.

1. Introduction

The dissociative recombination (DR) of the rare gas hydride ions is very interesting both from a fundamental and from an applied point of view. HeH$^+$ and NeH$^+$ do not have curve crossings [1, 3] between the ion ground state and a repulsive neutral state that would lead to a strong direct recombination process (see figure 1). While it was originally believed that HeH$^+$ would exhibit a very small recombination rate [4], experimental studies using the merged beams method both in a single pass [5, 6] and multi-pass mode [7,8] have revealed that in fact at low collision energies the measured recombination cross section is quite large and has a highly resonant structure. This observation has received support from theoretical studies [9, 12]. In addition to low energy cross sections, HeH+ also exhibits a high energy peak (centered at 20 eV) that is well reproduced by theoretical calculations [13, 14].

Recently, the cross section for the DR of NeH$^+$ was measured at the heavy-ion storage ring ASTRID by Mitchell et al. [15]. From an applied point of view, the interest of this process resides in its role in the plasma chemistry of future thermonuclear reactor divertors, as it is explained in [15].

We shall present here the first theoretical evaluation of the DR cross section in the electron energy region of 5–25 eV, considering the first three doubly excited states of NeH as dissociative states. Details of the calculation are presented in the next section.

In the last section, we present a comparison between our preliminary theoretical calculations and the experimental data and discuss these results.
2. Theoretical evaluation of the DR cross section

In order to understand the nature of the DR process in this system, we have begun a theoretical study with a wave packet 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. Our preliminary results will be reported here.

Detailed descriptions of the Complex Kohn method have been given in previous publications (see, for example, [16, 17]), so only a brief outline will be given below. The method uses a stationary principle for the $T$-matrix:

$$T_{\text{stat}} = T_{\text{trial}} - 2 \int \Psi(H - E)\Psi.$$  \hspace{1cm} (1)

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

$$\Psi = A\Phi_0(\vec{r}_1 \ldots \vec{r}_N)F(\vec{r}_{N+1}) + \sum_{\mu} d_{\mu}\Theta_{\mu}(\vec{r}_1 \ldots \vec{r}_{N+1})$$  \hspace{1cm} (2)

where $A\Phi_0(\vec{r}_1 \ldots \vec{r}_N)F(\vec{r}_{N+1})$ represents the antisymmetrized product of $\Phi_0$, the initial target wave-function of the ion and the scattered wave function $F(\vec{r}_{N+1})$ ($P$-space) and the 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. The scattering function, $F(\vec{r}_{N+1})$, is further expanded in a combined basis of Gaussian $\phi_i$ and continuum (regular $f_i$ and outgoing $g_i^+$ Coulomb functions) basis functions:

$$F(\vec{r}) = \sum_{l} c_{l}\phi_l(\vec{r}) + \sum_{l,m} f_{l}(kr)\delta_{lm} + T_{l,mn}g_{l}^+(kr)\frac{Y_{lm}(\vec{r})}{r}$$  \hspace{1cm} (3)

where $Y_{lm}(\vec{r})$ are spherical harmonics. The $T$-matrix elements are the fundamental dynamical quantities from which all fixed-nuclei cross sections are derived.

The ground state configuration of NeH$^+$ is (1$\sigma$)$^2$(2$\sigma$)$^2$(3$\sigma$)$^2$(1$\sigma$)$^4$ while excited states involve excitation from the highest lying $\pi$ orbital into an unoccupied $\sigma$ orbital. We carried out an SCF calculation on the ion. These orbitals were then used in an all singles and doubles configuration interaction (CI) calculation to obtain the natural orbitals. In order to produce a balanced treatment of the ground and excited states, we took natural orbitals produced from averaging the density matrices for the lowest three states of the ion with the ground $\Sigma$ state weighted 0.98 and each component of the next $\Pi$ state weighted 0.01. This was necessary to maintain the relative energy position of the excited state. Three natural orbitals (4$\sigma$, 2$\pi_e$, 2$\pi_c$) were included as well as the occupied orbitals. The basis set was expanded to include additional diffuse orbitals. The two lowest orbitals were frozen and the target states were determined from a full CI in the natural orbital space (of six orbitals). Both “penetration terms” [17] needed to relax any constraints implied by the orthogonality of the scattered wave to the target orbitals and “CI relaxation terms” [17] were used to construct $Q$-space, the correlation part of the trial wave function.

Since the $\Sigma$ resonances dominated, we performed preliminary calculations only in this symmetry over a range of internuclear distances and the resonance parameters extracted by fitting the eigenphase sums to a Breit-Wigner form. Only the three lowest resonances were fitted. The resonance curves are shown in figure 1 compared to the ionic ground state. The autoionization widths $\Gamma(R)$ are shown in figure 2.

The dissociation dynamics were calculated using the wave packet method. The wave packets are propagated by solving numerically the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(R,t) = H(R)\Psi(R,t)$$  \hspace{1cm} (4)
Figure 1. (color online) Potential energy curves of calculated NeH$^+$ resonance states (blue) and the ground state of NeH$^+$ (red).

Figure 2. Autoionization widths.

where

$$H(R) = -\frac{1}{2\mu} \frac{d^2}{dR^2} + V(R)$$

by using the Crank-Nicholson method [18]. At $t = 0$ the wave packets are initiated on the resonant states

$$\Psi(R, t = 0) = \sqrt{\frac{\Gamma(R)}{2\pi}} \chi_{\nu=0}(R).$$

The vibrational wave function $\chi_{\nu=0}(R)$ for the $\nu = 0$ vibrational level in the ground state of NeH$^+$ is calculated using a finite difference method [19] to solve the time-independent Schrödinger equation for the one-dimensional ion potential shown in figure 1. Autoionization can be included in the local complex approximation, by using a complex potential of the resonant state

$$V(R) = E_{\text{res}} - i \frac{\Gamma(R)}{2}.$$
The wave packets are then propagated out to the asymptotic region where the autoionization width is zero [20]. In order to compare with the experiment we calculate the cross section by projecting the asymptotic wave packet on the resonant state onto the scattering wave functions. The cross section is given by

$$\sigma(E) = \sum_{i=1}^{3} \sigma_i(E) = \frac{2\pi^3}{E} \sum_{i=1}^{3} \left| \langle \Phi_E(R) | \Psi_i(R,t_f) \rangle \right|^2$$

where the sum is over the three resonant states included in the calculation, $\Psi_i(R,t_f)$ is the wave packet at the end of the propagation, evaluated at a time $t_f$ and

$$\Phi_E(R) = \sqrt{\frac{m}{2\pi k(E)}} e^{ik(E)R}$$

where $(1/2m)k^2(E)$ is the relative kinetic energy of the fragments.

3. Comparison with the experiment. Discussion

Figure 3 shows a comparison between the experimental data and the preliminary calculation. The preliminary theoretical result includes only the three lowest $2\Sigma$ doubly excited states. The position and magnitude of the dominant peak in the high energy portion of the experimental cross section is well represented. More extensive calculations including the higher $2\Sigma$ and the $2\Pi$ resonances (which have smaller autoionization widths) will be reported elsewhere. In addition, as can be seen in figure 1, no resonant curves cross the ion in the Frank-Condon region, therefore, in this low energy region DR is induced by non-adiabatic couplings between the ion and Rydberg and valence state [9, 11]. This is not described within the current calculation; hence no zero-energy peak was seen. A different theoretical treatment must be used to obtain the necessary couplings and will be discussed in a future paper.

Acknowledgments

AIF warmly thanks J Royal for very useful discussions. AEO acknowledges support from the National Science Foundation, Grant No. NSF-02-449111. 

Figure 3. (color online) Measured [15] and calculated cross sections for the dissociative recombination of NeH$^+$. The solid curve (red) shows the result of smoothing of the raw experimental data points. This smoothing was accomplished by taking a moving average along the energy range.
References

[1] Michels H H 1989 Dissociative Recombination: Theory, Experiment and Applications ed J B A Mitchell and S L Guberman (Singapore: World Scientific) p 97 and references therein

[2] Petsalakis I D, Theodorakopoulos G and Buenker R J 1988 Phys. Rev. A 38 4004

[3] Petsalakis I D, Theodorakopoulos G, Li Y, Hirsch G, Buenker R J and Child M S 1998 J. Chem. Phys. 108 7607 and references therein

[4] Roberge W and Dalgarno A 1982 Astrophys. J. 255 489

[5] Yousif F B and Mitchell J B A 1989 Phys. Rev. A 40 4318

[6] Yousif F B, Mitchell J B A, Rogelstad M, Le Padellec A, Canosa A and Chibisov M I 1994 Phys. Rev. A 49 4610

[7] Tanabe T, Katayama I, Inoue N, Chida K, Araki Y, Watanabe T, Yoshizawa M, Ohtani S and Noda K 1993 Phys. Rev. Lett. 70 422

[8] Tanabe T et al. 1998 J. Phys. B 31 L297 (corrigendum 1999 J. Phys. B 32 5221)

[9] Guberman S L 1996 The Physics of Electronic and Atomic Collisions: XIXth Int. Conf. (AIP Conf. Proc. 360) ed L J Dubé et al. p 307

[10] Sarpal B K, Tennyson J and Morgan L A 1994 J. Phys. B 27 5943

[11] Sarpal B K and Tennyson J 1996 Dissociative Recombination III: Theory, Experiment and Applications ed D Zajfman et al. (Singapore: World Scientific) p 164

[12] Orel A E, Kulander K C and Rescigno T N 1995 Phys. Rev. Lett. 74 4807

[13] Larson Å and Orel A E 1999 Phys. Rev. A 59 3601

[14] Mitchell J B A, Novotny O, Angelova G, Le Garrec J L, Rebrion-Rowwe C, Svendsen A, Andersen L H, Florescu A I, Orel A E, submitted to J. Phys. B

[15] Rescigno T N, McCurdy C —, W, Orel A E and Lengsfield B H 1995 Computational Methods for Electron-Molecule Collisions ed W M Huo and F A Gianturco (Plenum)

[16] Rescigno T N, McCurdy C W and Turner J L 1983 J. Chem. Phys. 78 6773