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Dissociative Recombination Mechanisms

An Introduction and Overview

Steven L. Guberman
Institute for Scientific Research, 22 Bonad Road, Winchester, MA 01890
slg@sci.org

1. INTRODUCTION

This chapter presents an introduction to dissociative recombination (DR) and to the papers in this volume by reviewing how DR works. In DR a molecular ion, AB^+, captures an electron, e^-, and breaks up,

$$AB^+ + e^- \rightarrow A + B. \tag{1}$$

Process (1) is dissociative in the exit channel and recombinative in the entrance channel. The Process involves the interaction of two continua, an electron in a nearly coulomb field on the left side of (1) with a nuclear continuum, i.e. “free” heavy particles on the right side of (1). AB^+ can be a diatomic or polyatomic molecular ion. The product fragments are often neutral and if energetically allowed, they can also be excited. Indeed, if the electron energy is high enough, both positively and negatively charged fragments, i.e. ion pairs, can be produced. Because Reaction (1) is driven by the coulomb attraction between the ion and the electron, it often proceeds without a barrier to electron capture. In DR, energy must be released in order to conserve energy and momentum. The release is often accomplished rapidly by the molecular dissociation, which finalizes the process since after dissociation, the electron can no longer be emitted (autoionization). The absence of a barrier and the rapid fragmentation allows DR rate coefficients to often (but not always) be high, i.e. about $1 \times 10^{-7} cm^3/sec$.

The theoretical study of DR is both a dynamics problem and a bound state problem involving many current areas of research in chemical physics. For the dynamics, it is necessary to describe the scattering of the incident electron. Is the electron elastically scattered without capture? Is the electron temporarily captured and emitted before dissociation? How is the electron captured? At energies just above the lowest vibrational level of an ion, many superexcited states are accessible. These include states having more than a single electron excited from the ground state neutral configuration in addition to those in which a single inner shell electron is excited. States with a single excited outer shell electron may also be found in this energetic region if they are vibrationally excited. If the electron is captured into these states, how do they decay? Do the different decay mechanisms interfere with each other? Does the interference affect the quantum yields of the products? Can the electron be captured only by its interaction with the other electrons or can it be captured by its interaction with the vibrating nuclei? If the electron is emitted (autoionization) does it leave behind a molecular ion that has been rovibrationally relaxed or excited? If the electron is permanently captured leading to dissociation to neutrals, the motion of the neutrals on potential curves or surfaces needs to be described. For polyatomic ions, the product neutral molecules can be both electronically and rovibrationally excited. Highly accurate potential curves and surfaces are needed if accurate rate coefficients are to be calculated.

Considerable progress has been made by both experiment and theory in answering many of these questions and that progress is described in the papers in this volume. Below, several of the questions raised above are answered and the mechanisms that drive DR are elucidated.

2. THE DIRECT MECHANISM

The possibility that molecular ions could undergo DR was suggested by Bates and Massey[1] 55 years ago. They were exploring a chemical model of the Earth’s ionosphere and needed a mechanism for removing the electrons at night, which photoionization by the Sun’s rays had produced during the day. They recognized the possibility that DR could play an important role, but they were uneasy with the mass mismatch between the electron and the molecular nuclei. How could an electron, several thousand times smaller than the nuclei, cause the molecule to fall apart? The explanation was given by Bates in a one page paper.[2] His mechanism is shown in Fig. 1 for the capture of an electron with energy, å. The incoming electron is captured through its interaction with the other electrons and not through its interaction with the nuclei. Capture occurs into a repulsive state upon which the nuclei can fly apart following the solid arrow in Fig. 1. After capture and prior to dissociation, the electron can be emitted (autoionization). Once the internuclear distance is greater than the distance at which the ion and neutral curves cross, autoionization is unlikely, and DR is completed. Note that the

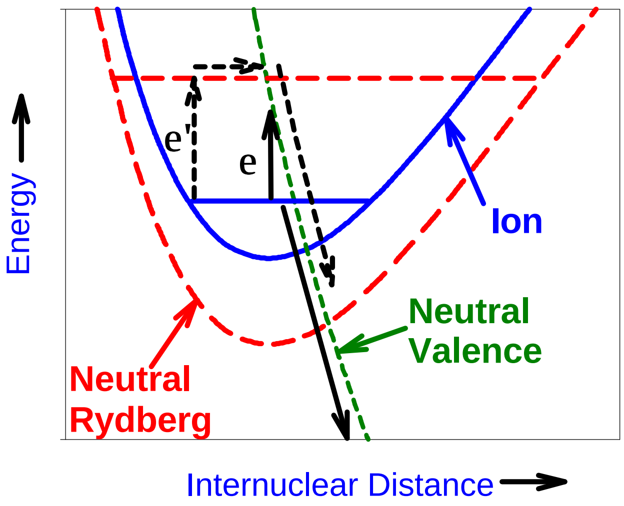

Figure 1. DR mechanisms. å and å' are electron energies.

mechanism requires a neutral potential curve to cross the ion curve. By the non-crossing rule, this situation is forbidden for a fully optimized state since it must cross through an infinite number of Rydberg states of the same symmetry. The crossing state must therefore be a diabatic state, i.e. a state that does not optimize the full electronic Hamiltonian. In practice, these states are taken to be fully optimized valence states that omit Rydberg character. Nevertheless, DR can also be described by fully optimized states, with Rydberg character, which do not cross the ion. This adiabatic picture is described below. For now, however, we will use the diabatic approach.

The diabatic process of Bates,[2] shown by the solid arrows in Fig. 1, is known as direct DR. In this case, the rate coefficient is approximately proportional to the square of a matrix element between the vibrational wave functions for the ion and neutral states. A high direct DR rate coefficient is often possible if the repulsive state crosses the ion curve between the turning points of the ion vibrational level, giving a high vibrational wave function overlap. The matrix element describing capture is given by

$$< \Psi_{ie}(x,R)\, X_v(R) \mid H(R) \mid \Psi_d(x,R)\, F_d(R) > \qquad (2)$$

which can be rewritten as

$$<X_v(R) \mid ('_{ie,d}(R)/2B)^{1/2} \mid F_d(R) >. \qquad (3)$$

Here H is the electronic Hamiltonian, R is the internuclear distance, x represents the electron coordinates, Ψ_{ie} is the electronic wave function for the ion plus a “free” electron, Ψ_d is the electronic wave function for the dissociative state, $X_v(R)$ is the ion bound vibrational wave function, $F_d(R)$ is the continuum vibrational wave function in the dissociative state and $'_{ie,d}(R)$ is the electronic width. A small electron capture width will lead to a small probability for capture while a large width will increase the possibility of autoionization. A favorable width for DR is between these two extremes.

3. THE BORN-OPPENHEIMER BREAKDOWN INDIRECT MECHANISM

The dashed arrows of Fig. 1 show the pathway for indirect recombination, introduced by Bardsley,[3] in which an electron of energy ε' is captured into a neutral, vibrationally excited Rydberg state. This state is predissociated by the repulsive state of the direct DR mechanism. Capture occurs by a Born-Oppenheimer breakdown mechanism [Bardsley, 1968] involving the interaction between the electronic and nuclear motion. The electrostatic matrix element, analogous to (2) but with a Rydberg state replacing the dissociative state, is zero. The appropriate matrix element is given by

$$< \Psi_{ie}(x,R)\, X_v(R) \mid T_N(R) \mid \Psi_{ryd}(x,R)\, X_{v'}(R) > \qquad (4)$$

where T_N is the nuclear kinetic energy operator. Alternatively, the matrix element in (4) can be determined from the variation of the quantum defect, μ with R. The quantum defect is determined from the energy difference between the ion and the neutral potential curves, $\mu(R) = n - (2E)^{-1/2}$, where n is the principal quantum number. Once capture occurs, the electron can autoionize via the coupling in (4) or the Rydberg state can predissociate via the electrostatic coupling in (2) with $\Psi_{ryd}(x,R)$ replacing $\Psi_{ie}(x,R)$ on the left side of the matrix element. Once in the dissociative state, autoionization can occur by this electrostatic mechanism or dissociation can take place along the route shown by the dashed arrow in Fig. 1.

Note that for Born-Oppenheimer breakdown capture, the propensity rule, $\Delta v = 1$ applies.[4] For electron capture by an ion in v=0, this coupling is largest if the electron enters the v=1 level of a Rydberg state.

The Rydberg states are the source of structure in the DR cross sections. The resultant cross section shape near a Rydberg resonance is due to the interference between direct and indirect recombination. The interference induced shape can be understood by calculating the Fano profile index from the above matrix elements[5] using the same approach than Fano introduced for understanding atomic photoionization cross sections near resonances.[6] This approach is successful if the resonances are isolated and not overlapping.

4. THE ELECTRONIC INDIRECT MECHANISM

In this mechanism, the same states are excited as in the Bardsley indirect mechanism except that the nuclear kinetic energy operator is not involved. In the electronic indirect mechanism, the electron is captured first into the dissociative state, which then “leaks” into the vibrationally excited Rydberg state by an electrostatic mechanism. The flux eventually returns to the dissociative state and the process is completed. This process has been discussed previously[7,8] and has been included in the Multichannel Quantum Defect Theory (MQDT) approach for calculating DR cross sections.[5] The matrix element takes the form[5]

$$\iint X_v(R)\langle\Psi_{ie}|H(R)|\Psi_d\rangle F_d(R_<)G_d(R_>)\times\langle\Psi_d|H(R')|\Psi_{ryd}\rangle X_{v'}(R')\,dR\,dR' \qquad (5)$$

where $R_<$ and $R_>$ are the lesser and greater of R and R' respectively and G_d is the irregular continuum dissociative wave function. Because the electronic Hamiltonian acts twice in (5), this mechanism is often referred to as the second order indirect mechanism. The magnitude of the matrix element in (5) often exceeds that for the indirect Born-Oppenheimer breakdown mechanism.[5]

A very important aspect of the electronic indirect mechanism is that the propensity rule for the Bardsley indirect mechanism no longer applies. Indeed transitions with $\Delta v >> 1$ occur often. In these cases, the energetics are such that transitions to high v states with low n are very important. Resonances with low n can have large widths and can cover a large section of the cross section versus electron energy plot.

The second order electronic mechanism is now included in most MQDT calculations of DR cross sections where its interference with direct recombination and the Born-Oppenheimer breakdown indirect mechanism is fully taken into account. Approaches that calculate the full K matrix, account for higher order indirect electronic coupling.

5. CORE EXCITED STATES

In the indirect mechanisms discussed above, the Rydberg states of interest have as the core, the ion state undergoing recombination. Each rovibrational state of the ion is the limit of an infinite series of these Rydberg states. But there are other Rydberg states that can also play a role. These are states having excited ion states as the core.[9] For ions with excited states lying less than 4 eV above the ground state, Rydberg states with an excited core can affect the DR of the lowest ground state ion vibrational levels. However, these states differ in a fundamental way from the Rydberg states discussed in earlier sections. These states differ by at least a double excitation from the ground state ion plus a free electron. In this situation the Born-Oppenheimer breakdown matrix elements (4) are zero. Therefore the coupling matrix elements for populating these states are electrostatic and are given by

$$< \Psi_{ie}(x,R)\ X_v(R)\ |\ H(R)\ |\ \Psi_{ryd}^{ex\,core}(x,R)\ \ X_{v'}(R) > \qquad (6)$$

This is the same matrix element as in (2) except that the excited ion core Rydberg state replaces the dissociative state on the right side. These Rydberg levels will cause structure in the cross section, as do the levels discussed in the prior Sections. However, for Rydberg states with the ground state ion core, the v = m resonances cannot appear in DR of the v = m level of the ion since these must lie below the ion level. However, for excited core states, only the energetics determine which excited core Rydberg vibrational levels lay above the recombining ion level. These excited core states have already been included in MQDT cross section calculations. For N_2^+, a partial inclusion of the $A\,^2\Pi_u$ Rydberg states (i.e. only $^3\Pi_u$ Rydberg states were included) increases the rate coefficient at room temperature by about 10%.[10] The assignment of cross section structure to core excited states has also been discussed in storage ring studies of OH^+ [11] and CD^+ [12] and excited core states have been included in a theoretical study of CH^+ and CD^+ DR.[13]

6. DISSOCIATIVE STATE MIXING

If there are more than two dissociative routes of the same symmetry, the dissociative routes can mix via the Rydberg states of the same symmetry. These dissociative routes predissociate the same symmetry Rydberg states and as a result, they are all connected together in the region of the ion. This leads to the interesting situation in which capture into a favorable crossing dissociative state can lead to partial dissociation along another dissociative route of the same electronic symmetry but with an ion curve crossing that is unfavorable to direct recombination. Another interesting effect, which has been demonstrated for N_2^+,[14] occurs in the case where one dissociative route has a favorable ion intersection and another of the same symmetry has an unfavorable intersection. Without the presence of the favorable crossing route, the cross section structure for DR along the unfavorable route consists of narrow resonances, which are dips. However, with the favorable route included in the calculations, the dips change to peaks since in the energy region of the resonance, the unfavorable dissociative route mixes in some of the favorable route via the Rydberg resonances.

A similar situation can occur if multiple routes of different electronic symmetries drive DR if a nonzero coupling is present which couples the intermediate Rydberg states together. This situation occurs in O_2^+ where spin-orbit coupling couples together ${}^1\Sigma_u^+$ and ${}^3\Sigma_u^-$ dissociative states by coupling together the Rydberg states of these symmetries.[15] The ${}^1\Sigma_u^+$ state crosses the ion between v=1 and v=2 and dissociates to O(^{1}S) + O(^{1}D). Therefore, the quantum yield of O(^{1}S) from DR of v=0 along ${}^1\Sigma_u^+$ is very small. The ${}^1\Sigma_u^+$ state is the only state that generates O(^{1}S) from the low ion levels. The ${}^3\Sigma_u^-$ state has a favorable intersection with v=0 and dissociates to O(^{3}P) + O(^{1}D). However, after favorable capture of the electron into the ${}^3\Sigma_u^-$ dissociative state, some of the flux transfers into the ${}^3\Sigma_u^-$ Rydberg states, which are connected by spin-orbit coupling to the ${}^1\Sigma_u^+$ Rydberg states. The latter are predissociated by the ${}^1\Sigma_u^+$ dissociative state leading to the O(^{1}S) + O(^{1}D) products. This spin-orbit coupling mechanism causes over an order of magnitude increase in the quantum yield for O(^{1}S).[15] This mechanism will, of course, occur in other molecular ions but it requires that the molecular ion have nonzero spin and angular momentum projection upon the internuclear axis.

7. DR IN THE ABSENCE OF A CURVE CROSSING

For many molecules, there are no diabatic states that cross though the ion potential. Examples include HeH$^+$ [16-18] and H_3^+.[19] At first glance, one might therefore expect that the DR rate coefficients would be very small. However, it is known from studies of DR in several molecular ions that when direct recombination is slow, the Rydberg resonance states often appear as peaks in DR cross sections. DR occurs by electron capture into a Rydberg resonance, which is predissociated by a curve that does not intersect the ion curve (see Fig. 2). Therefore, in the vicinity of each resonance, DR suddenly becomes possible and the cross section increases, yielding a peak. The question to be answered in these cases is: are there enough of these peaks and are they high and broad enough to give a high rate coefficient?

In the case of HeH$^+$, the matrix element that describes direct DR is given by

$$< \Psi_{ie}(x,R)\, X_v(R) \mid T_N \mid \Psi_{ryd}(x,R)\, F_d(R) > . \qquad (7)$$

For HeH$^+$, there are no valence dissociative routes that cross the ion and dissociation takes place on the repulsive wall of Rydberg states with asymptotes that lie below the ion v=0 level.[16,17] Fig. 2 shows two Rydberg curves, one of which is dashed and the other has dashes and dots. Direct recombination is shown for an electron with energy, ε. By Born-Oppenheimer breakdown coupling, the electron is captured into the dash-dot

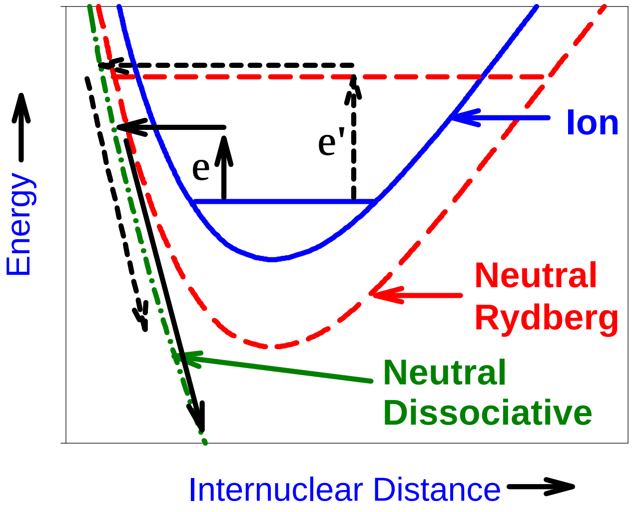

Figure 2. Dissociative recombination without a curve crossing.

potential curve. The dash-dot state is a member of the Rydberg series that has the ion as its limit. The electrostatic coupling between these states is zero. The ion plus a free electron and the Rydberg state are connected by Born-Oppenheimer breakdown coupling. The direct recombination cross section calculated with the matrix element in (7) is small. DR is primarily driven by capture of an electron (with energy ε' in Fig. 2) into a vibrationally excited Rydberg state followed by dissociation upon the dash-dot Rydberg state. Both Rydberg states are members of the same series and are connected by the Born-Oppenheimer breakdown coupling. For HeH^+, there is a strong coupling between these Rydberg states and the rate coefficient for HeH^+ DR is not negligible. The theoretically calculated rate at room temperature is 2.6 x 10^{-8} cm^3/sec[16,17] for ^3HeH and the experimentally derived rate coefficient is 3 x 10^{-8} cm^3/sec for ^4HeH.[20] Note that the theory did not include rotational effects and isotope effects are large in these systems. So the agreement between theory and experiment may be fortuitous. The same mechanism described here for HeH^+ also drives the DR of H_3^+. However, DR of the latter is, of course, considerably more complicated because of the need to account for more than one nuclear motion coordinate. The magnitude of the DR rate coefficient for H_3^+ is controversial and is the subject of several papers in this volume.

8. OTHER SOURCES OF CROSS SECTION STRUCTURE

Rydberg vibrational levels are not the only sources of structure in DR cross sections. As the electron energy increases, the cross section drops abruptly as new autoionization channels (i.e. ion vibrational levels) become accessible. Broad cross section structure can also arise from the variation of the Franck-Condon factor between ion and continuum vibrational wave functions as the electron energy changes.[21]

A very interesting contribution to cross section structure has been described recently in studies of HD^+ DR to $H^+ + H^-$.[22-24] In H_2, DR occurs on states that are mostly doubly excited near the ion.[25] The lowest dissociative state, $Q_1\,{}^1\Sigma_g^+$, crosses the ion near the outer turning point of the v=1 vibrational level and has a well at R=4-5a_o. The outer wall of this potential is mostly due to the $H^+ + H^-$ coulomb attraction. Several Rydberg states of H_2 are crossed twice by this Q_1 potential so that there is more than one way to dissociate to $H^+ + H^-$. An electron can be captured into the Q_1 state followed by transfer of some of the dissociating flux to a Rydberg state at the first crossing. At the second crossing with the Q_1 state, the flux partially returns to the Q_1 state and dissociation continues to $H^+ + H^-$. Alternatively, the flux can diabatically follow the Q_1 state out to the asymptotic limit. The interference resulting from these different paths causes ripples in the theoretically[24] determined cross section, which compares well to the experimentally derived cross section.[22] This type of interference will be important in the DR of many other molecular ions.

9. CONCLUSIONS

The mechanisms discussed here will take place in the DR of many molecular ions that have not yet been studied. However, the list of mechanisms described here is undoubtedly incomplete; it is likely that as more ions are studied, the detailed energetics and interactions involved in each case will reveal still more mechanisms. It is important to keep in mind, in future studies, that very small interactions can play a large role in DR. The indirect mechanisms discussed here often involve Rydberg states with high n. These Rydberg states, of different electronic symmetries, can be separated in energy by only a few wave numbers. In these cases, small interactions can completely mix these states, as discussed above, for the spin-orbit coupling in O_2.

The mechanisms discussed here also occur in the DR of polyatomic ions, but they are more complicated due to the additional degrees of freedom in the nuclear motion. For example, intramolecular energy transfer can compete with dissociation in polyatomic ions so that DR may not be the most likely event to occur after electron capture. For polyatomics, rules are needed to describe how the excess energy is distributed. Under what conditions and for what molecular structures will recombination lead to rovibrational excitation or dissociation? Can capture of an electron in one part of a molecule lead to dissociation in another part? How do the polyatomic superexcited states decay? Clearly, much remains to be learned about DR.

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