Dissociative Recombination of Small Polyatomic Molecules

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Abstract. Simplified analytical expressions for dissociative recombination driven by the Jahn-Teller and Renner-Teller interactions are discussed. These expressions allow straightforward predictions of isotope effects, and the results are discussed for both H$_3^+$ and HCO$^+$ and their isotopomers. Although the predicted effects are generally in good agreement with experiment, discrepancies indicate areas worthy of more extensive investigation. Some general features of isotope effects in the dissociative recombination of other systems are also discussed.

1. Introduction

The dissociative recombination of an electron and a molecular ion involves the coupling of ionization and dissociation continua. As it was originally envisioned [1], this process can occur by capture of the electron into a dissociative electronic state of the neutral, resulting in the production of neutral fragments. Subsequently, it was realized that indirect processes can also play an important role in this process [2]. In this scheme, the electron is captured into a quasi-bound Rydberg state of the neutral, which is subsequently predissociated by a dissociative state. The accurate theoretical description of dissociative recombination is thus exceedingly difficult, and a full treatment of the process is limited to diatomic ions and a small number of polyatomic ions like H$_3^+$. Because dissociative recombination is important in a wide range of applications such as interstellar chemistry, planetary atmospheres, low-temperature plasmas, and plasma-assisted combustion [3], there is a significant desire to treat larger polyatomic systems. This situation provides motivation for the development of approximate approaches to predict dissociative recombination rate constants. We have recently developed such an approach to describe resonance capture processes at low collision energy ($<\sim$1eV) in systems like H$_3^+$ and HCO$^+$, where the dominant capture processes into vibrationally excited neutral Rydberg states are driven by the Jahn-Teller [4] and Renner-Teller interactions [5], respectively.

In this approximate approach, it is assumed that the indirect process for dissociative recombination dominates, that capture of slow electrons into vibrationally excited Rydberg states is the rate limiting step, and that dissociation is sufficiently fast that re-ionization can be ignored. Thus, the dissociative recombination cross section is equal to the capture cross section. The cross section for capture into vibrationally excited Rydberg states is related to the matrix elements for the inverse process of vibrational autoionization, that is, the decay of a vibrationally excited Rydberg state through the conversion of vibrational energy of the ion core into electronic energy of the Rydberg/escaping electron. The vibrational autoionization width is given by a variation of the formula originally developed by Herzberg and Jungen [6], but generalized to include processes driven by the Jahn-Teller or Renner-Teller effect. With this approach, the dissociative recombination cross section can be calculated with a minimal amount of input data. In our previous papers, these data were obtained from
spectroscopic analyses of low-lying, bound Rydberg states of the species of interest. However, the input data can also be obtained from quantum chemistry calculations, as has been demonstrated recently by Douguet and coworkers [7].

Such simplified calculations are in no way aimed at replacing high-level benchmark calculations like those of Kokoouline, Greene, and coworkers [8-11]. Rather, such calculations are meant to provide a first-order picture of what is expected, and thus provide a means of highlighting unexpected experimental results. One of the useful aspects of these approximate expressions is that they allow the simple prediction of isotope effects, which can then be compared with experiment. In contrast, for example, a fully developed calculation of the dissociative recombination cross section for D$_3^+$ requires nearly as much effort as the original calculation for H$_3^+$ [8]. In what follows, we focus on this aspect of the work. We begin by reviewing the expressions for electron capture in H$_3^+$, and then compare the predicted isotope dependence with experiment. The isotope dependence for H$_3^+$ vs. D$_3^+$ is straightforward to predict, but the isotope dependence for the mixed isotopomers H$_2$D$_1^+$ and HD$_2^+$ involve more subtle approximations. Comparison of these predictions with experiment serves to illustrate surprising aspects for the latter, and suggests areas for future experimental and theoretical efforts. Following the discussion of the isotopomers of H$_3^+$, we present a brief discussion of expectations for isotope effects in other systems, and compare these with experiment.

2. Dissociative recombination H$_3^+$ and its isotopomers

Kokoouline, Greene, and coworkers [9] showed that the Jahn-Teller interaction provides the key mechanism for electron capture by H$_3^+$ at low energies, and they performed high-level calculations that produced dissociative recombination cross sections that were for the first time in good agreement with experiment [10]. In our simplified description of dissociative recombination, we included only the linear Jahn-Teller effect, and were thus limited to capture processes with $\Delta v = 1$. However, the propensity rule for vibrational autoionization (the inverse of this capture process) suggests that $\Delta v = 1$ processes will dominate [6,12].

For efficient dissociative recombination, the electron partial wave must be penetrating, which requires $l = 0$ or $1$ for H$_3^+$. Of these, only the $l = 1$ channel has a degenerate component, pe', that can have a Jahn-Teller interaction, and our analysis is limited to that channel. The Jahn-Teller interaction is described by the parameter $D$, which measures the lowering of the potential by the linear Jahn-Teller interaction in units of the vibrational frequency, $\omega$. The quantity $D\omega$ is purely electronic and independent of isotope. For H$_3$ and D$_3$, analysis of bound state spectroscopic data by Herzberg et al. [13,14] allowed the characterization of the Jahn-Teller interaction in the 3pe' Rydberg states, and the isotopic independence of $D\omega$ was confirmed. This information was used to describe the Jahn-Teller interaction throughout the pe' channel by scaling the quantity $D^{1/2}$ by the spacing between levels $2R/n^3$, as required by quantum defect theory. Here $R$ is the Rydberg constant and $n^*$ the effective principal quantum number. With this scaled interaction, the golden rule expression for the vibrational autoionization rate of a single level is [4]:

$$\Gamma_a = 4\pi \frac{2R}{n^*^3}(D\omega^2)$$  \hspace{1cm} (1)$$

When used with the Breit-Wigner cross section formula, and averaged over all the resonances in a single series, this expression leads to an average cross section

$$\langle \sigma \rangle = \frac{2\pi^2}{k^2} \left( \frac{\Gamma_a}{\Delta} \right)$$  \hspace{1cm} (2)$$

where $\Delta = 2R/n^*$, the spacing between levels in the series, and $k$ is the wavenumber of the electron. The $1/n^*$ dependence of $\Delta$ is cancelled by the $1/n^*$ dependence of $\Gamma_a$, making the term in parentheses
in equation 2 constant. The cross sections are converted to rate coefficients by multiplying by the relative velocity of the collision. The isotope dependence of $<\sigma>$ is contained in $\Gamma$, and goes as $D\omega^2$. Because $D\omega$ is isotope independent, the isotope dependence simply reduces to that of $\omega$.

For $H_2D^+$ and $D_2H^+$, there is strictly speaking no true Jahn-Teller effect. However, the electronic surfaces have the same shape and similar $\Delta v = 1$ couplings between the surfaces. Although the degenerate $\nu_2$ vibration of $H_3^+$ and $D_3^+$ is split into two components in $H_2D^+$ and $D_2H^+$, the splittings are quite small (~130 cm$^{-1}$ and 110 cm$^{-1}$, respectively, out of ~2000 cm$^{-1}$). As a result, we use the $D\omega$ value from the spectroscopic analysis of $H_3$ and $D_3$ for all four isotopomers, and use the average $\omega$ values for $\nu_2$ and $\nu_3$ in $H_2D^+$ and $D_2H^+$.

![Figure 1](image.png)

Figure 1. The rate coefficients for the four isotopomers of $H_3^+$ calculated by using equation 2 and spectroscopic data for the required input parameters. The drop in the cross section occurs at the energy of the fundamental frequency of the corresponding $\nu_2^+$ vibration of the ion.

Figure 1 shows the rate coefficients for the four isotopomers as predicted by using equation 2, the value of $D\omega$ from Herzberg et al. [13,14], and the experimental vibrational frequencies for the ions. Two features of these curves deserve mention. First, the rate increases with decreasing mass of the ion. This result is consistent with the expectation that vibrational excitation in electron-ion collisions is more difficult for heavier molecules. Second, the rate coefficients drop to zero at the $\nu_2^+ = 1$ vibrational threshold. Because we consider only $\Delta v = 1$ processes, there is no mechanism to capture higher energy electrons. Although other mechanisms exist for the capture of higher energy electron, the $\Delta v = 1$ propensity rule suggests that the cross sections will fall considerably at the $\nu^+ = 1$ thresholds if capture into vibrationally excited Rydberg states is a dominant mechanism.

In the experimental determination of dissociative recombination cross sections and rate coefficients, there is typically a finite spread in the velocity distribution, and in ion-beam and storage ring experiments, the longitudinal and transverse velocity spreads are typically different. Thus, the theoretical cross sections must be convoluted with this velocity distribution to make a useful comparison with experiment. When this convolution is made, the agreement of the $H_3^+$ curve in Figure 1 with the experimental data is quite good, as seen in figure 2 of reference [4]. Figures 2 - 4 show the comparison of the convoluted theoretical curves and the experimental data for $H_2D^+$, $D_2H^+$,
an \( D_3^+ \), respectively [16,17]. Overall, the agreement is quite good, but several features are evident that deserve further consideration.

First, while the magnitude of the rate coefficient is reproduced extremely well for \( H_2D^+ \), the experimental curve [16] shows no drop near the \( v_2^+ = 1 \) threshold, a feature that is evident in all of the other isotopomers. The otherwise excellent agreement between experiment and theory suggests that this might be an experimental issue. Indeed, the \( H_2D^+ \) cross section is the most difficult to measure due to interferences from \( D_2^+ \).

The second issue is that the \( D_3^+ \) data [16] appear to have a much larger velocity spread than originally specified. For figure 4 we have used the velocity spread chosen by Kokoouline and Greene [8] in their high-level calculation of \( D_3^+ \). Again, the overall agreement between the simple calculation and the experiment is quite good.

Finally, the last issue is that the experimental data for \( D_2H^+ \) [17] show a much higher rate coefficient than the corresponding data for the other isotopomers. Indeed, the \( H_3^+ \), \( H_2D^+ \), and \( D_3^+ \) data follow the predicted trend of decreasing rate coefficients. In contrast, the \( D_2H^+ \) rate coefficients actually lie higher than both \( H_2D^+ \) and \( H_3^+ \). While this observation suggests that the experimental results might be flawed, a new storage ring experiment [18] is in excellent agreement with (actually
slightly higher than) the earlier measurements. This observation thus suggests that the dissociative recombination mechanism for D₂H⁺ may involve additional processes.

The observations on the isotopomers of H₂⁺ demonstrate the utility of simple formulae like equation 2. While such equations cannot be expected to reproduce the detailed experimental results, they provide a baseline from which to consider the experimental results, and thus highlight features or issues of real importance where the expectations break down, and where there is still more work to be done.

3. Dissociative recombination of HCO⁺ and DCO⁺

In a series of papers, Mikhailov et al. [15] and Douguet et al. [19,20] have performed an ever improving series of calculations on the low-energy dissociative recombination of HCO⁺ and DCO⁺. Key to these calculations was the realization that the dissociative recombination process was dominated by the indirect mechanism involving capture into vibrationally excited Rydberg states, and that the Renner-Teller interaction in the bending vibration is the driving force for the electron capture process. This observation led us to consider a simplified description for dissociative recombination in HCO⁺ that is similar in spirit to the one developed for H₂⁺. In particular, it was assumed that electron capture was the rate-limiting step in the dissociative recombination process, that capture driven by the Renner-Teller interaction in the πτ channel was the dominant factor, and that the parameters required to describe the interactions could be obtained by properly scaling parameters extracted from the spectroscopic analysis of low-lying, bound Rydberg states of HCO. The dissociative recombination cross section can be written in the same form as equation 2, but with the autoionization width given by a somewhat more complicated expression describing the Renner-Teller interaction.

The Renner-Teller interaction is described by using the three-state model of Gaugayocq and Jungen [21] adapted to the quantum defect framework. The expression for the vibrational autoionization width in a single channel is given by:

$$
\Gamma_v = 2\pi \frac{2R}{n^3} \left[ \frac{d\mu_{\alpha/\beta}(Q_2)}{dQ_2} \right]_0^2 \left| \langle \ell\nu'\ell', K | Q_2 | \nu\nu'^* \ell', K \rangle \right|^2.
$$

Here, $\mu_{\alpha/\beta}(Q_2)$ is an off-diagonal element of the quantum defect matrix describing the Renner-Teller interaction, $Q_2$ is the mass-weighted normal coordinate for bending, $\ell$ is the orbital angular momentum of the Rydberg electron, and $\lambda$ is the projection of $\ell$ on the molecular axis. The matrix elements of $Q_2$ can be evaluated in a harmonic oscillator basis [22], and the quantum defect matrix elements can be extracted from the spectroscopic data as discussed in [5]. As in the case of H₂⁺, only $\Delta v = 1$ processes were considered initially, although expressions for larger $\Delta v$ were also developed.

Expressions 2 and 3 provide dissociative recombination rates that are in excellent agreement with the theoretical rate coefficients of Mikhailov et al. [15]. The theoretical curves reproduce the shape of the experimental dissociative recombination data for HCO⁺ for energies below approximately 0.1 eV (the fundamental bending frequency of HCO⁺), but the magnitude of the theoretical cross section is too low by a factor of approximately 3-5. Above ~0.1 eV, the simple formula for the cross section goes to zero, while the experimental cross section does not fall nearly as fast. The improved calculations of Douguet et al. [19,20], which include the other vibrational modes of HCO⁺ as well as the effect of the large dipole moment of HCO⁺, lie only marginally closer to the experimental curve in the energy region below 0.1 eV, where our simplified approach gives a non-zero cross section. However, their new calculations do reproduce the slower falloff of the cross section above the $v^+ = 1$ bending threshold where the simplified approach, which includes only $\Delta v^+ = 1$ processes associated with the bending mode, predicts the cross section to go to zero. Interestingly, because the input parameters (and in particular the quantum defect matrices) in our earlier work were derived from experiment, they should have effectively already included the effects of the ion dipole moment.
Thus, the improved agreement observed by the isotope effect can be readily evaluated. The mass dependence of the vibrational frequencies of HCO$_3^+$ is assumed that the quantum defect derivative in equation 3 can be simplified. The quantum defect derivative is also squared in equation 3. In this expression, both the quantum defect derivative and the matrix element of the displacement, $Q_2$, have a mass dependence. In a harmonic oscillator basis, the mass dependence of the matrix element of $Q_2$ is contained in a factor of $1/\omega_2$, which is squared in the expression for the autoionization width. The mass dependence of the quantum defect derivative in equation 3 can be shown explicitly by changing from the mass weighted normal coordinate to the bending angle as follows:

$$\frac{d\mu_{\partial \rho/\gamma_2}}{dQ_2} \cdot \frac{d\mu_{\partial \rho/\gamma_2}}{dp} = \frac{m_{H}m_{C}m_{O}^2 \Gamma_{\mathrm{HC}}^2}{m_{H}m_{C}^2 r_{\mathrm{HC}} + m_{H}m_{O}^2 (r_{\mathrm{HC}} + r_{\mathrm{CO}})^2 + m_{C}m_{O}^2 r_{\mathrm{CO}}^2} \cdot \frac{d\mu_{\partial \rho/\gamma_2}}{dp}.$$  \hspace{1cm} (4)

In this expression, $\rho$ is the bending angle, the $m_i$ are the masses of the different atoms, and $r_{ab}$ is the bondlength between a and b. The quantum defect derivative with respect to $\rho$ is an electronic quantity that is independent of the atomic masses. If it is assumed that $r_{\mathrm{HC}} = r_{\mathrm{DC}}$ in HCO and DCO, respectively, and that $r_{\mathrm{CO}}$ is the same in both species, the isotope effect on the quantum defect derivative can be readily evaluated. The quantum defect derivative is also squared in equation 3.

Using the known vibrational frequencies of HCO$^+$ and DCO$^+$, Equation 2 predicts the dissociative recombination cross section for HCO$^+$ will be 1.26 times faster than that for DCO$^+$. This value can be compared with both previous theory and experiment. In particular, Mikhailov et al. predicted the dissociative recombination rate for HCO$^+$ is ~30% higher than that for DCO$^+$, in good agreement with the present result. Later, the improved calculations of Douguet et al. [19] gave a rate for HCO$^+$ that was only ~10% higher than that for DCO$^+$. To our knowledge, there are only two measurements of the thermal rates for the dissociative recombination of HCO$^+$ and DCO$^+$. Adams et al. [23] reported thermal rates $\alpha$ (95 K) that are ~10% higher for HCO$^+$ than for DCO$^+$, while Korolov et al. [24] reported thermal rates $\alpha$ (300 K) that are ~18% higher for HCO$^+$ than for DCO$^+$. In any event, the simple model discussed here appears to provide a reasonable first order estimate of the isotope effect in this system. Storage ring measurements for DCO$^+$, and perhaps new measurements for HCO$^+$, are expected to provide more insight into this behavior.

4. Isotope effects in the dissociative recombination of other systems

Capture into vibrationally excited Rydberg states is generally expected to show isotope effects, particularly in hydride ions. However, the relatively simple isotope effects observed in H$_2^+$ and HCO$^+$ will not necessarily be observed in larger polyatomic ions. In particular, because the mass dependence can depend on the vibrational mode, the isotope effect may become more complicated when capture occurs through multiple vibrational modes. Nevertheless, if one mode dominates the capture process, the observed isotope effect in the dissociative recombination cross section may still have a relatively simple form. Indeed, experimental data on several small polyatomic ions do show relatively simple isotope effects.

As an example, between approximately 0.1 and 0.3 eV, the dissociative recombination rate for H$_2$O$^+$ is approximately 40% higher than that for D$_2$O$^+$ [25]. Above 0.3 eV, the D$_2$O$^+$ cross section falls off at slightly lower energy than the H$_2$O$^+$ cross section, owing to the smaller vibrational frequency of the former and the decreased efficiency for capture with $\Delta \nu > 1$. However, below about 0.1 eV, the two cross sections are nearly equal, which suggests some other effect may be important at very low energies.
In contrast, up to the \( v' = 1 \) vibrational thresholds, the dissociative recombination rate for NH\(_4^+\) is consistently nearly a factor of two greater than that for ND\(_4^+\) \[26\]. Similarly, in the same low-energy region, the dissociative recombination rate for CH\(_5^+\) is also approximately a factor of two greater than that for CD\(_5^+\) \[27\]. The simplicity of the isotope effect suggests that a small number of vibrational modes dominate the capture process. The direction of this isotope effect is also consistent with expectations, but it remains to be seen if it can be reproduced either with simple models or high-level calculations. As a final example, the dissociative recombination of the protonated ammonia dimer shows a somewhat unexpected isotope effect, with the cross section for D\(^+(\text{ND}_3)_2\) actually somewhat greater than that for H\(^+(\text{NH}_3)_2\) for all energies below \(~0.3\) eV \[28\]. In contrast, the protonated ammonia trimer shows the expected behavior, with the H\(^+(\text{NH}_3)_3\) cross section above the D\(^+(\text{ND}_3)_3\) cross section. These observations suggest that additional work is necessary to understand the low-energy dissociative recombination of these species.

5. Conclusions

We have discussed how simple formula for indirect dissociative recombination via capture into vibrationally excited Rydberg states can provide insight into isotope effects in dissociative recombination cross sections. As discussed above, such formulae are not a substitute for high-level, first principles calculations of these cross sections. However, they can provide a valuable first order prediction that can be readily compared to experiment. In addition, for many larger hydrocarbon systems that may be important in planetary atmospheres, plasma-assisted combustion, and other applications, large-scale calculations are currently not feasible. In such cases, we believe these simple expressions can play an important role.

Finally, the simple formulae discussed here only include indirect capture into vibrationally excited Rydberg states, and are not expected to work well in all cases. In particular, if the direct process for dissociative recombination is important, the true cross section will deviate significantly from the prediction of the present model. Indeed, the direct capture process is known to be important for the dissociative recombination of NO\(^+\) \[29,30\], which is isoelectronic with HCO\(^+\). When the direct mechanism is important, the comparison of the predictions of the present model with experiment will provide an estimate of the relative importance of the two mechanisms.

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