Resonances in dissociative recombination: trends and patterns

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Abstract. In dissociative recombination, the kinetic energy of the incident electron is transferred into excitation of the electrons of the target ion and then into kinetic energy of the fragments. In general, this proceeds via a resonance where the electron is temporarily trapped by the ion, leading to efficient energy transfer. The study of dissociative recombination is the study of these resonances, Rydberg states converging to the ground and excited states of the ion. For a number of systems, we have studied the electronic states involved in dissociative recombination, including the ground and excited states of the ion, the resonant states and the bound Rydberg states of the system, by combining electron scattering calculations with multi-reference configuration interaction quantum chemistry calculations. We will report on trends and patterns in these resonance states. We will discuss studies of dissociative recombination of the rare-gas ions, moving down the periodic table from He\textsuperscript{+} to Ne\textsuperscript{+} to Ar\textsuperscript{+}, where the ground electronic state of the ion is constant, but its polarizability increases. We will also present results on isoelectronic polyatomic systems, such as HCO\textsuperscript{+} and HCNH\textsuperscript{+}, as well as the effects of changing the electronic structure slightly such as HCN\textsuperscript{+}/HNC\textsuperscript{+} and H\textsubscript{2}CO\textsuperscript{+}.

1. Introduction

Electronic energy must be transferred into the kinetic energy of the nuclei in order for dissociative recombination to occur. The mass of the electron is more than 1800 times lighter than the mass of the hydrogen atom, and this mass ratio is even larger when heavier diatomics or polyatomics are considered. Therefore, the time scale for the electron collision is very different than the time scale for molecular motion, such as vibration. So in the case of non-resonant electron collisions with molecular ions, there would be inefficient transfer of energy. However, in the case of resonant collisions, the electron is temporarily attached to the molecular ion, changing the forces that the atoms in the molecule feel. This leads to an electron collision time which is commensurate with molecular vibration, allowing the electron collision to drive dissociation and vibration. Therefore the study of dissociative recombination is the study of the resonant states of the system.

Unlike the case of dissociative attachment, where there are only a handful of anion states, often only one that are involved in the process, dissociative recombination is dominated by series of Rydberg states. These resonances can include repulsive states, usually a Rydberg series converging to the first excited state of the ion. These are, in many cases, the resonances which are responsible for direct dissociative recombination. There is also an infinite series of Rydberg states converging to the ground state of the molecular ion. This leads to structure in the dissociative
recombination cross section as a function of initial electron energy. These structures are the signature of the indirect recombination process. In general, they can be assigned to excited rovibrational levels of bound Rydberg states with a ground-state ion core, which couple to the initial ground-state electronic continuum by non-adiabatic interactions only. In addition, these Rydberg states play a critical role in the non-crossing mechanism of dissociative recombination, seen in systems such as $\text{HeH}^+[1]$, $\text{H}_2^+[2, 3]$ and $\text{LiH}^+[4]$. In addition, there exists another class of resonances. These are members of a Rydberg series converging to higher excited states of the ion, generally referred to as core-excited states. These states are bound with respect to dissociation, if the ion to which the series converges is bound. They are coupled both to the electronic initial continuum and to the dissociative resonance states and tend to produce broader and more prominent structures in the dissociative recombination cross section[5, 6]. Since the energy dependence of the Rydberg states mirror that of the state of the ion to which they converge, the shape and position of the excited states of the ion can yield information about resonant states.

Our process for studying dissociative recombination divides the calculation into two parts. First we use electron scattering at fixed nuclear geometries to calculate the position and lifetime of the Feshbach resonances by fitting the eigenphase sum to a Breit-Wigner form. We then use standard quantum chemistry techniques at fixed nuclear geometries to calculate the potential energy curves for the bound Rydberg states and the resonance states (after they have crossed the ion ground state so they are electronically bound) and finally to diabatize the resonances. These calculations yield potential energy curves, quantum defects, and the couplings between the states, and between the states and the continuum (autoionization widths). Using this information as input we then calculate the quantum molecular dynamics leading to dissociative recombination. These calculations are carried out using Multi-Channel Quantum Defect Theory (MQDT)[7], wave packet methods[8], and for polyatomics, the Multi-Configuration Time Dependent Hartree (MCTDH) method of Meyer et. al.[9]

In the following sections, we will briefly describe a series of examples of such calculations and

**Figure 1.** Potential energy curves for $\text{He}_2^+$ ground and low-lying excited states and lower $\text{He}_2$ resonance states. Ground state of ion heavy solid line —— , excited states of ion dashed line - - - - , resonance states light solid line ——.

**Figure 2.** Potential energy curves for $\text{Ne}_2^+$ ground and low-lying excited states and lower $\text{Ne}_2$ resonance states. Ground state of ion heavy solid line —— , excited states of ion dashed line - - - - , resonance states light solid line ——.
In our first example, we consider dissociative recombination of electrons with the rare gas ions, He\(^{2+}\), Ne\(^{2+}\) and Ar\(^{2+}\). These systems have been previously studied\([10, 11, 12]\), the results are summarized here. The ground state, for these ions is:

\[
\text{[core]}(n\sigma_g)^2(n\sigma_u)
\]

For He\(^{2+}\), there is no core, for Ne\(^{2+}\), there are 16 electrons in the core, and and Ar\(^{2+}\) has 32 core electrons. The lowest excited ion state is:

\[
\text{[core]}(n\sigma_g)(n\sigma_u)^2
\]

for He\(^{2+}\) and Ne\(^{2+}\). In Ar\(^{2+}\), this is one of the low-lying excited states, but the lowest excited state is:

\[
\text{[core]}(n\pi_g)^3(n\sigma_u)^2
\]

Moving from He\(^{2+}\), Ne\(^{2+}\) to Ar\(^{2+}\), the polarizability of the molecule increases and the excited states drop in energy. This causes the resonance states to lower in energy also. This can be seen in Figures 1-3, where the ground state and first excited state of each ion and the low lying resonant states are plotted. Each curve is shifted such that the zero of energy for each system is the energy of the ground state of the ion at its equilibrium separation. Note that the first resonance of He\(^{2+}\) crosses at much larger internuclear distance, outside of the Frank-Condon region, while in the case of Ne\(^{2+}\), the state crosses just to the right of the equilibrium position, but in the Frank-Condon region. In the case of Ar\(^{2+}\), the curve drops further in energy, and now crosses at smaller distances. This effects the dissociative recombination cross section dramatically as can be seen in Figure 4, where the three systems are compared. He\(^{2+}\) has almost zero cross section at low energy, while Ne\(^{2+}\) and Ar\(^{2+}\) have a significant value even at the lowest energy studied. The cross section at the lowest energy studied for Ne\(^{2+}\) is higher than that of Ar\(^{2+}\) due to the more favorable crossing.
3. HCNH\(^+\)

The ground state of HCNH\(^+\) is a closed shell with \(^1\Sigma\) symmetry,

\[
(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)(1\pi)^4
\]

The low-lying excited states involve the excitation of an electron from the highest lying orbital \((1\pi)\) to higher orbitals,

\[
(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)(1\pi)^3(2\pi)
\]

and

\[
(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)(1\pi)^3(6\sigma)
\]

with symmetries \(^1,3\Sigma,^1,3\Pi\) and \(^1,3\Delta\).

Details of this calculation have been published\[13\]. The target wave function was constructed by first carrying out a self-consistent-field (SCF) calculation on the ion using a contracted set of triple zeta plus polarization (TZP) basis set. These orbitals were then used in a multi-reference Configuration Interaction (CI) calculation, where the lowest three orbitals were frozen, and all single and double excitations from a reference space generated by a full CI for eight electrons in the \(4\sigma,5\sigma,6\sigma,7\sigma,1\pi_{x,y},2\pi_{x,y}\) space. Natural orbitals were generated from averaging the density matrices for the lowest two states of the ion. The five lowest orbitals were frozen and the target states were determined from a full CI calculation in the natural orbital space of eleven orbitals with the largest occupation number. The basis set was expanded to include more diffuse orbitals. The Complex Kohn variational method\[14\] was used to study the electron scattering at fixed geometries. The position and lifetime of the Feshbach resonances was obtained by fitting the eigenphase sum to a Breit-Wigner form. Additional structure calculations were carried out to determine the dominant character of the states and to obtain the resonant curves after crossing the ion.

An example of the results are shown in Figure 5. We have plotted the ground and first excited state of the ion as a function of the C–H bond distance, keeping all other bonds frozen at their equilibrium geometry and in the second panel, the variation with N–H bond distance. Only the states with \(^1\Sigma\) symmetry are shown. The states have been diabatized using information from the configuration-interaction coefficients of the wave function. There are no crossings at low energy, but there are multiple resonances starting at approximately 3 eV. The resonance curves reflect the ion states to which they converge. The ion states change character and have several curve crossings as the bonds of the system are stretched. Future calculations will study the
structure and dissociative recombination mechanisms of the $\text{H}_2\text{CN}^+$ isomer, which has a similar geometry to the $\text{H}_2\text{CO}^+$ ion.

![Figure 6](image1.png)
![Figure 7](image2.png)

**Figure 6.** Potential energy curves for HCO$^+$ ground and low-lying excited states and HCO resonance states of $^1\Sigma$ symmetry. Ground state of ion heavy solid line ——, excited states of ion dashed line - - - -, resonance states light solid line ——.

**Figure 7.** Potential energy curves for HCO$^+$ ground and low-lying excited states, and HCO resonance states of $^1\Pi$ symmetry. Ground state of ion heavy solid line ——, excited states of ion dashed line - - - -, resonance states light solid line ——.

4. HCO$^+$

HCO$^+$ is isoelectronic to HCNH$^+$ and therefore has similar ground and low-lying excited states. Our level of calculation in this system is the same as in HCNH$^+$. Again, as in HCNH$^+$, the excited states of the ion lie approximately 10.5 eV above the ground state of the ion, and exhibit curve crossings between the lower energy states that are bound in the Frank-Condon region and higher lying dissociative states. These results are shown in Figures 6 and 7.

5. HCN$^+$/HNC$^+$

HCN$^+$ and HNC$^+$ have one fewer electron than HCO$^+$ and HCNH$^+$. In these systems, the $(1\pi)$ and the $(5\sigma)$ orbitals are very close in energy and switch positions between the two systems. The ground state of HNC$^+$ is:

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

with a low-lying excited state

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

There exists a series of Rydberg states converging to this excited state of the ion with configurations

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

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

with symmetries $^1\Sigma^+_1,^3\Pi$ and $^1\Delta,^3\Delta$. In contrast, 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

\[(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)\]

and a series of Rydberg states converging to this state,

\[(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(n\sigma)\]

\[(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)(n\pi)\]

with symmetries \(1\Sigma, 1\Pi\) and \(1\Delta\). Since the first excited state of the ion is low-lying, the resonances are also expected to be low in energy. Again, the level of calculation was similar to that of HCNH. The results of the calculation are shown in Figures 8 and 9.

These calculations were carried out in linear geometry and fixed C-N bond distance. Calculations which considered the variation in energy with the H--CN (or NC) distance fixed but for varying C–N bond distances showed no qualitative differences. Further calculations will study the effect of bend on the system, breaking the degeneracy of the \(\Pi\) states and allow the interaction of \(\Sigma\) states with one component of the \(\Pi\) states. It is interesting to note that although HCN and HNC are different chemical species, they represent two stable points on a three-dimensional potential energy surface. The effect of the bend must be considered to understand the dynamics of dissociation.

6. \(\text{H}_2\text{CO}^+\)

\(\text{H}_2\text{CO}^+\) has one more electron than \(\text{HCO}^+\) and \(\text{HCNH}^+\). This system is no longer linear, but bent, leading to \(C_{2v}\) not \(C_{\infty v}\) symmetry. The ground state of the ion is:

\[(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(1b_1)^2(2b_2)^1\]

The \((1b_1\text{ and }2b_2)\) which are roughly \(\pi\) orbitals, either oriented in or perpendicular to the molecular plane are close in energy, leading to a low lying excited state,

\[(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(1b_2)^2(1b_1)(2b_2)^2\]
The low-lying resonances in this system, consist of the Rydberg series converging up to this excited ionic state. These are shown in Figures 10 and 11.

The initial calculations on this system held all angles and bond distances fixed at the equilibrium geometry of the ground state of the ion and varied the C–O bond distance. Only the singlet resonant states have been calculated so far. These studies show a number of resonances, that as in HCO+ and HCNH+ interact, showing evidence of curve crossings as the C–O bond is stretched. Further calculations on this system are necessary to both understand how the triplet resonance states vary with C–O stretch, but also, how the resonances change as other bond distances and angles are modified.

7. Conclusions
Electron resonances are ubiquitous in the scattering of low-energy electrons from molecules and molecular ions. These resonances provide an efficient path for channeling energy from the electron collision into nuclear motion leading to dissociative recombination, vibrational excitation or resonant dissociative excitation. Dissociative recombination is driven by Rydberg states, either converging to the ground or excited states of the ion. Therefore, calculations on the ground and excited states of the ion can yield information about the resonance states. It is clear much more work remains in the study of both diatomic and polyatomic systems, particularly studies leading to information not just on total dissociative recombination cross sections, but branching ratios into the various excited fragment states.

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