Resonant enhanced electron impact dissociation of molecules

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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. We have carried out calculations on the resonant
process leading to dissociative attachment and dissociative recombination. We separate the
problem into two steps. First, the resonance parameters are obtained from accurate electron
scattering calculations using the Complex Kohn variational method. Then these parameters are
used as input to the dynamics calculations. We will illustrate the method with two examples,
dissociative attachment in CO₂ and dissociative recombination in O₂⁺.

1. Introduction
In the past, both theory and experiment have been limited in their study of how energy
flows in a reaction following electron impact. In early experiments, the initial state of the
molecule or molecular ion was unknown or was an admixture of states often, in the case of a
molecular ion, not even in a Boltzmann distribution. The experiments measured total cross
sections or rate coefficients. This allowed theory to average their state-to-state results, often
averaging out errors in the calculations. As experiments have improved, the tests on theory have
become more stringent. Modern experimental techniques such as COLTRIMS (cold target recoil
ion momentum spectroscopy) sometimes referred to as a 'reaction microscope', allow detailed
measurements of the dynamics of the reaction. It is now possible to record, in coincidence,
the momenta of all charged molecular fragments. These studies are an excellent probe of the
dynamics in the interaction of electrons with molecules and the subsequent flow of energy
between the vibrational modes of the system. These measurements pose a new challenge to
theoretical predictions. For dissociative electron attachment and vibrational excitation, detailed
final state distributions, including angular distributions, are available with well-determined
initial targets and well-defined energies. We can now obtain a time-dependent map of the
reaction, watching how the initial energy of the electron couples to the molecular system,
how it is interchanged among the degrees of freedom of the system and the effect of this
interchange on the dynamics and outcome of a variety of scattering processes. Recent dynamical
studies [1] have shown that dissociative electron attachment (DEA) to fundamental polyatomic
systems can exhibit complex electronic and nuclear dynamics involving symmetry breaking target deformations [2] and, in some cases, conical intersections [3]. In the case of dissociative recombination, molecular ion storage rings have allowed the cooling of the molecular ion target and the control of the electron-molecular ion collision energy. In addition, it is possible to use fragment counting imaging detectors[4] to determine the final state branching ratios.

In the case of non-resonant electron collisions with a molecule, there is usually inefficient transfer of energy from the electron into the motion of the nuclei, leading to little vibrational excitation or dissociation. This is due to the large difference in mass between the electron and the nuclei. However, in certain special 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 leads to a large 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. This can lead to resonant vibrational excitation and dissociative attachment and recombination.

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 follow the comparable calculations at fixed internuclear geometries to determine the resonant energy surfaces and the corresponding surface of autoionization widths, using the Complex Kohn variational method. We then study the dynamics using either time-independent methods (usually for diatomic systems) or time-dependent wave packet methods for polyatomic systems with multiple degrees of freedom.

2. CO\textsubscript{2} Dissociative Electron Attachment

The first example will be the dissociative electron attachment to carbon dioxide. Most work on this system, both experimental and theoretical have concentrated on the short-lived \(^2\Pi_u\) state near 4 eV. This is a shape resonance which can be well-described as a state with the extra electron in the lowest unoccupied (\(\pi_u\)) orbital. This resonance provides the dominant mechanism for vibrational excitation. Scattering calculations [5] have shown that the \(^2\Pi_u\) resonance becomes electronically bound for configurations where the CO bonds are symmetricaly stretched and that CO\textsubscript{2} \(^-\) ion is stable for bent geometries. Sommerfeld et al. [6] has shown, that this stable anion correlates with a second, lower energy \(^2\Sigma^+_1\) state which, in linear geometry, becomes a virtual state that dominates electron scattering below 1 eV [7]. Recent experiments at LBL have shown that the dominant DEA channel in CO\textsubscript{2} is observed at 8.2 eV[8]. Since this energy is less than the 10.0 eV required to produce electronically excited CO\textsuperscript{A} + O\textsuperscript{−}, the 8.2 eV resonance must necessarily result in electronic ground-state products. However, there are only three electronic states that can correlate to the CO(\(^1\Sigma^+\)) + O\textsuperscript{−}\(^{(2}\Pi\)) asymptote. One is the \(^2\Sigma^+_1\) state that, in linear geometry, becomes the virtual state. If the \(^2\Pi_u\) resonance accounts for the other two states, how can the dominant DEA channel at 8.2 eV also produce ground state products?

In order to understand the experiments and understand the mechanism leading to DEA at 8.2 eV we carried out both \textit{ab initio} electronic structure and fixed-nuclei electron scattering calculations. The results of these calculations are summarized in Figure 1a, which shows a cut through the potential energy surfaces in linear geometry where one CO distance is fixed and the other varied. In addition to the \(^2\Pi_u\) anion, we find a doubly excited (\(^{2}\Pi_{g}\sigma^2\)) \(^2\Pi_g\) negative ion state, whose parent is the \(^3\Pi_g\) excited state of the neutral target. We note that near the equilibrium geometry of the neutral, the \(^2\Pi_u\) state lies below all the electronically excited CO\textsubscript{2} states and can thus only autodetach into the e\textsuperscript{−} + CO\textsubscript{2} (X\(^1\Sigma_g^+\)) continuum. The surprising
result is that it is the $^2\Pi$ Feshbach state, along with the $^2\Sigma^+$ virtual state, that correlate with CO$(^1\Sigma^+)$ + O$^-$ ($^2P$) in linear geometry. There is a sharp avoided crossing between the $^2\Pi$ shape resonance and the $^2\Pi$ doubly excited state in linear geometry, the former correlating with a short-lived CO$^-$, $^2\Pi$ anion + O ($^1D$). There is in fact a conical intersection between the $^2\Pi$ states close to the point where they avoid in linear geometry.

To further characterize the doubly excited state, we carried out fixed-nuclei complex Kohn scattering calculations with the same prescriptions for constructing the N-electron target states and N+1-electron scattering states that were employed in the structure calculations. Figure 1b shows the $^2\Pi_g$ component of the elastic cross section at equilibrium geometry near the resonance energy. A Breit-Wigner fit to the results confirmed the resonance to be extremely long-lived, with a width of $\sim 0.004$ eV. We must emphasize that these results are for a single geometry. When convoluted over vibrationally weighted geometries in the Franck-Condon region, no sharp features would be expected to be seen in the elastic cross section, which explains why the observed 8.2 eV DEA peak is not visible in the transmission spectrum [9].

In order to compare with the observed laboratory-frame angular distributions, we calculate the entrance amplitude, formally defined as $V(\theta, \phi; S) = \langle \Psi_{bg}^+ (\theta, \phi; S) | H_{el} | \Psi_{res} (S) \rangle$, where $\Psi_{bg}$ is a background scattering function with a plane-wave incident on the target in the direction $\theta, \phi$, $\Psi_{res}$ is the resonance wavefunction, $H_{el}$ is the electronic part of the Hamiltonian and $S$ labels the internal coordinates of the molecule. The electron attachment probability, a function of $\theta$ and $\phi$ expressed relative to the dissociation axis in the molecular frame, is computed from the squared modulus of the entrance amplitude, which is obtained from an analysis of the calculated fixed-nuclei S-matrix [10]. If the axial recoil approximation is valid, the laboratory angular distribution is obtained by averaging the attachment probability over initial and final target rotational states, which eliminates its dependence on $\phi$.

In order to include the zero-point bending and asymmetric stretch motion we obtained the entrance amplitudes from scattering calculations with the nuclei located at their root-mean square (RMS) values, assuming harmonic asymmetric stretch and bending potentials. Figure 2 shows the calculated entrance amplitudes at the RMS geometries. Figure 3 shows a comparison
Figure 2. (Color online) Entrance amplitudes for CO$_2$ DEA through the $^2$II Feshbach resonance. Left to right: real and imaginary parts of the entrance amplitude calculated at RMS values of bend and asymmetric stretch (see text).

Figure 3. (Color online) Angular distributions for CO$_2$ DEA through the $^2$II Feshbach resonance. Left to right: calculated O$^-$ angular distributions at equilibrium and RMS geometries; comparison of calculated and measured angular distributions (see text).

between the angular distribution computed at the equilibrium and RMS geometries. The observed asymmetry clearly implies that there must be post-attachment bending involved in the dissociation dynamics. To show this effect, the rightmost panel of Fig. 3 shows results (labelled ‘convolved’) in which the angular distribution is calculated by adding 3 degrees to the axial recoil angle and convolving the computed values with a 55$^\circ$ FWHM Gaussian distribution. The agreement with the experimental distribution at 0.7eV O$^-$ KE is quite good. These results indicate that it is likely that the electron attaches preferentially on the stretched side of the molecule and subsequent dynamics involve a strong breakdown of the axial recoil that broadens the two peaks.

This shows again that, even with small polyatomic targets, dynamics beyond one-dimensional
models are needed to fully characterize the dissociation mechanism. Our results, coupled with the momentum imaging spectroscopy clearly show that the 8.2 eV DEA peak in CO$_2$ is initiated by electron attachment to a dissociative, doubly excited $^2\Pi$ state that interacts with a lower $^2\Pi$ shape resonance through a conical intersection and dissociates to electronic ground-state products. Mapping out the conical intersection(s) is complicated since bending breaks the degeneracy of the $^2\Pi$ states, resulting in a pair of $A'$ and $A''$ states with different topologies. In order to understand this process, further calculations, both scattering and structure are needed to fully characterize the surfaces. In addition, dynamics in three-dimensions, including the coupling between the resonant surfaces is required. This will be the subject of our future work in this area.

3. O$_2^+$ Dissociative Recombination

The dissociative recombination of O$_2^+$ has a long history. For a recent review see reference [4]. It is an important process in the modeling of planetary atmospheres. Not only the total cross section as a function of energy for the low-lying vibrational states is needed for these modeling efforts, but also the branching into the various atomic states. Most sources of O$_2^+$ are not vibrationally cold, which has complicated the interpretation of experiments. Much of the theoretical work has concentrated on the branching into the O($^1S$) atomic state, which is responsible for air-glow in the Earth’s atmosphere.

The ground state of the oxygen molecular ion is $^2\Pi_g$

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\sigma_u)^2(3\sigma_g)^2(1\pi_u)^4(1\pi_g)$$

There are low-lying $\pi_g$ and $\sigma_u$ orbitals, giving rise to a number of low-lying resonant states of valence character, which correlate to the low-lying atomic states of O, $^3P$, $^1D$ and $^1S$. We carried out a series of Complex Kohn scattering calculations at fixed bond distance and fit the eigenphase sum to a Breit-Wigner form to determine the position and widths of these resonances. These calculations were coupled with quantum chemistry calculations to determine the potential energy curves once the resonances have crossed. These results were compared to the results of Saxon[11] after the curves have crossed the ion and were found to be in excellent agreement. Multiple resonances were found. The case of scattering in $^3\Pi_u$ symmetry was quite interesting. As can be seen in Figure 4, the eigenphase sum shows a single broad resonance that crosses near the equilibrium bond distance as well as a number of sharp resonances. This can be contrasted to the case of scattering in $^1\Sigma_u^+$, shown in Figure 5, where there are fewer resonances and no broad resonances.

We then used a time-independent, non-local treatment of the dynamics on the adiabatic curves with no couplings between them to determine the cross section. Theoretical treatments of dissociative recombination are generally based on rigorous resonance scattering theory [12], 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. The dynamics of this system is governed by the nuclear wave equation at total energy $E$,

$$(E - K_R - V_{res})\xi_\nu = \phi_\nu$$

where $K_R$ is the nuclear kinetic energy operator, and $\xi_\nu$ is the nuclear wave function associated with the electronic resonance state.

The driving term for the nuclear wave equation, or “entry amplitude”, $\phi_\nu$ is defined as

$$\phi_\nu(R) = \left(\frac{\Gamma(R)}{2\pi}\right)^{1/2}\eta_\nu(R),$$

where $\Gamma(R)$ is the nuclear potential energy function, $\eta_\nu(R)$ is the nuclear wave function, and $\nu$ is the electronic state index.
Figure 4. (Color online) Left: Eigenphase sum for scattering in $^3\Pi_u$ symmetry for three bond distances, red $R=1.8$ bohr, blue $R=2.0$ bohr and green $R=2.33$ bohr. Right: Potential energy curves, black $^2\Pi_g$ state of $O_2^+$, red, resonant states $O_2^*$, $^3\Pi_u$ symmetry.

Figure 5. (Color online) Left: Eigenphase sum for scattering in $^1\Sigma_u$ symmetry for three bond distances, red $R=1.8$ bohr, blue $R=2.0$ bohr and green $R=2.2$ bohr. Right: Potential energy curves, black $^2\Pi_g$ state of $O_2^+$, red, resonant state $O_2^*$, $^1\Sigma_u$ symmetry.

where $\eta_{\nu}$ is the initial vibrational wave function of the ion target.

Since many of the resonances cross at low energies, it is necessary to go beyond the local model and use the nonlocal versions of these theories. In this case, $V_{res}$ is a complex, energy-dependent, nonlocal potential, defined as

$$
V_{res}(R, R') = E_{res}^{\text{open}}(R)\delta(R - R') - i\pi \sum_{\nu} U_{\nu}(k_{\nu}, R)U_{\nu}(k_{\nu}, R').
$$

(3)

$E_{res}$ is the real part of the potential energy curve of the resonance from electron-molecule scattering calculations (or bound-state calculations in its bound region), and $k_{\nu}$ is the momentum of the scattering electron when the molecule is left in the final vibrational state $\eta_{\nu}$. The sum
runs over the energetically open vibrational states of the ion.

Following Hazi et al. [13] we approximate \( U_\nu(k_\nu, R) \), the matrix element coupling the resonance to the non-resonant background associated with a vibrational level \( \nu \), as

\[
U_\nu(k_\nu, R) = \left( \frac{\Gamma(R)}{2\pi} \right)^{1/2} \eta_\nu(R)
\]  

At sufficiently high incident energy one can assume that the sum over vibrational states in Eq. 3 is complete to show that in the high-energy limit the nonlocal potential produces the local width function, where

\[
V_{res}(R) = E_{res}(R) - i\Gamma(R)/2
\]

The position and width of the resonance are \( E_{res} \) and \( \Gamma \) respectively.

When we go beyond the local approximation, we have made use of a finite-element method, implemented using a discrete variable representation (DVR) [14]. In the case of dissociative recombination, the generalization of this method to use exterior complex scaling (ECS) gives the additional advantage of avoiding the need for explicit imposition of asymptotic boundary conditions. Details of this very efficient numerical representation can be found in the work of Rescigno and McCurdy [14], the recent review of McCurdy et al. [15], and the references therein.

The ECS transformation to the equation whose solution now describes a purely outgoing wave is given by

\[
R \rightarrow T(R) = \begin{cases} 
R & R < R_0 \\
R_0 + (R - R_0)e^{i\eta} & R \geq R_0 
\end{cases}
\]

where \( R \) is the internuclear distance, while \( R_0 \) and \( \eta \) are fixed parameters of the transformation. In this way, the transformed Schrödinger equation is solved on a grid that extends beyond \( R_0 \), into the region in which the outgoing wave falls off exponentially. Making the radius \( R_0 \) large enough to enclose the entire interaction region allows the collision dynamics to be extracted from the region inside that radius, where coordinates are real.

A solution of Eq. 1 is constructed that is regular at the origin and subject to purely outgoing boundary conditions. The integrated cross section for dissociative electron recombination from vibrational state \( \nu \) is then expressed as

\[
\sigma_{\nu \rightarrow DR} = g^2 \frac{2\pi^2}{k_\nu^2} \frac{K}{\mu} \lim_{R \rightarrow \infty} |\xi_\nu(R)|^2
\]

where \( g \) is the ratio of resonance state to initial state statistical weights and \( K^2/2\mu \) is the asymptotic kinetic energy of the dissociated fragments with reduced mass \( \mu \), i.e.,

\[
K^2/2\mu = E - V_{res}(R)|_{R \rightarrow \infty}.
\]
Figure 6. (Color online) Left: Total dissociative recombination cross section from ground vibrational state of $\text{O}_2^+$ compared to the experimental results from CRYRING. Right: Variation of the total dissociative recombination cross section as a function of vibrational excitation.

the $^3\Pi_u$ symmetry, there will be strong mixing between the states. Since one state goes to the $^3\Pi_u$ limits and other to the $^1\Sigma_u^+$ limits, the branching ratios will be modified by these couplings. In the case of the $^1\Sigma_u^+$ symmetry, leading to $^1\Sigma_u^-$, there is only one resonance state that contributes, so the effect will be smaller. To characterize the branching ratios, further work is needed to determine these couplings and include them in the dynamics.

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