Non-adiabatic effects in dissociative recombination of molecular ions

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Abstract. The article discusses the role of non-Born-Oppenheimer couplings in dissociative recombination (DR) of triatomic and diatomic molecular ions. For highly symmetric molecular ions the couplings play an important role, which results in a high rate for the indirect DR process. The non-Born-Oppenheimer couplings are particularly strong in highly-symmetric ions owing to the degeneracy of electronic and vibrational states at the equilibrium configuration of the nuclei. This is a generic property of polyatomic molecular ions, frequently associated with the Jahn-Teller or Renner-Teller effect, although analogous situations should occur in other species having conical intersections. In this respect, DR in triatomic ions differs significantly from DR in diatomic systems, where indirect DR is usually slow, although one exception to this rule is reviewed here. We concentrate here on the dissociative recombination of two highly symmetric triatomic ions: H$_3^+$ and HCO$^+$. In both ions, non-adiabatic couplings between doubly-degenerate vibrational and doubly-degenerate electronic states play an important role and produce a fast indirect DR. We also compare DR in these triatomic ions with the exceptional diatomic ion LiH$^+$, where non-adiabatic effects are strong due to f-mixing between p and d waves and this contributes to a high indirect DR rate. For all the systems considered, good agreement with experiments has been achieved, although some discrepancies remain to be resolved in the future.

1. Introduction
The theory of dissociative recombination for diatomic ions, e.g.

$$AB^+ + e^- \rightarrow AB^* \rightarrow A + B,$$

is relatively well-developed and has now successfully interpreted experimental DR rate coefficients for several such ions, including H$_2^+$ and its isotopologues, HeH$^+$, LiH$^+$, O$_2^+$, and NO$^+$. Historically, it was first suggested that only the direct DR mechanism could lead to a high DR rate[1]. In this mechanism, the dissociative surface crosses the ionic potential surface in the Franck-Condon region of the nuclear configuration space. In this case, the DR process can occur without proceeding through any other intermediate state AB$^*$. The importance of the indirect mechanism, which proceeds through intermediate Rydberg states (Eq. 1) that exhibit no such crossing between the ionic and the dissociative neutral potential curves, was recognized later [2] and found to be important in such diatomic systems as HeH$^+$ [3] and LiH$^+$ [4].

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The quantitative theory of polyatomic DR, e.g.,

\[ \text{ABC}^+ + e^{-} \rightarrow \text{ABC}^* \rightarrow \text{dissociation}, \quad (2) \]

arrived much later [5, 6], although earlier qualitative and semi-quantitative discussions exist in the literature [7]. For example, the high DR rate for the simplest triatomic ion \( \text{H}_3^+ \) proved difficult to interpret theoretically at electron energies below 2 eV. Although the experimental DR rate coefficient measured in storage rings was large (\( \sim 10^{-7} \text{cm}^3/\text{s} \) at 300 K), it was recognized [5] that direct DR is not possible in that energy range: there is no favorable crossing between the ground ionic potential surface and the dissociative state of the neutral molecule. This property seems to be the generic feature for closed shell polyatomic target ions: the dissociative state(s) of the neutral molecule usually lies (lie) far below the energy of the closed-shell target ion, which makes the Franck-Condon factor for direct DR quite small at low incident electron energies. The high value of the experimental DR rate coefficient, despite the absence of a favorable Franck-Condon factor, indicates that the non-adiabatic couplings driving the predissociation of \( \text{ABC}^* \) in Eq. (2) should play an important role. Nevertheless, the first attempts to interpret experimental data in \( \text{H}_3^+ \) at energies below 2 eV were not very successful [6]. The situation with another closed-shell molecular target ion, \( \text{HCO}^+ \), is similar: The experimental thermal DR rate is about \( \sim 10^{-7} \text{cm}^3/\text{s} \) at 300 K, but the dissociative potential does not cross the ionic potential [8] in the Franck-Condon region.

Recently, we have developed a theoretical method [4, 9, 10, 11] to study indirect dissociative recombination in diatomic (Eq. 1) and highly-symmetric triatomic (Eq. 2) molecular ions, where strong non-adiabatic effects lead to relatively high DR cross-sections. In this article we review the theoretical approaches developed and discuss the manner in which these non-adiabatic couplings control the DR reaction in small molecular ions, in particular, in highly symmetric triatomic as well as diatomic ions.

This article is organized as follows. The next section is devoted to a qualitative discussion of non-adiabatic effects in highly symmetric triatomic ions. Section 3 discusses the formalism describing the way that non-adiabatic couplings are included in our theoretical model. In sections 4 and 5 we briefly review the way we calculate vibrational wave functions of the molecular ions and the final DR rate coefficients. Section 6 presents the calculated DR rate coefficients. Section 7 contains concluding remarks.

2. The role of non-adiabatic effects in dissociative recombination of triatomic and diatomic ions

Experiment has shown that DR cross-sections for \( \text{H}_3^+ \) and \( \text{HCO}^+ \) are quite large at energies below 2 eV. In the absence of any direct DR mechanism in this energy range for these molecules, it was suggested [5] that non-adiabatic couplings should be responsible for the fast DR rate. Theory that included only the direct mechanism gives a very low DR rate coefficient [6], orders of magnitude lower than storage ring measurements. The first attempt to include non-adiabatic couplings via intermediate Rydberg state potential surfaces in the theoretical description of \( \text{H}_3^+ \) DR was carried out by Ref. [6]. That calculation obtained a greatly increased cross-section, far above that obtained by the initial exponentially small estimates that had ignored such non-adiabatic Rydberg state couplings; but the result of this improved calculation was still orders of magnitude smaller than the storage-ring experiments. A similar situation arose with the \( \text{HCO}^+ \) ion. Larson et al. [8] have considered DR in \( \text{HCO}^+ \) and included non-adiabatic coupling among the \( \text{nss}, \text{nps}, \text{and nds} \) states. The resulting theoretical DR rate coefficient was still much lower than the available experiments [12, 13]. It appeared, therefore, that the theoretical approach which had successfully described the indirect DR mechanism for diatomics might not be adequate for these triatomic ions.
In 2001 [9], it was suggested that the Jahn-Teller mechanism, which is specific to an electron in the field of the H$_3^+$ ion (or other symmetric ions), can play a role in the H$_3^+$ DR reaction. From the point of view of Born-Oppenheimer potential surfaces, Jahn-Teller coupling has essentially the same meaning and implications as non-adiabatic coupling in diatomic ions. However, a major difference from diatomics comes from the fact that some triatomic (or more generally polyatomic) systems possess degenerate vibrational modes. If the state of the incident electron is also nontrivially degenerate in the equilibrium nuclear geometry, as is the case for $p\pi$ states of the incident electron in the field of either the HCO$^+$ or H$_3^+$ ion, the symmetric configuration of the system exhibits a phase instability (owing to the Jahn-Teller theorem, [14]). This instability causes efficient electron capture by the ion, followed by rapid dissociation of the HCO or H$_3$ states that are formed. From the perspective of the Born-Oppenheimer surfaces of the neutral system (i.e., of the ion plus incident electron), the presence of degenerate electronic states of the incident electron means that the bound Rydberg state potential surfaces of the neutral system exhibit the topology of a conical intersection. Moreover, this property of the bound state surfaces carries over into the fixed-nuclei electron-ion reaction- or scattering-matrix, as one expects on the basis of quantum defect theory. The position of the conical intersection corresponds to the nuclear configuration of the highest symmetry. For all other configurations, the symmetry is lower and therefore the electronic states are not degenerate. Since the non-adiabatic couplings are inverse proportional to the splitting between electronic states, they become very strong near the conical intersection. In reality, the coupling is dynamic because the system vibrates going through the conical intersection back and forth (dynamical Jahn-Teller and Renner-Teller effects). This mechanism does not exist in diatomic molecules because they cannot have degenerate vibrational modes. It is also usually not effective for molecular ions whose symmetry group does not have doubly or triply-degenerate irreducible representations. (In certain polyatomic molecules that do not have degenerate irreducible representations, similar phenomena may also be present provided there is a conical intersection of electronic states in the Franck-Condon region. However, it is not a general situation in such non-symmetric molecules.) Therefore, in highly symmetric triatomic (and polyatomic) ions the electron-vibration coupling is much stronger than in diatomic ions, and this is likely to be the case in other species possessing low energy conical intersections.

3. How to include Jahn-Teller and Renner-Teller coupling in DR treatment of triatomic ions, and non-adiabatic effects into the DR of diatomic ions

The Renner-Teller and Jahn-Teller couplings are generic non-adiabatic couplings between electronic and vibrational degrees of freedom when a $p$-wave electron moves in the field of a linear (e.g., HCO$^+$) or equilateral (e.g., H$_3^+$) polyatomic molecules. The couplings involve electronic states with non-zero projection on the molecular axis of symmetry. Such states are doubly-degenerate when the nuclear configuration is symmetric: linear configuration for HCO and equilateral configuration for H$_3$. The strongest Renner-Teller and Jahn-Teller couplings involve $np\pi$ states in HCO$^+$ and H$_3^+$ correspondingly. In particular, $np$-wave electronic states of the continuum are responsible for the large DR cross-section in both of these ions. In the following, we limit our considerations to $np$ electronic states only.

In the present treatment the couplings are taken into account using the reaction or scattering matrix, which describes the collision of the molecular ion (HCO$^+$ or H$_3^+$) with the electron. The starting point for the construction of the scattering matrix is of course the fixed-nuclei Hamiltonian containing the non-adiabatic coupling physics in either a diagonalized (adiabatic) or off-diagonal (diabatic) representation.

For the closed-shell linear ion HCO$^+$, its interaction Hamiltonian $H_i$ with a bound $np$-electron depends on the configuration $Q$ of the three nuclei and has the following form in the basis of
the \(np\pi^{-1}, np\sigma\) and \(np\pi^{+1}\) states [15]

\[
H_\varepsilon(Q) = \begin{pmatrix}
E_\pi & \delta e^{i\varphi} & \gamma e^{2i\varphi} \\
\delta e^{-i\varphi} & E_\sigma & \delta e^{i\varphi} \\
\gamma e^{-2i\varphi} & \delta e^{-i\varphi} & E_\pi
\end{pmatrix},
\]

(3)

where \(E_\sigma\) and \(E_\pi\) are the electronic energies of the \(np\sigma\) and \(np\pi^{\pm1}\) states at the linear ionic configuration; \(\delta\) and \(\gamma\) are the real, non-Born-Oppenheimer coupling elements [16]. The couplings \(\delta\) and \(\gamma\) depend on the three internuclear coordinates, the distance \(R_{\text{CH}}\) between C and H, the distance \(R_{\text{CO}}\) between C and O, and the bending angle \(\theta\) of the ion. The non-diagonal elements in the above Hamiltonian have additional phase factors \(e^{\pm i\varphi}\) and \(e^{\pm 2i\varphi}\), where \(\varphi\) is the polar angle of the bending orientation.

The non-diagonal coupling parameters \(\delta\) and \(\gamma\) vanish at the linear configuration \((\theta = 0)\). Thus, at the linear geometry two eigenvalues of the Hamiltonian are degenerate. For small non-zero bending angle \(\theta > 0\), the coupling \(\delta\) is proportional to \(\theta\). The coupling \(\gamma \sim \theta^2\) is much smaller than \(\delta\) in HCO.

The diagonalization of \(H_\varepsilon(Q)\) gives three eigenvalues \(V_{\pi''}, V_\sigma, \) and \(V_{\pi'}\) and is accomplished by the unitary transformation matrix \(U\) [15]:

\[
U^\dagger[H_\varepsilon]U = \text{diag}\{V_{\pi''}, V_\sigma, V_{\pi'}\},
\]

(4)

with eigenvalues

\[
V_{\pi''} = E_\pi - \gamma, \\
V_\pi = \frac{1}{2} \left( E_\pi + E_\sigma + \gamma + \sqrt{(E_\pi - E_\sigma + \gamma)^2 + 8\delta^2} \right), \\
V_\sigma = \frac{1}{2} \left( E_\pi + E_\sigma + \gamma - \sqrt{(E_\pi - E_\sigma + \gamma)^2 + 8\delta^2} \right).
\]

(5)

The eigenvalues \(V_{\pi''}, V_\sigma, \) and \(V_{\pi'}\) depend on three internuclear coordinates and represent the adiabatic potential energy surfaces. In this approach, they are obtained from \textit{ab initio} calculations [8]. The matrices \(U\) in Eq. (4) and \(H_\varepsilon\) in Eq. (3) can be reconstructed from the adiabatic potential surfaces \(V_{\pi'',\pi',\sigma}(Q)\). For example, we obtain from Eq. (5)

\[
E_\sigma = V_\sigma(\theta = 0), \\
E_\pi = V_{\pi'}(\theta = 0), \\
\delta = \frac{1}{\sqrt{8}} \sqrt{(V_\pi - V_\sigma)^2 - (E_\pi - E_\sigma + \gamma)^2}, \\
\gamma = E_\pi - V_{\pi''}.
\]

(6)

The next step is the calculation of quantum defects \(\mu_{\pi'}(Q), \mu_{\pi''}(Q), \) and \(\mu_\sigma(Q)\). To obtain them, in addition to \(V_{\pi'',\pi',\sigma}(Q)\), one also needs the potential surface \(V'(Q)\) of the ground state of the ion:

\[
\mu_{\pi'',\pi',\sigma}(Q) = n - \frac{1}{\sqrt{2(V'_+ - V_{\pi'',\pi',\sigma})}},
\]

(7)

where \(n\) is the principal quantum number of the corresponding electronic state. The three values \(\mu_{\pi''}, \mu_{\pi'}, \mu_\sigma\) make the diagonal matrix of quantum defects \(\hat{\mu}(Q)\). The scattering \(\hat{S}(Q)\) and reaction \(\hat{K}(Q)\) matrices in the basis of the \(np\pi^{-1}, np\sigma\) and \(np\pi^{+1}\) electronic states are then obtained as

\[
\hat{S}(Q) = U \exp[2\pi i \hat{\mu}(Q)] U^\dagger, \text{ and } \hat{K}(Q) = U \tan[\pi \hat{\mu}(Q)] U^\dagger.
\]

(8)
The matrices depend on the three internuclear distances and, in addition, on the polar angle \( \varphi \) of the bending orientation.

The structure of the \( K \)-matrix is similar to the structure of the Hamiltonian:

\[
\hat{K}(Q) = \begin{pmatrix}
K_\pi & K_{\sigma\pi}e^{i\varphi} & K_{\pi\pi}e^{2i\varphi} \\
K_{\sigma\pi}e^{-i\varphi} & K_\sigma & K_{\sigma\sigma}e^{i\varphi} \\
K_{\pi\pi}e^{-2i\varphi} & K_{\sigma\pi}e^{-i\varphi} & K_\pi
\end{pmatrix}.
\]

(9)

For the small angle \( \theta \ll 1 \), the diagonal elements \( K_\pi \) and \( K_\sigma \) are almost independent on \( \theta \); the non-diagonal elements \( K_{\sigma\pi} \) and \( K_{\pi\pi} \), representing the Renner-Teller coupling, are proportional to \( \theta \) and \( \theta^2 \) correspondingly, similar to the coupling coefficients \( \delta \) and \( \gamma \) in Eq. 3.

For \( H^3_5 \), the electron-ion scattering matrix is constructed in a similar way. The ground electronic state of the ion is the closed-shell state. The ion has the equilateral configuration at the equilibrium position. The interaction between the ion and the \( np \) electron is described by the following Hamiltonian in the basis of \( np\pi \) states:

\[
H_e(Q) = \begin{pmatrix}
E_\pi & \delta e^{i\varphi} \\
\delta e^{-i\varphi} & E_\sigma
\end{pmatrix},
\]

(10)

where the non-diagonal elements represent the Jahn-Teller coupling between the \( np\pi \) states. In contrast to the Renner-Teller coupling, the \( np\sigma \) states are not involved in the Jahn-Teller physics. The real coupling parameters \( \delta \) are zero at the equilateral configuration and linear with respect to the asymmetric stretch normal coordinate \( \rho \) [11, 17] (assuming that the symmetric stretch coordinate is fixed). The angle \( \varphi \) is the polar angle of asymmetric stretch mode [11, 17]. The diagonal elements \( E_\pi \) depend weakly on the asymmetric stretch \( \rho \) for small values of \( \rho \). The two eigenvalues of the Hamiltonian are

\[
V_{1,2} = E_\pi \pm \delta.
\]

(11)

Using a procedure similar to the one applied to matrix of Eq. (3), parameters \( E_\pi(Q) \) and \( \delta(Q) \) as well as the matrix \( U \) diagonalizing the Hamiltonian \( H_e(Q) \) can be reconstructed from \textit{ab initio} calculation. Then, the body-frame \( K \)-matrix is obtained applying Eqs. (7) and (9). It has the structure similar to Eq. (10):

\[
K_e(Q) = \begin{pmatrix}
K_\pi & K_{\pi\pi}e^{i\varphi} \\
K_{\pi\pi}e^{-i\varphi} & K_\pi
\end{pmatrix},
\]

(12)

where the non-diagonal elements \( K_{\pi\pi} \) are linear with \( \rho \), the diagonal elements depend weakly on \( \rho \).

4. Vibrational states in theory of DR in triatomic ions

Since degenerate vibrational modes have to be taken into consideration, a reduced dimensionality treatment should only be applied with caution. The included vibrational degrees of freedom should be able to represent the required degenerate modes. It means that at least two vibrational coordinates have to be explicitly taken into account. In addition, some dissociation coordinate has to be included into consideration. This makes at least three vibrational coordinates (or three vibrational modes) that must be treated explicitly. Two of the three vibrational modes can probably be approximated by normal harmonic modes for simplicity.

The complete set \( Q \) of vibrational coordinates for the HCO\(^+\) ion includes the \( R_{CH} \) and \( R_{CO} \) distances, the bending angle \( \theta \) of the molecule, and the polar angle \( \varphi \) of the bending. To represent the vibrational motion of \( H^3_5 \) we use the hyper-spherical coordinates: the hyper-radius and two hyperangles [9, 10, 11]. In the HCO\(^+\) case, we consider the \( R_{CH} \) distance as the dissociation
coordinate, because experiment shows that the main DR channel for HCO$^+$ is H + CO. (It would be possible to utilize the hyperradius for the dissociation coordinate in the HCO calculation also, but if so, it will be essential to not adopt an adiabatic hyperradial approximation as was done in the initial calculations for H$_3^+$. For H$_3^+$, the dissociative coordinate is the hyper-radius. The hyper-radius represents uniformly both sets of H$_3^+$ DR channels: H$_2$ + H and H + H + H. To discuss the DR in HCO$^+$ and H$_3^+$ in the same way, we use symbol $R$ for the dissociative coordinate, and $\Omega$ for the remaining vibrational coordinates $Q$.

The two different approaches to calculate the DR rate coefficients discussed in the following account for the vibrational dynamics in slightly different ways. The “simplified” [18] approach utilizes vibrational states for which the dissociative coordinate $R$ is not quantized, but all other vibrational coordinates must be quantized. We call such partially-quantized vibrational states as adiabatic states, meaning that the dissociative coordinate $R$ is treated as a slow-changing coordinate. The adiabatic vibrational states $\varphi_a$ are obtained by diagonalizing the fixed-$R$ vibrational Hamiltonian in the space of the $\Omega$ coordinates:

$$H^\text{ad}_a(R; \Omega) = U_a(R) \varphi_a(R; \Omega). \tag{13}$$

$U_a(R)$ are adiabatic energies depending parametrically on the dissociation coordinate $R$.

In the second approach, the exact vibrational eigenstates $\Phi_{\text{vib}}(R, \Omega)$ of the vibrational Hamiltonian of the ion are needed. These states are represented as an expansion in the basis of the functions $\varphi_a(R; \Omega)$. The coefficients of expansion $\psi_a(R)$ depend on the coordinate $R$

$$\Phi_{\text{vib}}(R, \Omega) = \sum_a \psi_a(R) \varphi_a(R; \Omega) \tag{14}$$

and are obtained by solving the multi-channel one-dimensional Schrödinger equation using the slow-variable discretization technique [19] (see also Refs. [20, 21]).

Note that we do not need only the bound states of the multi-channel Schrödinger equation for the ion. To allow this approach to obtain outgoing continuum states also, an complex absorbing potential is placed at a large value of the dissociative coordinate; thereby one also obtains states with complex energies whose real part lies well above the dissociation threshold of the ion. Such states of the vibrational ionic continuum are of course very highly excited with respect to the ground vibrational level of the ion. These ionic states cannot be populated in the DR process at low energies of the incident electron. But the lower Rydberg states of the neutral molecule that are “attached to” these states can be populated and, in fact, they represent the only possible dissociation pathways during the electron-ion scattering. The inclusion of these states in the electron-ion scattering matrix makes the matrix subunitary. The ”defect” of unitarity is then interpreted as the DR probability [10, 11, 22].

5. Calculation of rate coefficients

Once the scattering (or reaction) matrices of Eqs. (9) and (12) are available, the rate coefficients for HCO$^+$ and H$_3^+$ have been calculated in the following way.

In the first theoretical approach discussed here, we take into account only the vibrational motion of the molecular ions. Rotation is neglected. The body-frame scattering $S$ (or reaction $K$) matrix (Eqs. (9) or (12)) is then transformed into the representation of adiabatic states

$$S_{j,j'}(R) = \langle \Phi_i(R; \Omega)|S_{\Lambda,\Lambda'}|\Phi_{i'}(R; \Omega)\rangle_{\Omega}. \tag{15}$$

The indices $\Lambda$ and $\Lambda'$ numerate the electronic states included into the treatment. The indices $j, j'$ correspond to the basis of that representation and include the quantum numbers describing the electronic state ($\Lambda$ or $\Lambda'$) and the vibrational quantum number $i$ or $i'$ of the adiabatic state.
Formally, the amplitude $S_{j,j'}(R)$ represents the scattering of the electron from one vibronic state $j$ to another $j'$, while the dissociative coordinate $R$ is unchanged.

The scattering (or reaction) matrix $S_{j,j'}(R)$ is then used to obtain the potential curves $U_d(R)$ of the neutral molecule HCO$^+$ or H$^+$ as discussed in Refs. [9, 18, 16]. These potential curves have usually a non-zero autoionization width $\Gamma_d(R)$. The autoionization width is proportional to the probability to capture the electron into the corresponding state of the neutral molecule. If the electron is captured, the neutral molecule can autoionize or undergo the pre-dissociation process. Assuming that the autoionization is negligibly slow compared to pre-dissociation, from the curves $U_d(R)$ and widths $\Gamma_d(R)$ we calculate DR cross-sections and rate coefficients. We have estimated that for H$^+$, the pre-dissociation is fast relative to the autoionization [9] for the states important to DR. For HCO$^+$, only a partial analysis has been done so far, and it suggests that the two processes are competitive.

For H$^+$, we also used a second approach for calculation of the DR rate coefficients, which accounts for the competition between autoionization and pre-dissociation. The DR cross-section and rate coefficient are obtained directly from the actual physical scattering matrix $S^{phys}$, which is calculated from the body frame matrices of Eqs. (9) and (12) by the techniques of rovibrational frame transformation [11, 23, 24] and closed-channel elimination [25]. This approach is discussed in detail in Refs. [11, 26]. An important advantage of this approach is that one obtains the DR cross-section (and the rate coefficient) directly from the scattering matrix: There is no need for the resonance search as in the first approach. Another advantage is that the competition between autoionization and predissociation is accounted for implicitly: There is no need to estimate the effect of the autoionization on the DR cross-section that is obtained. The disadvantage of the approach is that the size of the scattering matrix, after implementation of the rovibrational frame transformation, could be very large (in the thousands, typically). In addition, many rotational states have to be included in the calculation to obtain the DR rate coefficient for high temperatures. This requires extensive numerical calculations, and the high density of narrow resonances means that a dense energy grid is required as well.

6. Results

6.1. H$^+$

Figure 1. Theoretical (line) and experimental (symbols) H$^+$ DR rate coefficients given as functions of the parallel component of electron energy (for details, see Ref. [26]). Circles correspond to the CRYRING experiment [27], diamonds correspond to the TSR experiment [28]. In the experiments, the rotational temperature of the ions is estimated to be 40 K in CRYRING and 13 K in TSR. The theoretical curve is calculated for a higher temperature, 1000 K.

Figure 1 compares the theoretical H$^+$ DR rate coefficient with experimental data from two storage ring experiments [27, 28]. The theoretical curve is calculated using the second
"improved" approach. The $H_3^+$ rate coefficient calculated within the "simplified" approach is presented in Refs. [9, 18]. Agreement between theory and experiment is generally quite good. However, the temperature of rotational excitation is 1000 K for the theoretical curve, and only 40 K and 13 K in the experiments. The theoretical curve calculated for a lower rotational temperature, < 100 K, has much more pronounced resonance structure than is observed experimentally (see the detailed discussion in Ref. [26]). Another important difference between the theoretical and experimental curves is their behavior at energies below 0.2 meV. The experimental curves raise steeply when the energy approaches to zero in contrast to the theoretical curve, which is almost flat at low energies. It should be mentioned that in the experiments the electrons have a finite-width energy distribution (2 meV at CRYRING and 0.5 meV at TSR). Therefore, a change 0.1 meV in parallel component of the electron energy should not have a large effect on the rate coefficient. This is what the theoretical rate demonstrates, but the experimental rate coefficients behave approximately as $E^{-1/2}_\parallel$ at even smaller parallel energies. The reasons for the two disagreements, (1) the sharper resonance structure in the theoretical rate and (2) the $E^{-1/2}_\parallel$ behavior in the experimental data at low energies, remain unresolved.

The results presented in Fig. 1 correspond to the $H_3^+$ ion initially prepared in the ground vibrational level. Figure 2 shows the calculated DR rate coefficients for two different excited vibrational states of the ion. The DR rate coefficients for excited vibrational states are significantly larger than for ion initially in the ground vibrational state.

6.2. HCO$^+$

The HCO$^+$ DR rate coefficients have been calculated so far only in the "simplified" approach. An additional simplification was made in the calculation: the $R_{CO}$ distance was fixed at the equilibrium position $R_{CO} = 2.0877$ a.u. This additional simplification makes the system more "rigid" in the calculation, which seems likely to unphysically lower the calculated probability to capture the incident electron. The results (thermal rate coefficients) of the calculation are demonstrated in Fig. 3 and compared with two different experiments [12, 13]. The theoretical results are calculated and presented for both the ground and vibrationally exited states of the ion.

As was the case for $H_3^+$, and not surprisingly, the DR rate coefficient is larger for the vibrationally excited state. Agreement with experiment is poorer than was the case for $H_3^+$. The

![Figure 2. Theoretical $H_3^+$ DR rate coefficients obtained for three different initial vibrational states of the ion. The theoretical curves are all calculated for 1000 K rotational temperature. The experimental curve is from Ref. [27] and obtained for $H_3^+$ initially prepared in the ground vibrational level $\{000\}$.](image-url)
reason could be due to the fixed $R_{CO}$ distance that was adopted in the present calculation. If the vibration motion along $R_{CO}$ is allowed, this should increase the density of available Rydberg states where the incident electron can be captured. On the other hand autoionization following the initial electron capture has been neglected in this approach. If it is account for, the DR rate becomes smaller. Currently, a better analysis of DR in HCO$^+$, including the vibration along $R_{CO}$, is under development. At the same time, we point out that the experimental DR rate coefficients are quite different in different experiments, so it is possible that some systematic experimental difficulties remain to be resolved as well. In any case, it is safe to say that the problem of HCO$^+$ DR is far from being solved.

6.3. Indirect DR for the diatomic ion LiH$^+$

Some diatomic molecular ions exist for which there are no discernable low-energy pathways that can produce a dissociative recombination reaction by the conventional direct mechanism of Bates. One famous example that has received considerable attention is the HeH$^+$ ion. This has been measured experimentally at both the CRYRING and TARN II storage rings, [29, 30] and tackled theoretically by Takagi and others [8, 31, 32]. The study by Takagi successfully extracted the total DR rate coefficient at low energies, and obtained good agreement with experiment, and in addition it clarified the relevant pathways and suggested that for HeH$^+$, both rotational coupling and the nonadiabatic coupling between different electronic partial waves can be important. Another example of a molecular ion with a comparatively fast low-energy DR rate is the LiH$^+$ ion. The 139K rate coefficient had been extracted from experimental measurements in 2001 at TSR [33, 34, 35] to be $(6 \pm 2) \times 10^{-7}$ cm$^3$/s, whereas the first theoretical attempt to describe this system gave a much lower rate coefficient more than an order of magnitude smaller. That discrepancy triggered our own studies[4, 36], with the two goals of (i) obtaining an independent theoretical calculation to see whether theory is in fact consistent with the lone existing measurement of the total DR rate, and (ii) pinpointing the DR mechanism and pathways for this simple molecular ion in order to gain insight into the dynamical indirect DR process as a whole.

To understand the problem, i.e. the reason why it is not obvious that the low energy DR process should be so efficient, consider Fig. 4. It shows the Born-Oppenheimer potential curves for the ionic ground state, for several molecular Rydberg states, and the lower electronically autoionizing potential curves that lie above the ionic ground state potential curve. One sees immediately in this figure that the singlet and triplet potential curves of excited LiH molecules do not cross the ionic ground state potential curve, unless it is at small internuclear distances.
Figure 4. Several singlet and triplet Σ Born-Oppenheimer potential energy curves (thin, solid) for LiH are shown along with the ground state of LiH⁺ (thick, solid). The potentials that lie above the ionic ground state are electronically autoionizing states (blue, dashed), whose width is not explicitly indicated in the figure. Because these exhibit no curve crossing between any neutral LiH potential curve and the ground state of the ion, direct DR is expected to occur rarely if at all. Two other important energies are shown as horizontal lines, the \( v = 0 \) vibrational level of LiH⁺ (dotted) and the dissociation threshold of LiH⁺ (thin, dark, solid). (From Ref.[36])

For many molecules without a curve-crossing in the Franck-Condon region of the ion, e.g. H₂⁺, there are often one or more that become relevant at higher energies, but for the LiH system, no crossing occurs at radii beyond the ionic potential curve minimum, even in that higher energy range.

In studies to date of DR carried out using multichannel quantum defect theory in conjunction with the rovibrational frame transformation, it has usually been possible to identify a single dominant partial wave of the incident electron that plays a controlling role. In our LiH⁺ DR calculations, however, this was not found to be the case, as coupling between different incident orbital momenta has vital importance for determining the correct rate. This has been adequately documented elsewhere, e.g. in Fig.4 of Ref.[36], where a strong avoided crossing occurs between the \( ns \) and \( nd \) partial waves, precisely at the internuclear distance where the ionic potential curve has a minimum, \( R \approx 4 \) a.u. While both the \( 1Σ \) and \( 3Σ \) symmetries show such a crossing, our calculations suggest that the sharper avoided crossing for the \( 3Σ \) symmetry is the one which dominates low energy DR for this system.

The DR rate has been calculated using elements from the theoretical toolkit discussed above, including MQDT and the rovibrational frame transformation based on vibrational Siegert pseudostates calculated within a finite radius box in \( R \). The resulting plot of the rate versus the parallel energy component, convolved with the experimental parallel and perpendicular energy resolutions as described above, is shown in Fig. 5. This shows that the new calculations reported in Refs. [4, 36] have in fact reproduced the observed experimental results from TSR. What we would like to focus on here, however, is more what we have learned from our analysis of the DR pathways, rather than dwelling on this question of agreement or disagreement between theory and experiment. The main point is that the agreement gives reason to take seriously the conclusions we have been able to draw about the DR mechanism in LiH⁺, which presumably still has relevance to other indirect DR species.

The following is our physical picture for how we now view the DR process in LiH⁺. First, the incident electron can be written as a partial wave expansion, and typically only one or just a few partial waves dominate the capture processes that ultimately result in DR. In these
LiH$^+$ calculations, we have included up to $l = 2$, and in fact it is the $d\sigma$ partial wave that is the strongest, although couplings off-diagonal in $l$ are also important. The $d$-wave electron is captured into a Rydberg state, predominantly one that is attached to the closed $v^+ = 1$ vibrational threshold. In other words, there is an energy exchange between the electronic and vibrational energy, which in the frame transformation is largely mediated by the $R$-dependence of the quantum defect or body-frame scattering matrix. As is typical of an MQDT calculation, an “unphysical” scattering matrix is utilized which has closed channel as well as energetically-open channel indices. The initial capture can be viewed as a simple scattering excitation process in which the incident electron strikes the molecule in a $|v^+ = 0\rangle$ state and then leaves it in a $|v^+ = 1\rangle$ state, with the important difference from ordinary scattering theory that this excitation happens when the electron is at small-$r$, and eventually as the electron recedes towards infinity, the fact that this channel is closed will ultimately turn the electron back around to recollide with the molecular ion again. What has just been described is all familiar to those who have followed the Rydberg capture picture of indirect DR for the past decade or two or three. However, a new aspect of this problem was unraveled in the course of the study presented in Refs.[4, 36], namely the role of the so-called “complex resonances” of multichannel spectroscopy, which have an intermingled nature with a (low-$v$, high-$n$) Rydberg channel that is quasi-degenerate with a (higher-$v$, lower-$n$) Rydberg channel. We were able to see that such a quasi-degeneracy tends to correspond to regions of enhanced indirect DR, by factors ranging from 3-20, and in this sense, the complex resonances of multichannel spectroscopy can be viewed as providing the dominant “doorway” for indirect DR reactions.

Another insight gleaned from this new study of LiH$^+$ is the fact that the $R$-dependent angular coupling among the different partial waves is also decisively important. A test calculation conducted in Ref.[4] was to artificially turn off that coupling; once it was omitted, the resulting calculation gave a DR rate for LiH$^+$ that was very close to the earlier theoretical results obtained by Florescu et al. [37], i.e., which was more than an order of magnitude smaller than the experimental rate (and our full LiH$^+$ DR calculation) at low energies. This shows that an avoided crossing which happens to fall right in the middle of the Franck-Condon region can be extremely important in its affect on the low-energy DR rate; this is quite likely a general result that is applicable to other systems in addition to this particular molecular ion.

7. Concluding remarks
We have reviewed two different theoretical approaches for calculation of DR cross-sections in triatomic ions, discussed the results obtained for two different triatomic ions, H$_2^+$ and HCO$^+$, and compared them with the diatomic system of LiH$^+$ where the non-adiabatic effects are also strong.
The two approaches presented are generic and can be applied to theoretical DR studies for other small polyatomic molecular ions, where only a limited number (3-4) of vibrational modes can realistically be taken into account. The “doorway” mechanism of complex multichannel resonances, identified through the prototype system of an electron that collides with LiH\(^+\), appears to show promise for understanding this frequently surprising indirect DR process.

In general, the DR mechanism in highly symmetric triatomic molecular ions is different from DR in diatomic ions owing to the presence of degenerate vibrational modes. The incident electron arriving in a degenerate electronic state such as \(\pi^\pm\) (or \(d\delta^\pm\)) is strongly coupled to the degenerate ionic vibrational modes because of the Jahn-Teller theorem. The strong non-adiabatic coupling causes rapid energy transfer from the electronic to the vibrational degrees of freedom. In HCO\(^+\) and H\(_3^+\) the coupling produces recombination that is comparatively faster than will normally be the case for systems where the direct DR process is impossible.

The theoretical DR rate coefficients for both H\(_3^+\) and LiH\(^+\) are in good agreement with existing experiments. For HCO\(^+\) the theoretical DR rate coefficient is approximately a factor of 2-3 smaller than the experimental values [12, 13]. However, at the present time, different experiments disagree on the value of the HCO\(^+\) rate coefficient, so it remains unclear how seriously one should view the current discrepancy between theory and experiment.

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