Wave packet studies of dissociative recombination

A E Orel
Department of Applied Science, University of California, Davis, USA
E-mail: aeorel@ucdavis.edu

Abstract. The study of dissociative recombination is complicated by the high energy and large number of channels that are open. Theory in this area has not kept up with experiment with few molecules studied. We will present our work on the study of the ‘direct’ dissociative recombination process, where one or more resonant states exist. The resonance parameters are taken from accurate electron scattering calculations and used as input to the dynamics calculations. We will illustrate the method with the study of DR in the HCN\(^+\) and HNC\(^+\) systems.

1. Introduction
Accurate quantum chemistry calculations exist for the ground states of rather large polyatomic systems. Spectroscopically accurate potential energy curves exist for a number of diatomics, and a smaller yet still significant number of triatomic and polyatomic systems. In the area of electron scattering, accurate elastic differential cross sections exist for systems ranging from diatomics such as \(\text{H}_2\), to larger polyatomic systems such as ethylene, benzene, and silane. However, accurate calculations of dissociative recombination exist on only a handful of diatomics. Calculations for partial branching ratios are even rarer. There are still discrepancies between theory and experiment for the simplest of diatomics HD\(^+\) [1], and there exists only one accurate ab initio calculation in full-dimensions on a triatomic, \(\text{H}_3^+\) [2].

What are the differences that so complicate the study of dissociative recombination reactions? The basic reason lies in the energy of the process that is being studied. Although the collision energy of the incoming electron can be very low (meV range), when the electron recombines the total energy is at the ionization potential of the neutral. Therefore, there exist a large number of open electronic states in the system. Indeed, there exist an infinite number of Rydberg states converging to each state of the ion. In addition, the states may lie close in energy, leading to breakdown of the Born-Oppenheimer approximation and large non-adiabatic couplings between states. Finally, one must address both bound electronic states, but also states with a free electron and the resonance states that lying embedded in the free electron plus ion continuum.

We will concentrate in this work on the resonance or ‘direct’ mechanism. Since the mass of the electron is some three orders of magnitude less than that of the nuclei, there is inefficient transfer, in general, of energy from the electron into the motion of the nuclei, leading to little vibrational excitation or dissociation. However, in certain special cases, there is an intimate coupling between the electron interaction with the target and the nuclear dynamics of the target. The results of such an interaction can be quite dramatic. In these cases, the electron can temporarily attach to the molecule and change the forces felt between its atoms for a period of time comparable to a vibrational period. This can lead to resonant vibrational excitation and dissociative attachment, for neutral targets, or dissociative recombination in the case of ions.
Therefore we can simplify the calculation by first considering the capture of the electron into a resonant dissociative state, and then describing the dynamics of the molecule moving on the excited state (resonant) potential energy surface. The dynamics must be able to describe autoionization since the molecule can re-emit the electron. If no autoionization occurs, the molecule fragments into products, during which the probability may be distributed into various product states due to non-adiabatic coupling.

Our studies of this process will follow the comparable treatment of quantum reactive scattering. First we will carry out \textit{ab initio} electron scattering calculations at fixed internuclear geometries to determine the resonant energy surfaces and the corresponding surface of autoionization widths. This will then be used as input to a dynamics study to determine the cross-section and product distributions for the DR process. In the following sections, we will describe the methods we have used to study this process.

2. Method

2.1. Fixed-nuclei electron scattering calculations

The fixed-nuclei electron scattering cross sections were computed using the complex Kohn variational method [3]. In this method, the electronic trial wave function of the scattering system is expanded as

$$\Psi = \sum_{\Gamma} A \left[ \Phi_{\Gamma}(x_1..x_N)F_{\Gamma}(x_{N+1}) \right] + \sum_{\mu} d_{\mu} \Theta_{\mu}(x_1..x_{N+1}) \quad (1)$$

where the $\Phi_{\Gamma}$ are $N$-electron target eigenstates, $x_i$ denote space-spin coordinates, $A$ antisymmetrizes the coordinates of the target and scattered electrons and the $\Theta_{\mu}$ are square-integrable $N+1$-electron configuration state functions (CSFs) described further below. The first sum, which we denote as the $P$-space portion of the wave function, runs over the energetically open target states. We denote the second sum as the correlation portion of the wave function.

In the Kohn method, the $F_{\Gamma}$, which represent the wave functions of the scattered electron, are expanded as a linear combination of symmetry-adapted molecular orbitals (Gaussians) and numerical continuum functions. The $N+1$-electron CSFs describe short-range correlations and the effects of closed channels and are critical to striking a proper balance between intra-target electron correlation and correlation between target and scattered electrons.

For the correlation part of the wave function, we included two classes of terms. 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” [3]. Since the scattering functions $F_{\Gamma}$ are constructed from bound and continuum functions which are, by construction, orthogonal to the target orbitals, the penetration terms are needed to relax any constraints implied by this strong orthogonality. In addition to the penetration terms, we included a second class of “CI relaxation terms” [3]. The target ground state is built as a fixed linear combination of a number of CSFs, say $M$, from the active space. The target CI calculation can also produce $(M-1)$ excited states, which are presumed to be energetically closed. The CI relaxation terms are constructed as the direct product of these states and the orbitals used to describe the scattered electron. In other words, this class of CI relaxation terms is simply the complement (1-$P$) of the $P$-space portion of the wave function. This complement, combined with the penetration terms, constitutes the correlation part of the trial wave function. In solving the variational equations, we use Feshbach partitioning to combine the penetration and relaxation terms into an optical potential. For more detail on this subject, we refer the reader to [3].

From the results of these scattering calculations, we obtain elastic and inelastic (transition to excited target states) cross sections and eigenphase sums. Near a resonance these quantities show dramatic structure in their energy dependence. An example is shown in figure 1 and 2. Here the elastic cross section and eigenphase sum are shown as a function of energy for scattering of electrons from Ne$_2^+$ in overall $^1\Pi_u$ symmetry. The three curves are calculations done at three different fixed internuclear geometries of Ne$_2^+$.

Note the two peaks that move to lower energy as the bond distance is increased. The position of these peaks is the resonance energy and their width yields the autoionization width which
is inversely proportional to the lifetime. Figure 2 shows the eigenphase sum, which shows steps of $\pi$ at the resonance energy. The steepness of the rise determines the autoionization width. In practice, it is the eigenphase sum (not the elastic cross section) which is fit to a Breit-Wigner form to abstract this information.

2.2. Dissociation Dynamics

We have used two methods to study the dissociation dynamics, the time-dependent wave packet method (TDWP) and Multi-Channel Quantum Defect Theory (MQDT). These two techniques have different areas of application that allow a broad range of problems to be studied. MQDT is extremely effective at low energy, where the local approximation inherent in the standard TDWP breaks down. MQDT, though, is most useful where only one bond distance is important in the dissociation. TDWP can handle multi-dimensional problems, and is extremely effective in determining branching ratios into final channels.

The wave packet method proceeds by direct integration of the time-dependent Schrödinger equation, propagating a wave packet on a complex potential energy surface. The complex energy surface reflects the fact that the resonant state can release the electron as long as the resonance energy lies within the continuum. The cross section is calculated by the projection of the wave packet onto final states for long times when the wave packet has reached the asymptotic region of the potential and the autoionization loss has gone to zero [4].

In many cases, in particular when the resonance lies at very low energy above the ion and the approximations in the ‘local’ wave packet method described above break down, MQDT is an efficient and accurate alternative. The MQDT method has been described elsewhere [5]. It includes both the direct recombination through the resonance and the indirect where the electron first captures into a vibrationally excited Rydberg state and then to the resonance on an equal footing. The simultaneous treatment of these two processes is critical since they represent indistinguishable paths to the same final state and hence cause interference structure in the cross section.

We have studied a number of systems using these methods. These include studies of DR in the rare-gas diatomic ions, He$_2^+$ and Ne$_2^+$, and NeH$^+$ which are described elsewhere in this volume [7–9]. We will describe in the next section our preliminary work on HCN$^+$ and HNC$^+$. 

Figure 1. Elastic cross section as a function of energy for electron scattering from Ne$_2^+$ for several internuclear geometries

Figure 2. Eigenphase sum as a function of energy for electron scattering from Ne$_2^+$ for several internuclear geometries
3. Dissociative Recombination of HCN$^+$ and HNC$^+$

As an example we will show results on electron scattering from HCN$^+$ and HNC$^+$. This example was motivated by one of the most puzzling questions in contemporary interstellar chemistry, the HNC/HCN abundance ratio. Both species are known to be involved in synthesis of more complex organic molecules. The hydrogen isocyanide HNC isomer is less stable than the hydrogen cyanide HCN isomer by 0.63 eV. Thus, HNC should have negligible abundance with respect to HCN if both of them are formed in thermal equilibrium conditions. However, the HNC/HCN abundance ratio observed in interstellar media drastically changes from one source to another. For example, the HNC/HCN ratio is about 1.55 in cold clouds [10] (where cold refers to a temperature of about 10 K) yet drops to around 0.0125 in warmer (around 200 K) clouds [11]. In order to understand the non-zero HNC/HCN abundance ratio in dense interstellar clouds, it has been proposed that both species are produced with the same efficiency in the dissociative recombination of HCNH$^+$. This system is addressed elsewhere in this volume [13].

It is also necessary to consider the DR of the HNC$^+$ and HCN$^+$ systems. This has been studied by Talbi et al. [12], however only structure not scattering calculations were carried out. These calculations suggest that the HCN$^+$ DR proceeds both through a direct mechanism and indirect mechanism, while the HNC$^+$ DR proceeds via only an indirect mechanism. This may indicate that the HCN$^+$ DR is more efficient, however until the couplings are known this must remain speculation.

The ground state of HCN$^+$ is:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(1\pi)^3$$

with a low-lying excited state:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)(1\pi)^4$$

The (5\sigma) and (1\pi) are quite close in energy and these two states are switched in energy for HNC$^+$. The potential energy curves for the two ions are shown in figures 3 and 4.

We first performed an SCF calculation on the neutral. This resulted in an equivalent treatment of $\pi_x$, $\pi_y$, and $\sigma$ orbitals. We then froze the lowest four orbitals, and performed an all singles and doubles...
CI calculation. We obtained natural orbitals by averaging over the density matrices for the lowest three states of the ion, \(^2\Pi_x\), \(^2\Pi_y\) and \(^2\Sigma\). The lowest four orbitals were frozen and the next six orbitals with the highest occupation numbers were used for the natural orbital space, \(1\pi_x\), \(1\pi_y\), \(2\pi_x\), \(2\pi_y\), \(5\sigma\) and \(6\sigma\) orbitals. The basis set was expanded to include additional diffuse orbitals. The target states were determined from a full CI in the natural orbital space.

Calculations were carried out in all symmetries and with both possible spin couplings, \(^1\Sigma\), \(^1\Pi\) and \(^1\Delta\) for both HCN\(^+\) and HNC\(^+\). For HNC\(^+\) resonances were found in all cases, lying between the ground state of the ion and the first excited states. For HCN\(^+\), our preliminary results show low energy resonances only in the \(^1\Sigma\) and \(^3\Pi\) cases, but further calculations are necessary. The behavior of the resonances as a function of internuclear geometry was studied. An example is shown in figure 5 and 6, where the elastic cross section and eigenphase sum as a function of incident electron energy are shown for the case of electron scattering from HNC\(^+\) with \(^1\Pi\) overall symmetry. Note that in contrast to the case shown in figures 1 and 2, there is a strong background in the elastic scattering. However, it is still possible to see two resonances in the elastic cross section. These resonances move to lower energy as the H–N bond is stretched and should lead to dissociation.

In figure 7 and 8 we show our preliminary results for the low-lying resonances in these systems. Figure 7 shows the resonances in \(^1\Sigma\) and \(^3\Sigma\) for electron scattering from HCN\(^+\) compared to the ion potential energy curves. The lowest lying \(^1\Sigma\) and \(^3\Sigma\) resonances cross very near the equilibrium geometry of the ion. In figure 8 we show the resonances in \(^1\Sigma\) and \(^1\Pi\) for electron scattering from HNC\(^+\) compared to the ion potential energy curves. The two lowest \(^1\Sigma\) resonances appear to cross the ion close to the equilibrium geometry, the \(^1\Pi\) appear at higher energies and parallel to the first excited state of the ion.

4. Conclusion

The preliminary results presented here indicate the presence of low lying resonances in both the HCN\(^+\) and HNC\(^+\) systems. Further calculations are necessary to determine the behavior, repulsive or bound, of these resonant states and where they cross the ion if at all. Additional structure calculations are needed at larger internuclear geometries to determine the asymptotic behavior of the states. In addition, it is important to determine the effect of bending away from the linear geometry and the effect of stretching.
the C–N bond. Finally, dynamics calculations must be carried out to produce cross sections for the DR process and final state distributions.

Acknowledgments

The work presented here was in part due to the efforts of Å Larson, J Royal, A Florescu and V Ngassam. The work would not have been accomplished without the support and participation of A Suzor-Weiner. The author acknowledges support from the National Science Foundation, Grant No. PHY-02-44911. We acknowledge the financial support of the NATO Science programme, through the Collaborative Linkage Grant No. PST.GLG.9794033.

References

[1] Ngassam V, Motapon O, Florescu A, Pichl L, Schneider IF and Suzor-Weiner A 2003 Phys. Rev A 68 032704
[2] Kokouline V and Greene C H 2003 Phys. Rev. A 68 012703
[3] Rescigno T N, Lengsfeld B H and McCurdy C W 1995 Modern Electronic Structure Theory vol 1 ed Yarkony D R (Singapore: World Scientific) p 501
[4] Larson and Orel A E 1999 Phys. Rev. A 59 3601
[5] Giusti A 1980 J. Phys. B: At. Mol. Phys. 13 3867
[6] Ngassam V, Florescu A, Pichl L, Schneider IF, Motapon O and Suzor-Weiner A 2003 Eur. Phys. Jour. D 26 165
[7] Florescu A I and Orel A E 2005 J. Phys.: Conf. Series this volume
[8] Ngassam V, Orel A E, Motapon O and Suzor-Weiner A 2005 J. Phys.: Conf. Series this volume
[9] Royal J and Orel A E 2005 J. Phys.: Conf. Series this volume
[10] Irvine W M and Schloerb F P 1984 Astrophys. J. 282 516
[11] Schilke P, Walmsley M C, Pineau des Forets G, Roueff E, Flower D R and Guilloteau S 1992 Astron. Astrophys. 256 595
[12] Talbi D, Le Padellec A and Mitchell J B A 2000 J. Phys. B: Atom. Molec. Opt. Phys. 33 3631
[13] Ngassam V, Orel A E and Suzor-Weiner A 2005 J. Phys.: Conf. Series this volume
[14] Cunningham A J, O’Malley T F and Hobson R M 1981 J. Phys. B: At. Mol. Phys. 14 773
[15] Carata L, Orel A E and Suzor-Weiner A 1999 Phys. Rev. A 59 2804
[16] Chang J S, Hobson R M, Ichikawa Y, Kaneda T, Maruyama N and Teii S 1989 J. Phys. B: At. Mol. Phys. 22 L665