Dissociative Excitation of NeD⁺

J. Lecointre¹, V. Ngassam⁴, J.J. Jureta¹,², J.B.A. Mitchell³, A.E. Orel⁴ and P. Defrance¹

¹ Université Catholique de Louvain, Département de Physique, unité PAMO, Chemin du Cyclotron 2, B-1348 Louvain-la-Neuve, Belgium.
² Institute of Physics, P.O.Box 68, 11081, Belgrade, Serbia.
³ PALMS, 'Equipe d’astrophénie expérimentale', UMR No 6627 du CNRS, Université de Rennes I, F-35042 Rennes, France.
⁴ Department of Applied Science, University of California, Davis, Davis CA 95616 USA.

Abstract. Measurements of NeD⁺ dissociative excitation cross section were obtained in Louvain-la-Neuve (UCL, Belgium) by using the animated crossed electron-ion beam method. The electronic structure of the system was calculated by using quantum chemistry calculations for the NeD⁺ ion and ab initio electron scattering calculations using the complex Kohn variational method for the resonant NeD neutral complex formed by the temporary capture of the electron by the ion. The cross section for dissociative excitation are then calculated below the second excitation thresholds of the ion where the process is dominated by a series of doubly-excited resonance states. Theory and experiment are then compared.

1. Introduction
Dissociative excitation (DE) has been much less studied than dissociative recombination (DR). Its higher energy threshold makes it not amenable to plasma techniques and the advantages of merged beam techniques for achieving very low collision energies and the particular importance of DR to low temperature plasma chemistry have meant that the scarce beamtime available at heavy ion storage rings has been mostly devoted to this latter process, as far as electron-molecular ion studies are concerned. It is however particularly attractive for study using crossed beam experiments which cannot go low enough in energy to effectively study DR and yet, not requiring high energy accelerators, can be set up with much less capital and operating expenditure. Indeed, Louvain-la-Neuve in Belgium is one of the facilities where much of the experimental effort in recent years devoted to this subject has been performed. Neon may be used as a coolant gas in the divertor region of ITER to absorb the plasma energy by multiple ionization and excitation [1]. NeH⁺ is expected to be formed by collision of Neon atom with vibrationally excited molecular hydrogen in the divertor. We have recently studied the reaction:

\[
e^- + NeD^+ \rightarrow NeD^{**} \rightarrow Ne + D^+ + e^-\]  \hspace{1cm} (1)

both theoretically using a wave packet propagation method and, experimentally using a crossed electron-ion beam apparatus. The results are reported here after a brief discussion of both the theoretical methods and the experimental setup used.
2. Experimental procedure
In the experiment developed in Louvain-la-Neuve (UCL, Belgium) the animated crossed electron-ion beam method is applied [2]. Ions are extracted from an ECR ion source and accelerated to 12 keV. The fixed-energy molecular ion beam is selected by means of a first double focusing 90° magnetic analyser, additionally focused and purified by a 45° spherical electrostatic deflector. The ion beam is directed into the collision region where it crosses the ribbon-shaped electron beam at right angles. The electron energy ($E_e$) range extends continuously from the threshold of the initial reaction (excitation or ionization) up to 2.5 keV. Product ions are separated from the primary ion beam by means of a second double focusing 90° magnetic analyser. Due to the transfer of internal potential energy, dissociation fragments exhibit both a broad velocity and a broad angular distribution in the laboratory frame. Selected by the variable analyser slit, the angular acceptance of the magnet (0.1 radian) is large enough to transmit to the detector all ions with the maximum expected kinetic energy release produced by dissociation processes. Product ions are further deflected by a 90° electrostatic spherical deflector and directed onto a channeltron detector. Usually, only a fraction of the signal is detected, so that absolute cross sections are obtained after determination of the product ion transmission. For singly charged fragments, individual contributions of dissociative excitation and dissociative ionization processes are estimated separately [3].

3. Theory
The potential energy and the autoionization width of the resonant states were obtained from electron-scattering calculations using the complex Kohn variational method well described in Ref. [4]. In order to generate an accurate target wave function, we carried out an SCF calculation on the ion to generate a set of molecular orbitals. 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 Σ state weighted 0.98 and each component of the next Π state weighted 0.01. This was necessary to maintain the relative energy position of the excited state. Three natural orbitals (4σ, 2π_x, 2π_y) were included as well as the occupied orbitals. The basis set was expanded to include 10 additional diffuse orbitals: five s (exponents .299, .1, .033, .011, .0037), four p (exponents .113, .0519, .023, .005) and one d (exponent .170). The two lowest orbitals were frozen and the target states were determined from a full CI in the natural orbital space of six orbitals with the largest occupation numbers.

At the equilibrium geometry four resonance states of Σ symmetry and three of Π resonances are below the first excitation threshold of the ion (18.5 eV). No Δ resonances were found in this energy range. The resonance parameters (autoionization widths and resonance energies) were extracted by fitting the eigenphase sums to a Breit-Wigner form. Fig.1 shows the four Σ (left panel) and three Π (right panel) resonances calculated.

The nuclear dynamics are studied by solving the time dependent Schrödinger equation for each resonant state since they are not coupled to each other, that is:

$$i \frac{\partial}{\partial t} \Psi(R, t) = \left[ -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} + V_{res}(R) \right] \Psi(R, t),$$

where $\Psi$ represents the amplitude on each of the resonance states and $\mu$ is the reduced mass of the system. The resonance potentials appear as local complex potential curves, given by

$$V_{res}(R) = E_{res}(R) - \frac{i}{2} \frac{\Gamma(R)}{2},$$
Figure 1. Potential energy curves of $\Sigma$ (left panel) and $\Pi$ (right panel) resonance states of NeH. In each panel, the solid curve represents the ground $^1\Sigma$ state NeH$^+$. The dashed curves represent the resonance states in each symmetry. In these figures, energy is in eV where 1 eV = $1.602 \times 10^{-19}$ J and distance is in bohr where 1 Bohr = $5.291772 \times 10^{-11}$ m.

where $E_{res}(R)$ is the energy position of the resonance potential curve and $\Gamma(R)$ is the autoionization width. The initial wave packet is expressed as

$$\Psi_{\nu_i}(R, t = 0) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{\nu_i}(R), \quad (4)$$

where $\chi_{\nu_i}(R)$ is the initial vibrational wave function of the molecule.

For the initial vibrational level $\nu_i$, the cross section for dissociative recombination via a single resonance state is given by

$$\sigma_{\nu_i}(E) = \frac{4\pi^3}{k_i^2} g \left| \langle \phi_E(R) \mid \Psi_{\nu_i}(R, t) \rangle \right|^2. \quad (5)$$

where $\phi_E(R)$ is the energy normalized wave function given by

$$\phi_E(R) = \sqrt{\frac{\mu}{2\pi k_i(E)}} e^{ik(E)R}. \quad (6)$$

4. Results

In the present paper, absolute cross sections are reported for the particular dissociative excitation channel leading to the D$^+$ formation and results are shown in Fig. 2. The maximum of the DE cross section is found to be $(6.3 \pm 1.4) \times 10^{-17}$ cm$^2$ (at $E_e = 35.1$ eV) and two threshold energies are identified at $(10.0 \pm 0.5)$ eV and $(14.1 \pm 0.5)$ eV. The lowest dissociative states ($B^1\Sigma$ and $b^3\Sigma$) accessible via direct excitation leading to the Ne$^+(2p^53s, 1^3P)+H^+$ pair formation present a high dissociation limit, so that the threshold for dissociative excitation is much higher (around 30 eV). Vibrational excitation of the parent ion cannot be responsible for these observed low
energy thresholds, given that the potential well depth of NeD$^+$ is only slightly higher than 2.1 eV. Such low experimental thresholds can only be explained by resonant dissociative excitation. The lowest one (10.0 eV) can be attributed to capture into doubly excited states (about 11 eV) followed by autoionization to the $X^1\Sigma$ electronic ground state of NeD$^+$ (equation 1). The width of the Franck-Condon region may also explain the existence of the two experimental thresholds.

In Fig. 2, present absolute cross sections for dissociative excitation leading to Ne+D$^+$ products are compared with measurements performed on NeH$^+$ ions and obtained from an ASTRID storage ring experiment [5]. In that experiment, neutral Ne and Ne+H products are detected but not separately distinguished, so that the corresponding data contain both dissociative recombination and excitation contributions. DR, which is dominant in the low energy range (below 1 eV), cannot be observed in the present experiment as only ions are detected. The storage ring data shown in Fig. 2 have been normalised to the present absolute cross sections, at 20 eV. Several energy thresholds are observed around 7 eV, 20 eV, 33 eV and 42 eV. Below 20 eV, a distinct qualitative difference is clearly observable between the storage ring data and the present ones: the thresholds (10.0 eV and 14.1 eV) do not coincide with the above-listed ones and the broad peak centred on 14 eV is not seen. This is clearly a resonant contribution due to dissociative recombination which is highlighted by subtracting the present results from the storage ring data, assuming that there will be little difference between the NeH$^+$ data and what one would obtain using NeD$^+$ ions in the storage ring (left side insert, Fig. 2). The corresponding resonant states evidently lead to formation of two neutral products.

Figure 2. Absolute cross section for dissociative exitation versus electron energy: present measurements for D$^+$ fragments are represented with opened squares and normalized data of ref [5] are represented with plus sign. The insert on the left shows estimated resonant contributions (see text for details), the insert on the right is a comparison of the data with theory (solid line).
(Ne+H), because no resonant signal is observed in the present experiment. Above 20 eV, both experimental results give similar overall shapes for DE, except for the thresholds (33 eV and 42 eV) which cannot be observed in the present experiment due to larger statistical uncertainties.

On the theoretical side, the potential energy curves shown in Fig. 1 were used, as input into the wave packet method previously described, to determine the resonant DE cross section. The absolute cross section for dissociative excitation of NeD$^+$ from the ground vibrational state ($\nu=0$) of the ion are shown in the right side insert of Fig. 2. Also shown, opened square, is DE cross section for NeD$^+$ measured at Louvain-La-Neuve. The theoretical DE cross section for NeD$^+$ has a peak of $2.83 \times 10^{-18}$ cm$^2$ at 13 eV where the overlap between the wave function of the ion continuum and that of the lowest resonant $\Sigma$ state is maximum. There is also a structure in the DE cross section, located at about 16 eV and due to resonant states that contribute mostly at higher energy. The range of energy in which calculations has been done is smaller compare to experiment. Six excited states of NeD$^+$ are opened in the energy range of the experiment, and must be explicitly included in the close-coupling expansion. This is beyond the scope of this study. The experimental data from Louvain-La-Neuve shows a threshold in the cross section for DE at 10 eV that is clearly reproduce by the theory. This threshold is due to the fact that even though the DE channel is open at low energy, the cross section is smaller and cannot be detected in the present experiment. As the collision energy increases and the interaction between the lowest $\Sigma$ resonant state and the ion continuum become stronger; the cross section become significant and the process is detected by the experimental apparatus. These experimental cross sections peak at about 100 eV. This is attributed to the direct DE channels not included in the calculations. In the energy region around the threshold, the present calculation shows a good agreement with the experimental data.

5. References
[1] Mitchell JBA, in *Atomic and Plasma-Material Interaction for fusion*, (Vienna: International Atomic Energy Agency) 6 97 (2001)
[2] Defrance P, Brouillard F, Claeyss W and Van Wassenhove G, *J. Phys. B: At. Mol. Opt. Phys.* 14 103 (1981)
[3] Lecointre J, Belic DS, Cherkani-Hassani H, Jureta JJ and Defrance P, *J. Phys. B: At. Mol. Opt. Phys.* 393 275 (2006)
[4] Rescigno TN, Orel AE, McCurdy CW and Lengsfield BH, in *Computational Methods for Electron-Molecule Collision*, ed Huo WM and Gianturco FA (New York Plenum, 1995)
[5] Novotny O, PhD Thesis, Université de Rennes I (2006)