Electron-driven excitation and dissociation of molecules

S. Chourou1, Å. Larson2 and A. E. Orel1
1Department of Applied Science, University of California, Davis, USA
2Dept. of Physics, Stockholm University, AlbaNova University Center S-106 91 Stockholm, Sweden
E-mail: aeorel@ucdavis.edu

Abstract. In the collision of electrons with molecules and molecular ions, excitation and dissociation are dominated by resonant processes, where the electron becomes temporarily trapped, changing the forces felt by the nuclei. In this paper, we will outline our method for treating these collision processes, where one or more resonant states exist. We separate the problem into two steps. First we 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, using the Complex Kohn variational method. These resonance positions and widths are then used as input to a dynamics study to determine the cross section and product distributions for the dissociation or excitation process. We will present results on a number of systems, including HCCH, HCN/HNC and HCCCN as examples of dissociative attachment, and H$_2$O$^+$ for dissociative recombination.

1. Introduction

Electron collisions with molecules and molecular ions that lead to dissociation play a key role in a number of environments, since they produce the radicals and molecular fragments that initiate and drive the relevant chemistries. Examples of such systems can be found in biology as well as in chemistry and physics; they range from the technologically important plasmas used in plasma enhanced chemical vapor deposition [1], to planetary atmospheres and interstellar clouds [2]. Due to the difference between the mass of the electron and the nuclei, it is unlikely that there is a significant cross section for vibrational energy transfer or dissociation in electron-molecule or electron-molecular ion collisions. Nuclei move slowly compared to electrons, so the time scale for nuclear motion is very large compared to the time of an electron collision. However, in resonant systems where the electron temporarily attaches to the molecule, the forces felt between its atoms are changed for a period of time comparable to a vibrational period. This can lead to resonant vibrational excitation (VE), resonant dissociative excitation (DE) and dissociative attachment (DA), for neutral targets, or dissociative recombination (DR) in the case of ions. These processes can be studied by 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. First we 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, using the Complex Kohn variational method [3].
These resonance positions and widths are then used as input to a dynamics study to determine the cross-section and product distributions for the dissociation or excitation process. In the following section we will briefly describe the underlying theory used in these calculations. We will then illustrate the method with a series of examples.

2. Theory
Theoretical treatments of DR, DA, VE and DE are generally based on rigorous resonance scattering theory \[4\], formulated within the Born-Oppenheimer approximation. The principal result of the formal theory is the so-called nuclear wave equation that governs the nuclear dynamics on the resonance state(s). This is an inhomogeneous wave equation which, due to the presence of a nuclear Green’s function that operates on the nuclear coordinates, involves an effective Hamiltonian that is complex, non-local and energy dependent. In many resonant dissociative recombination/attachment problems, the heavy-particle dynamics can be treated within the local complex potential or “boomerang” approach\[5\]. In this approximation, the nuclear wave equation at total energy \( E \) is

\[
(E - K_R - V_{\text{res}})\xi_\nu = \phi_\nu \tag{1}
\]

where \( K_R \) is the nuclear kinetic energy operator, \( V_{\text{res}} \) is the (complex) resonant state potential,

\[
V_{\text{res}}(\vec{R}) = V_0(\vec{R}) - i\Gamma(\vec{R})/2 \tag{2}
\]

and \( \xi_\nu \) is the nuclear wave function associated with the electronic resonance state. (Note, in this discussion we have used atomic units (\( \hbar = m = 1 \)). The position and width of the resonance that form the resonant potential are \( E_{\text{res}} \) and \( \Gamma \) respectively. The driving term for the nuclear wave equation, or “entry amplitude”, \( \phi_\nu \) is defined as

\[
\phi_\nu(\vec{R}) \equiv (\Gamma(\vec{R})/2\pi)^{1/2} \chi_\nu(\vec{R}), \tag{3}
\]

where \( \chi_\nu \) is the initial vibrational wave function of the target. The local complex potential model is expressed in Eqs. (1-3) in its original or “boomerang” form, and provides the wave function \( \xi_\nu \) from which the cross sections can be calculated. The inhomogeneous differential equation given by Eq. (1), can be recast into this time-dependent form, as first shown by McCurdy and Turner \[6\]. We then proceed by the direct integration of the time-dependent Schrödinger equation. The time propagation must be carried out long enough for the wave packet to reach the asymptotic region of the potential where the autoionization loss has gone to zero. In the examples that follow, the dynamics calculations were carried out using the MultiConfiguration Time-Dependent Hartree (MCTDH) method \[7\] and the package of codes developed in Heidelberg by the group of Meyer. We have found this method to be extremely efficient in studying these processes.

The cross-sections resulting from the dynamics calculations are only as accurate as the resonance parameters used. We used the complex Kohn variational method \[3\] to calculate these parameters. The electronic resonance parameters, \( V_0(\vec{R}) \) and \( \Gamma(\vec{R}) \) are determined by analyzing the T-matrix from state-of-the-art electron-molecule or electron-molecular ion scattering calculations. For single, isolated resonances, the eigenphase sum is fit to a Breit-Wigner form.

3. Examples: Dissociative Attachment
3.1. HCCH
Recent experiments on DA of acetylene show a strong peak in the 3 eV energy range, with products HCC\(^-\) + H \[8\]. The electron is believed to attach to an antibonding \( \pi^* \) orbital, but
dissociation occurs not on the C-C bond but on the C-H bond. In addition, the fragments have $A'$ symmetry. These observations are similar to those seen in DA of formic acid, a system we have previously studied [9]. We carried out \textit{ab initio} calculations for elastic electron scattering from acetylene using the complex Kohn variational method at the static exchange level to obtain the resonance surface and autoionization width before the anion crosses the neutral. After it has crossed additional quantum chemistry calculations, at a consistent level, \textit{ie} SCF, were used to map out the rest of the surface. These calculations were done keeping one C-H distance fixed, reducing the problem to three (Jacobi) dimensions, the C-CH distance ($r$), the distance from the other hydrogen atom to the center of mass ($R$) and the angle in-between them ($\theta$). Note that since only total DA cross sections, not final state distributions were desired, the form of the anion surface away from the crossing is not relevant. We then carried out MCTDH calculations [7] to track the dissociation dynamics and obtain the dissociative attachment cross sections [10]. These results are shown in Figure 1. The apparent excellent agreement in the case of HCCH at 0K is fortuitous since the experiment was done at room temperature.

![Figure 1](image.png)

**Figure 1.** Total cross sections for DA to $C_2H_2$ (left) and $C_2D_2$ (right) at 300 K and 0 K compared to experiment [12].

More recently, we have performed nuclear dynamics calculations on $C_2H_2$ and $C_2D_2$ to study the isotope effect in DA [11]. Our previous calculations at 0 K led to an isotopic ratio of the cross section for $C_2H_2$ compared to the cross section for $C_2D_2$ of 28.9, a factor of 2 higher than recent measurements [12]. Since this reaction proceeds by bending, and this mode is populated at room temperature (the temperature where the experiments were performed), the discrepancy was attributed to the contribution of higher vibrational modes. We included the four lowest bending vibrational states that had non-vanishing populations at the experiment temperature of $T = 300$ K. The resulting ratio is found to be 17.9 in closer agreement to the experimental value. These results are shown in Figure 1. Although the agreement in absolute magnitude is not as good, this is to be expected since these calculations were carried out at the static-exchange level. In general, the addition of polarization and correlation effects causes changes in the resonance parameters. However, although the value of $\Gamma$ was found to be smaller by a factor of 0.93 at equilibrium geometry when we performed a Relaxed Self-Consistent-Field (RSCF) calculation, there was only a small shift in the resonance position. We attempted to obtain a rough estimate of the DA cross section by rescaling the $\Gamma$ surface using the 0.93 factor. This results in a cross section maximum of 4.9 pm$^2$ around 3 eV for HCCH. Future calculations will address this as well as the Feshbach resonances that are known to occur at higher energies.
3.2. HCN/HNC

We have previously carried out studies on dissociative electron attachment to ClCN and BrCN [13]. These calculations showed less effect of bending compared to the calculations on HCCH, since the Σ resonant states occurred at a lower energy relative to the ion. Even upon bending dissociation proceeded directly on the A′ state associated with the Σ state in linear geometry, with little interaction with the A′ state arising from the Π state when bent. We decided to study HCN and its isomer HNC to see how they compare to ClCN and BrCN. These systems are isoelectronic to HCCH. We were interested in a comparison to this system as well as studying the isomer effect between HCN and HNC. There exist previous electron scattering calculations on these systems [14, 15, 16]. However, we were interested in studying the dynamics of dissociative electron attachment in these systems.

We carried out calculations at the static exchange level for this system in Jacobi coordinates (three dimensions). Note that these systems share a common potential energy surface, that is, for an angle of zero degrees the system is HCN, at 180 degrees it is HNC. Figure 2 shows a two-dimensional slice of the potential energy surfaces as a function of two coordinates, the distance from H to the CN center of mass (R) and the Jacobi angle (θ). The C-N distance (r) is fixed at the equilibrium value of the neutral. As in the case of HCCH, in linear geometry the Π resonant state lies parallel to the neutral, while the Σ resonant state is higher in energy, but dissociative. Upon bending, the Π state splits into A″ which remains parallel to the neutral, and A′ which interacts with the A′ arising from the Σ. This produces a path to dissociation which has a barrier. The barrier reduces in height as the bending angle is increased.

![Figure 2](image-url)

**Figure 2.** Potential energy surfaces for the neutral and lower adiabatic anion resonant state. HCN (left) and HNC (right). The CN distance has been fixed at the equilibrium distance of the neutral.

However, the dynamics in these systems was quite different than that observed in HCCH, as well as BrCN and ClCN. As in HCCH, the dissociation occurs on the lowest A′ surface. This surface correlates in linear geometry to the Π state at bond distances close to and smaller than equilibrium, but to the Σ state at larger separations. However, instead of bending as was the case in HCCH, the molecule tunnels through the barrier to dissociation. We found that the DA cross section was larger for HCN than HNC. This can be explained by the barrier to dissociation...
which is lower in energy and more narrow as a function of internuclear separation in the HCN case.

3.3. HCCCN

Experiments on dissociative electron attachment (DA) to HCCCN below 12 eV have led predominantly to formation of CCCN\(^-\), CN\(^-\), HCC\(^-\) and CC\(^-\) negative ions [17]. It has been concluded that these fragments result mainly from the decay of a \(\pi^*\) shape resonance state upon electron attachment that involves distortion of the symmetry of the linear neutral molecule. In order to study the dynamics of dissociation in these channels, we subdivided the molecule into three fragments (H), (CC) and (CN); therefore, four internal coordinates consisting in the distances between the center of masses of (H) and (CC) fragments, (CC) and (CN) fragments, the (H)-(CC) angle and the (CC)-(CN) angle are included in the calculation. We have performed electron scattering calculations at the static exchange level using the complex Kohn variational method [3] to determine the resonance energies and autoionization widths for various geometries of the system and construct the complex potential energy surfaces relevant to the metastable HCCCN\(^-\) ion. In Figure 3, the eigenphase sum for elastic scattering of electrons with energy below 10 eV are shown. These calculations reveal two \(\sigma^*\) and two \(\pi^*\) resonances at energies consistent with ion fragments count peaks observed experimentally. As can be seen in the figure there are qualitative similarities in the topology of the adiabatic resonant surfaces of HCCCN and that of HCCH and HCN/HNC where the \(\sigma^*\) and the \(\pi^*\) states cross in linear geometry. The eigenphase sum for \(\Sigma\) symmetry show that these resonant states are dissociative, while the \(\Pi\) are not. It is expected that upon bending of the molecule the \(\pi^*\) resonant surfaces will split into an \(A'\) and \(A''\) manifolds forming a conical intersection at the crossing point. Further calculations are needed to include the angular degrees of freedom so as to describe the four main DA channels observed experimentally and to correctly describe the dissociation dynamics. Once the surfaces are constructed it will be possible to compute the dissociation dynamics on the coupled resonant surfaces and obtain the DA cross sections.

Figure 3. Eigenphase sum for elastic scattering of electrons as a function of incident electron scattering energy, solid curve equilibrium geometry, dashed curves other geometries, left figure \(\Sigma\) symmetry, right figure \(\Pi\) symmetry.
4. Examples: Dissociative Recombination

4.1. H$_2$O

The dissociation dynamics in recombination of H$_2$O$^+$ with low-energy electrons has been the subject of a number of experiments, especially in the case of ‘zero’ energy electrons. In the case of an ion storage ring, ‘zero’ energy is defined as the lowest collision energy that can be obtained in the ion ring. This varies between rings, but is roughly on the order of a few meV [2]. The X $^1A_1$ ground state of H$_2$O has the dominant configuration (1a$_1$)$^2$(2a$_1$)$^2$(1b$_2$)$^2$(3a$_1$)$^2$(1b$_1$)$^2$. The electron in the highest occupied molecular orbital (HOMO) is bound by 12.6 eV, and removal of this leads to the formation of H$_2$O$^+$ in its $^2B_1$ ground state. Dissociative recombination with a zero eV electron gives:

\[
\text{H}_2\text{O}^+ + e^- \rightarrow \text{OH} + \text{H}(^2\text{S}) + 7.5 \text{ eV} \\
\rightarrow \text{O}(^3\text{P}) + \text{H}_2 + 7.6 \text{ eV} \\
\rightarrow \text{O}(^3\text{P}) + \text{H}(^2\text{S}) + \text{H}(^2\text{S}) + 3.04 \text{ eV} \\
\rightarrow \text{O}(^1\text{D}) + \text{H}(^2\text{S}) + \text{H}(^2\text{S}) + 1.07 \text{ eV}
\]

where the energies are given for OH and H$_2$ in their zeroth vibrational levels and with negligible rotational energy. The ion storage ring experiments [18, 19] indicate a strong preference for three-body breakup, while the branching ratios from flowing afterglow indicate the two-body breakup dominates [20]. In addition, DR of HDO$^+$ shows a 2:1 preference to break the OH rather than the OD bond. There also exists data on the energy and angular distributions of the fragments in the case of three-body breakup at ‘zero’ energy. There is however no theory available for this system, no experimental data available at other energies, and limited information as to the branching between the final states of the O atom fragment. The existence of the three-body channel indicates that one must go beyond a simple one-dimensional picture in this system. The limited angular fragmentation pattern [19] also suggests it will be necessary to use a full three-dimensional surface to understand the dynamics of this reaction.

![Figure 4](image_url)

**Figure 4.** Potential energy curves for resonant states of H$_2$O compared to the ground state of the ion as a function of (left) symmetric stretch and (right) asymmetric stretch. The solid curve is the ground state of the ion, the dotted curves and dashed curves are resonances that are members of two separate Rydberg series that converge to different states of the ion. The curves have been diabatized.

We have carried out preliminary fixed nuclei Complex Kohn calculations on water to obtain the potential energy surfaces for the low-lying resonant states. The results for these calculations are shown in Figure 4 where the resonant states are shown compared to the ion. These
calculations were carried out as a function of symmetric stretch (shown on the left side of the figure), where the bond angle is held fixed at the equilibrium values and both O–H bond distances are changed together. Also we show results as a function of asymmetric stretch, where again the bond angle is fixed, but now one O–H bond distance is fixed and the other O–H is varied. These calculations show the existence of a number of resonant states that exhibit favorable crossings with the ion. In both symmetric and asymmetric stretch, there exist resonances that are members of two separate Rydberg series that converge to different excited states of the ion, and experience a strong interaction near the Franck Condon region. The curves shown have been diabatized by following the leading term in the configuration-interaction wave function to show the interaction. Further calculations are needed to form the three-dimensional potential energy surfaces and to compute the dynamics.

5. Summary
As we have shown in these examples, electron resonances are ubiquitous in low-energy scattering from molecules and molecular ions and provide an efficient path for channeling energy into nuclear motion. In order to treat this process accurately, ab initio theory requires both an accurate treatment of electronic scattering and nuclear dynamics. This is now possible for diatomic and small polyatomic systems. We have also show that in order to understand how energy flows in a polyatomic systems it is critical to go beyond one-dimensional models. Much work is still needed, both experimentally and theoretically to truly understand these critical collision processes.

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