General features of the dissociative recombination of polyatomic molecules

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Abstract. We discuss some aspects of a simple expression for the low-energy dissociative recombination cross section that applies when the recombination process is dominated by the indirect mechanism. In most previous applications, this expression has been applied to capture into vibrationally excited Rydberg states with the assumption that capture is always followed by prompt dissociation. Here we consider the dissociative recombination of larger polyatomic ions and electrons. More specifically, we consider capture into electronically core-excited Rydberg states, and begin to assess its potential importance for larger systems.

1. Introduction

Dissociative recombination of an electron and molecular cation can occur via a direct mechanism involving capture into a dissociative electronic state of the corresponding neutral molecule, or via an indirect mechanism involving capture into a resonant, highly excited state of the neutral molecule, followed by predissociation of that state into neutral fragments [1–4]. Often, one capture mechanism dominates the dynamics, and simplified expressions for the dissociative recombination cross section and rate can then be found. Several years ago, we reported a simplified expression for the low-energy dissociative recombination cross section of small polyatomic ions when the process is dominated by the indirect mechanism with capture into vibrationally excited Rydberg states [5–7]. Making use of the principles of quantum defect theory [8, 9], the key parameters that determine the recombination cross section from this expression can be extracted from spectroscopic or quantum chemical data on low-lying, bound Rydberg states of the neutral molecule. Using spectroscopic data, we showed that with this expression one could obtain good agreement with the observed dissociative recombination cross sections of H3+ + e−, as well as the related isotopically substituted systems [7]. As demonstrated in the pioneering work of Kokoouline et al. [10–12], the key factor in determining these cross sections is the Jahn-Teller mediated capture into vibrationally excited Rydberg states in which the degenerate ν2 vibrational mode is excited. We have also shown [6] that the Renner-Teller interaction involving the bending vibration of HCO drives the low-energy capture process for HCO+ + e−, and our simple expression for the

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dissociative recombination cross section is in reasonable agreement with detailed calculations of the cross sections [13–16], even though the results of all of the calculations are a factor of 2–3 lower than the experimental values. Recently, this simple two-channel expression for the dissociative recombination cross section has been extended to a three-channel model [17] in which the contributions of both the direct and indirect mechanisms can be included together, along with the interactions between the two mechanisms. This is important because one possible explanation for the discrepancy between the simple model and the experiments for HCO\(^+\) is that both the indirect and direct mechanisms contribute to the cross sections. However, the studies reported to date indicate that the direct mechanism should not be important at low energy because the calculated potential energy surfaces for the ground state ion and dissociative states of the neutral do not show any crossings near the equilibrium geometry of the ion [13–16, 18].

Indirect dissociative recombination can also occur via capture into Rydberg states converging to electronically excited states of the molecular ion [19, 20]. This process has been discussed by several groups [19] for the dissociative recombination of CH\(^+\) + e\(^-\). More recently, Guberman [20] has performed detailed calculations for this process in the recombination of N\(_2\)\(^+\) + e\(^-\). Guberman also discussed some general conditions under which indirect dissociative recombination via core-excited Rydberg resonances is likely to be important. In the present paper, we consider this indirect dissociative recombination process in larger polyatomic molecular ions, where the capture/stabilization/dissociation mechanisms may be somewhat different than in diatomic ions. In particular, we use the simple expression for the dissociative recombination cross section along with information from photoabsorption and photoionization studies to begin to assess the potential importance of this process in larger molecular ions.

2. Indirect capture into electronically core-excited Rydberg states

In many dissociative recombination experiments on larger molecular ions, the resolution of the collision energy has not been sufficient to resolve resonant structure. Assuming that a single Rydberg series contributes to the cross section, and averaging the cross section over the interval between series members, Mikhailov et al. [14] have derived a simple expression for the resonant dissociative recombination cross section:

\[
\langle \sigma \rangle = \frac{2\pi^2}{k_o^2} \left( \frac{\Gamma_{a,o} \Gamma_d}{\Gamma \Delta} \right),
\]

where \(k_o\) is the electron momentum in the continuum \(o\), \(\Gamma_{a,o}\) is the partial autoionization width of the capture state into the continuum \(o\), \(\Gamma_d\) is the predissociation width of the capture state, \(\Gamma\) is the total decay width of the capture state, and the spacing between series members, \(\Delta \sim 2R/n^3\), where \(R\) is the Rydberg constant and \(n\) is the principal quantum number of the resonance. In previous work, the partial autoionization width \(\Gamma_{a,o}\) was a vibronic width describing capture into vibrationally excited Rydberg states, whereas in the present case it is an electronic width describing capture into electronically core-excited Rydberg states.

If electron capture is assumed to be the rate-limiting step, i.e., the total ionization width into all channels \(\Gamma_a \ll \Gamma_d \sim \Gamma\), Eq. (1) becomes [14]

\[
\langle \sigma \rangle \approx \frac{2\pi^2}{k_o^2} \left( \frac{\Gamma_{a,o}}{\Delta} \right).
\]

Because \(\Gamma_{a,o}\) scales approximately as \(1/n^3\), the quantity in parentheses is approximately constant as a function of \(n\) and \(E\), and corresponds to the reduced partial width for the channel.
For efficient dissociative recombination via the indirect mechanism, the resonant state must be coupled (either directly or indirectly) to both the ionization and dissociation continua. The free electron interacting with the ion must excite the internal degrees of freedom of the ion core, so that the low-$\ell$, penetrating collisions will in general be most effective for resonant capture [21]. The balance between $\Gamma_{a,o}$ and $\Gamma_d$ is also important to maximize the dissociative recombination cross section. Ideally, $\Gamma_{a,o}$ should be large to maximize the capture rate. However, if it is too large, reionization of the resonant state will compete with dissociation, and thus reduce the overall cross section. On the other hand, if the dissociation width is much larger than the ionization/capture width (Eq. (2)), the molecule will dissociate before it has a chance to reionize. Thus, information on the relative and absolute magnitudes of $\Gamma_{a,o}$, and $\Gamma_d$ for the relevant low-$\ell$ Rydberg states is highly desirable.

Many of the low-$\ell$ states that provide the most efficient capture are accessible via optical excitation from the ground state of the corresponding neutral molecule. As a result, it is often possible to assess their behavior by using photoabsorption and photoionization data to provide insight into the values of $\Gamma_{a,o}$, and $\Gamma_d$. Of course, optical selection rules can limit what states are accessible, and the character of the MO from which the electron is ejected can strongly favor (or disfavor) certain series. Thus, such data are not expected to provide a comprehensive or quantitative assessment of the importance of dissociative recombination in these systems. However, these data certainly can show if at least some electronically core-excited resonances are likely to contribute to dissociative recombination in these molecules.

The comparison of photoabsorption and photoionization data allows the determination of the quantum yield for ionization [22]. Because the total energy of the recombining system is typically 10–15 eV, non-ionizing, non-radiative decay will ultimately lead to dissociation, and fluorescence is typically, though not always, much slower than non-radiative decay. Thus, at least for the states that can be accessed optically, comparison of the photoabsorption and photoionization spectra can provide information on the partial widths for ionization and dissociation.

The quantum yields for ionization in larger molecules have been discussed previously [22, 23], and the review of Berkowitz is instructive [22]. While the ionization quantum yield for resonances in diatomic and triatomic molecules varies from 0–1, for most large molecules Berkowitz [22] concludes that the super-excited resonant states do not autoionize substantially, and that dissociation is the dominant decay path. Nevertheless, Berkowitz acknowledges that some autoionization must occur, as evidenced by the signals in threshold photoelectron spectroscopy that occur in the Franck-Condon gap.

To estimate the dissociative recombination cross section, the partial dissociation width for all channels, $\Gamma_d$, is required, but the individual widths for different product channels are not necessary. However, more information is needed about the autoionization process than just the partial autoionization width ($\Gamma_a$) alone. Rather, what is really needed is the partial autoionization width into the continuum of the initial vibronic state of the ion ($\Gamma_{a,o}$). Unlike the case of purely vibronic capture, in the simplest approximation, the partial width for capture into a core-excited Rydberg state is determined by the product of an electronic factor and Franck-Condon factor between the corresponding vibrational level of the excited electronic state and the vibrational level of the vibronic ground state of the recombining ion [24]. Depending on the relative geometries of the two electronic states, this Franck-Condon factor can range from negligible to unity. However, a typical value is probably on the order of 0.1. Since the partial dissociation width is generally larger than the partial ionization width into all final states, $\Gamma_d$ will typically be much greater than $\Gamma_{a,o}$, and thus Eq. (2) will hold. Furthermore, even though $\Gamma_{a,o}$ is considerably smaller than $\Gamma_d$, it is still expected to be non-negligible, and thus lead to capture and dissociative recombination. As discussed by Lefebvre-Brion and Field [24], electronic autoionization (and the related process of spin-orbit autoionization) typically has a much greater total width ($\Gamma_a$) than vibrational autoionization. While the Franck-Condon factor between the resonant state and the vibronic ground state in electronic autoionization will generally result in a significantly smaller value of $\Gamma_{a,o}$, capture into electronically core-excited states is still expected to be significant when compared to...
capture into purely vibrationally excited state. As a result, dissociative recombination via electronically
core-excited states is likely to be important in many larger molecules.

For larger polyatomic ions, the dissociation process following electron capture is almost certainly
not as direct as in the case of a diatomic molecule. Indeed, stabilization against re-ionization is perhaps
most likely to occur through a radiationless transition from the resonant capture state to states with
lower electronic excitation and greater vibrational excitation. Because the density of such states can be
quite high at the total energy of interest (up to 10–15 eV), once such transitions occur, it is unlikely
that the molecule will make its way back to the initial resonance state, and thus the system will be
stabilized with respect to re-ionization. In this case, $\Gamma_d$ in Eq. (1) could be replaced with $\Gamma_{nr}$, the
non-ionizing radiationless transition width. This width will always be at least as big as $\Gamma_d$. Of course, in
isolated systems the total energy will still remain in the molecule (assuming radiative decay is slow),
and ultimately the molecule will dissociate. It would seem likely that larger molecules dissociate on
multiple electronic surfaces as relaxation to the electronic ground state progresses.

Finally, we briefly consider the location of the core-excited resonances. Assuming the recombination
process begins with a molecular ion in its ground electronic/vibrational state, the importance
of indirect recombination via electronically core-excited Rydberg states will depend on the
location of the resonances relative to the adiabatic ionization energy. Most medium- to large-
sized polyatomic ions have excited electronic states within $\sim 2$ eV of the ground state [25]. [For
example, to name just a few, the cations of ethane, propane, ethylene, propylene, methanol, aniline,
and phenol all have excited states within 2 eV of the ionization threshold [25]]. Using this value
and assuming a Rydberg series converging to this limit with a quantum defect of 0, the positions of
resonances converging to this limit that lie above the lowest ionization energy can be calculated by
using the Rydberg formula. For $n = 3, 4, 5, \ldots$, the binding energies relative to the excited state are
1.51 eV, 0.85 eV, and 0.54 eV, $\ldots$, respectively, corresponding to electron energies of 0.49 eV, 1.15 eV,
1.46 eV, $\ldots$, up to 2 eV relative to the ground state ion. Of course, the exact position of the resonances
will depend on the actual values of the quantum defects. Nevertheless, if, as seems likely, dissociative
recombination via these resonances is important, they could significantly affect the cross section at low
energy. The energy separation between the lowest energy resonances is sufficient to be resolved in many
dissociative recombination experiments. In this case, it is more appropriate to treat them as isolated
resonances with the standard formula:

$$\sigma_{\text{res}}(E) = \frac{4\pi}{k_0^2} \frac{\frac{1}{4} \Gamma_{a,o} \Gamma_d}{(E - E_{\text{res}})^2 + \frac{1}{4} \Gamma^2}, \quad (3)$$

where $E_{\text{res}}$ is the energy of the resonance. Of course, use of this expression ignores the complex
interactions between the electronically autoionizing resonances and the vibrationally autoionizing
resonances, which ultimately would be treated using methods similar to those described for CH$^+$ and
N$^+_2$, 19,20 and more generally in References [8] and [9].

3. Conclusion

We have considered some general features of dissociative recombination in larger polyatomic molecular
ions. While the arguments are qualitative, preliminary consideration of available experimental data
suggests that indirect dissociative recombination via electronically core-excited Rydberg states could
play a significant role at relatively low collision energies ($< 2–3$ eV) in many larger polyatomic ions.

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