

CHAPTER 1

DISSOCIATIVE ELECTRON–ION RECOMBINATION STUDIES USING ION SYNCHROTRONS

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The abstract should summarize the context, content and conclusions of the paper in less than 200 words. It should not contain any references or displayed equations. Typeset the abstract in 10 pt Times roman with baselineskip of 12 pt, making an indentation of 1.5 pica on the left and right margins.

1. Introduction

Many chapters in this book deal with photoionization, which is a process where an electron bound to an atom or molecule is transferred to the electronic continuum by means of photon absorption. For an atomic ion A^{q+} , radiative recombination of $A^{(q+)+}$ can be viewed as the inverse process of photoionization of A^{q+} . The free electron attaches to $A^{(q+)+}$ to form A^{q+} , and the excess energy is carried away by a photon. If the ion $A^{(q+)+}$ contains bound electrons, the free electron can excite one of these electrons while entering a bound atomic orbital. This is called dielectronic capture and results in the formation of a doubly excited ion $[A^{q+}]^{**}$, which is located in the ionization continuum of $A^{(q+)+}$.

When a molecular ion captures an electron, the molecular analogues of radiative and dielectronic recombination are in principle possible, however, they are usually completely overshadowed by a process which is far more effective than any of the atomic processes

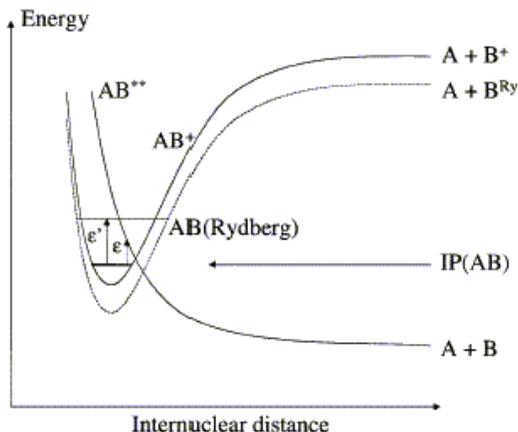


Fig. 1. A schematic illustration of dissociative recombination. The direct mechanism is initiated when the molecular ion AB^+ captures an electron with kinetic energy e . The potential energy function for the neutralized and electronically *doubly* excited molecule AB^{**} is strongly repulsive, which renders the two atoms A and B to rapidly depart from each other. When the potential energy has dropped below the ionization potential, denoted $IP(AB)$, the electron capture process has been stabilized. The indirect mechanism involves the capture of an electron with kinetic energy e' , so that a vibrationally and electronically *singly* excited molecule $AB(\text{Rydberg})$ is formed.



where $A \in B = q+1$ and B is in the radiative processes.

The reason for this process being so much more efficient than the atomic processes is that a molecular ion can stabilize the capture of an electron by making use of its internal structure, which allows for a radiationless rearrangement of the nuclei on a time scale (< 1 ps) much shorter than that for radiative transitions (> 1 ns). Figure 1 illustrates the process. The free electron can deposit its excess energy to the molecular ion either by exciting a bound electron or by exciting a vibrational mode. In order to prevent autoionization, the molecule must lower its electronic energy. This is achieved by rapid molecular dissociation along the repulsive potential energy curve of the doubly excited state (the direct mechanism), hence the name “dissociative recombination”. If the free electron loses its energy by vibrationally exciting the ion core, a radiationless transition (predissociation) from the vibrationally excited

Rydberg state to the repulsive doubly excited state is required before dissociative stabilization of the electron capture can occur (the indirect mechanism)^a. In contrast with the atomic case, the first step in the direct mechanism, dielectronic capture, is not sharply resonant in the molecular case.

Dissociative recombination involves radiationless transition(s) from a molecular ion and a continuum electron to a nuclear continuum, and it could involve a large number of Rydberg states. This renders the process very difficult to treat theoretically. A further problem for theoretical calculations is the sparsity of relevant molecular data.

A number of factors also conspire to make the process difficult to study experimentally. Molecular ions are difficult to prepare and maintain at high concentrations, and they are particularly difficult to prepare with a well-defined vibrational distribution. The ions should further be brought to interact with electrons with a *known* velocity distribution. Depending on the experimental technique, the production of neutral particles (beam techniques) or the removal of charge (afterglow techniques, ion traps) is monitored. In both cases there are other processes that give rise to the same effect, and these processes can be corrected for.

The technique relying on the monitoring of neutral particles is based on accelerated charged-particle beams. In order to have access to very-low-energy collisions (~ 1 meV), the ion and electron beams are merged at zero-degree angle over a known distance. Ion storage rings represent the most recent advancement of the merged-beams technique. In a storage ring, the molecular ions continuously circulate at very high speed in an extremely high vacuum. The ions all have nearly the same kinetic energy, and they occupy, for infrared active modes, the lowest vibrational quantum level. This very clean sample of ions serves as a well-defined target for a cold beam of electrons which interact with the molecular ion beam over a distance of about one meter. The application

^a The paper focuses on ASEAN because it is the only institutionalised regional grouping in Asia. Yet, because of data availability the empirical analysis is restricted to the five major- countries, namely Indonesia, Malaysia, Philippines, Singapore and Thailand, while Brunei, Cambodia, Laos Myanmar and Vietnam had to be excluded from the scope of the study.

of ion storage ring technology to the process of dissociative recombination, and related processes.

2. History and Applications of Dissociative Recombination

The mechanisms of dissociative recombination are shown schematically in the molecular ions. The direct mechanism was first suggested by Bates.¹ It is deceptively simple, but was long in coming, as described in some detail in Bates' final article on the subject.² It was not until the microwave experiments by Biondi and Brown^{3,4} that Bates was finally convinced that molecular ions effectively recombine with electrons. The direct dissociative recombination cross-section is inversely proportional to the electron energy, e , and proportional to the electronic which determines the process.

For dissociative recombination of polyatomic molecular ions it has so far been possible in storage rings to measure only the branching ratios into neutral products, but not their state of excitation. The technique used for doing these measurements will be described in Sec. 2.

3. Dissociative Recombination through a Crossing of Potential Curves

The mechanism for dissociative recombination has been given the descriptive name the *crossing mode*.² It was for a long time believed that a favorable crossing was a prerequisite for the occurrence of dissociative recombination. As we will see in the next section, a second mode of recombination, the *tunneling mode*, has recently been recognized as important. The recognition of this second mode came almost half a century after Bates' seminal paper.¹ Thus, it is natural that the majority of molecular ions for which theoretical and experimental dissociative recombination data are available belongs to the crossing mode category.

Table 1 lists all ion storage ring experiments known to the author concerning dissociative recombination that have resulted in a published paper, a paper that is in press, or a paper that has been submitted for publication (by August 1998), and the type of results that have been obtained in these experiments. Examples of the theoretically computed

Table 1. Calculated r -mode frequency corrections w_2 for constant density stars ($n = 0$) and $n = 1$ polytropes. Results are shown both for the full calculation (nC) and the Cowling approximation (C). The results are for barotropic perturbations and the fundamental $l = m$ modes.

	$w_2(n=0)$		$w_2(n=1)$	
	nC	C	nC	C
2	0.765	0.913	0.398	0.451
3	0.777	0.844	0.527	0.423
4	0.769	0.345	0.656	0.382
5	0.730	0.749	0.399	0.405

Doppler spectra. (Thick line: 0° crossing angle, thin line: 90° crossing angle). The results of the present model depend importantly on our assumption that the spectra retains a long-term interest.

3.1. Diatomic Hydrogen Ions

Being the simplest diatomic molecule, it is natural that H_2^+ and its isotopomers represent benchmark systems for dissociative recombination, in particular with respect to the comparison of experiment and theory. The experimental and theoretical studies of DR of H_2^+ and its isotopomers in their zeroth vibrational levels are described in some detail in two recent reviews,^{2,32} and only a brief summary of the present situation will be given here.

The development of a single-pass merged electron-molecular ion beams technique⁶⁵ played an important role for the understanding of DR of H_2^+ . Because of the rapid conversion of H_2^+ to H_3^+ by ion–molecule reactions, H_2^+ is inaccessible to the afterglow techniques. The merged beams (see Table 2) technique also allows the measurement of DR cross-sections or early experimental and theoretical papers^{6,7} provided the first qualitatively correct insight into the DR of H_2^+ , it was not until more than ten years later that a complete quantitative comparison of experiment and theory finally was accomplished by the research groups of Giusti-Suzor and Mitchell.^{66–69} The comparison revealed a good

Table 2. Predicted and observed order of errors for eigenvalues based on various combinations of stiffness and mass matrices.

Type	Predicted order of error in representing			Observed error for
	K	M	I	I
k2r-m2c	$O(h^2)$	$O(h^4)$	$O(h^2)$	$O(h^2)$
k2r-m2l	$O(h^2)$	$O(h^2)$	$O(h^2)$	$O(h^2)$
k3e-m3c	$O(h^2)$	$O(h^6)$	$O(h^2)$	$O(h^2)$
k3e-m3l	$O(h^2)$	$O(h^4)$	$O(h^2)$	$O(h^2)$
k3r-m3a	$O(h^4)$	$O(h^6)$	$O(h^3)$	$O(h^3)$
k3e-m3b	$O(h^5)$	$O(h^7)$	$O(h^4)$	$O(h^7)$
k3r-m3d	$O(h^7)$	$O(h^8)$	$O(h^6)$	$O(h^8)$

Note: The rapid conversion of $O(h^2)$ to $O(h^4)$ by ion-molecule reactions.

Source: Takagi (1996).

agreement both in terms of the absolute values of the cross-section and the positions of several ‘window’ resonances caused by the interference between the direct and indirect mechanisms.

The comparison concerned only DR at electron energies well below the ion dissociation energy, where the $(2p\mathbf{S}_u)^2\ ^1\Sigma_g^+$ resonant state completely dominates the recombination. It was not possible, however, to unambiguously assign the experimental results to H_2^+ populating only its zeroth vibrational level of the molecule.

3.2. Monohydride Ions

Dissociative recombination of monohydride ions has been reviewed recently.^{2,32} The process which involves an electronic excitation of the ionic core has not been further investigated since the last review.³² An imaging experiment with OH^+ in CRYRING led to discovery of a very small kinetic energy release when the electron energy was sufficient for the $O(^3P) + H(n=2)$ dissociation limit (see Table 3) to become energetically allowed.⁸⁴ Recombination of OH^+ is known to proceed through the $2\ ^2\Pi$ resonant state,⁸⁵ which dissociates diabatically to $O(^1D) + H(n=1)$. The imaging result (see Table 4) shows that part of the dissociating flux is redirected, probably at avoided crossings between

the $2^2\Pi$ state and the $3^2\Pi$, $4^2\Pi$ and $5^2\Pi$ states, which all correlate diabatically to the $O(^3P) + H(n=2)$ limit. It is thus reasonable to approximate the actual pressure with its time average over one period (that is, set $p=0$) provided the radius R .

These are generally accepted as the yardstick for determining whether or not a method qualifies as being intelligent. Neural-networks, genetic algorithms, tabu search, and ant systems are presented as being adaptive memory programming.

3.3. Nonhydride Diatomic Ions

This category is dominated by the three atmospherically important ions O_2^+ , N_2^+ , and NO^+ , but also CO^+ and CN^+ will be discussed.

The parameter estimates using Generalized Least Squares (GLS). As shown in the table, \hat{d}_1 is significantly positive at the 5% level, suggesting that A-share market beta is a good measure of risk for an individual firm's share. It is not a question simply of tracing funds but, rather, of assigning property rights. The competing claimants various government departments and agencies often cannot reach consensus on who the investor is.

It shows changes in proportions of the central government's projects and local projects in the total capital construction investment of state-owned sector. Investment decisions of central projects are generally made by the line ministries and the State Planning Commission, and that of local projects, (see Table 5) are made by local governments and enterprises.

Table 5. Probability of strength modification.

Probability of nonexceedance	f for Column	f For Beam	g for Column	g for Beam
90%	1.01	0.97	1.49	1.11
95%	0.94	0.95	1.55	1.13
99.9%	0.67	0.88	1.83	1.20

y : strength modification factor for dependable strength.

g : strength modification factor for upper bound strength.

3.3.1. Transition in the Theoretical Work

The thermal rate coefficient for O_2^+ occupies an unusual role in the respect that different experiments over a time span of thirty years almost unanimously agree² that $a(O_2^+) \approx 2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, the very recent measurement based on cross-section data from CRYRING being no exception.⁸⁶ With few exceptions,⁸⁷ most theoretical work has been devoted to the understanding of the formation of $O(^1S)$ in dissociative recombination of O_2^+ . It is the $O(^1S) \rightarrow O(^1D)$ transition in neutral atomic oxygen which gives rise to the green airglow at 5577 \AA in the terrestrial atmosphere. It is worth noting that the earliest mention of dissociative recombination was made in an attempt to identify a source of the green oxygen line.⁸⁸ Guberman showed^{89,90} that DR of $O_2^+(n < 10)$ leading to the production of $O(^1S)$ must occur through the $^1\Sigma_u^+$ state of O_2 that dissociates to $O(^1S) + O(^1D)$, and proceeded to calculate, using the MQDT approach, the partial rate coefficient for DR of O_2^+ through the $^1\Sigma_u^+$ state.⁹¹

Test for Lists and Theorem Environments

- item one,
- item two,
- item three.

Items may also be numbered in lowercase roman numerals:

- (i) item one
- (ii) item two
- (iii) item three
 - (a) lowercase roman letters for lists within lists,
 - (b) second item
- (iv) item four

Theorem 1: In any unital Banach algebra A , the spectrum of each $a \in A$ is a non-empty compact subset, and the resolvent function is analytic on $\mathbf{C} \setminus \text{sp}(a)$.

We see that the crucial assumption of the mechanism is that despite the vanishing of the bare fermion mass, the physical mass m of the fermion is nonzero. Since the bare fermion mass $m_0 = 0$, we have $A = C$, see Theorem 1 and so we obtain the self-consistency equation for the physical mass of fermion.

Proof: On $\mathbb{Y} \setminus (A \times \mathbb{P}^1)$, p is just h and its singularities are isolated. The notation A stays for $\hat{A} \cap Y$.

The first statement immediately follows from the definition of the spaces Y and X . As for the second statement, we have the homotopy equivalences

$$p_{i+1}(Y) \approx p_i(Y_s, X_a). \quad (2)$$

We need a condition which implies a certain level of connectivity of each pair $(B_i \cap Y_D, B_i \cap X_c)$. A condition that fits well is the rectified homotopical depth of the total space X . This condition does not depend on the stratification of the space.

Moreover,

$$\lim_{|I| \rightarrow \infty} R(I) \leq \lim_{|I| \rightarrow \infty} \frac{|I| \Gamma^1}{1 - (\frac{I}{I_0})} = 0. \quad (3)$$

Similarly, if $I_0 - a$ is invertible and $\|I - I_0\| \ll \frac{1}{(I_0 - a)^{-1}}$ then

$$(I - a)^{-1} = \sum_{n=0}^{\infty} (I_0 - I)^n ((I_0 - a)^{-1})^{n+1}.$$

This also shows that the resolvent is open. Since $\text{sp}(a)$ has been shown to be bounded, $\text{sp}(a)$ is compact. We have also shown that the resolvent function is analytic on the complement of the spectrum.

Definition 2: A Banach algebra A is said to be *unital* if it admits a unit 1 and $\|1\| = 1$ Banach algebras in 3.

Lemma 3: Let A be a unital Banach algebra and a be an element of A such that $\|1 - a\| < 1$. Then $a \in GL(A)$ and

$$a^{-1} = \sum_{n=0}^{\infty} (1 - a)^n.$$

Moreover, $\|a^{-1}\| \leq \frac{1}{1-\|a\|}$ and $\|1-a^{-1}\| \leq \frac{\|a\|}{1-\|a\|}$.

Remark 4: The Gelfand representation theorem for commutative C^* -algebras is fundamentally important. Even in a non-commutative A we often obtain useful information of A via the study of certain commutative C^* -subalgebras of A . So Theorem 1 certainly plays an important role in studying non-commutative C^* -algebras as well. Theorem 2 shows that to study commutative C^* -algebras, it is equivalent to study their maximal ideal spaces. So the commutative C^* -algebra, theory is the theory of topology. Much of general C^* -algebra, theory can be described as non-commutative topology.

Corollary 5: *The only simple commutative unital Banach algebra is \mathbf{C} .*

Proof: Suppose that A is a unital commutative Banach algebra and $a \in A$ is not a scalar. Let $I \in \text{sp}(a)$. Set $I = (a - I)A$. Then I is clearly a closed ideal of A . No element of the form $(a - I)b$ is invertible in the commutative Banach algebra A . By 3,

$$(a - I)b - 1 \geq 1.$$

So $1 \notin I$ and I is proper. Therefore, if A is simple, a must be a scalar, whence $A = \mathbf{C}$.

Example 6: Let X be a compact Hausdorff space and $C(X)$ the set of continuous functions on X . $C(X)$ is a complex algebra with pointwise operations. With $\|f\| = \sup_{x \in X} |f(x)|$, $C(X)$ is a Banach algebra.

4. Tunneling Dissociative Recombination

Convinced by overwhelming experimental evidence that HCO^+ recombines with a rate coefficient larger than $10^{-7} \text{ cm}^3 \text{ s}^{-1}$, and by theoretical predictions that its electronic ground state does not possess a favorable neutral state crossing, Bates introduced a multistep indirect mechanism which does not require a curve crossing.⁹⁷ He later gave this mechanism the descriptive name ‘tunneling dissociative recombination’.²

Figure 2 shows the relevant potential curves of O_2^+ and O_2 . The $^1\Sigma_u^+$ state crosses the ion ground state close to the right turning point of $n = 2$. It is immediately obvious from the potential curves that $n = 0$ is expected to have a much lower quantum yield than are $n = 1$ and 2 (neglecting for a moment the new mechanism shown in Fig. 2).

The aim of the present notes is to allow the variable R to have quantum fluctuations around the classical trajectory and modify the expressions of the general formalism. Of course, it would be much more interesting to allow for inhomogeneous fluctuations, but this would inevitably render the system intractable analytically and is left for future developments.

4.1. HeH^+

The FALP measurement³⁸ of a thermal rate coefficient less than $1 \times 10^{-10} \text{ m}^3$ for HeH^+ was seemingly in perfect harmony with the absence of a curve crossing. The sizeable cross-section measured in a merged beams experiment therefore came as a surprise. The findings inspired theoretical work,^{40,41} which finally identified coupling by the nuclear kinetic-energy operator of the HeH^+ ground state to close lying (but not crossing) Rydberg states of HeH as the driving mechanism.

Let S_j be such a close neighbor and $\mathcal{L}(S_j)$ be the local packing of (S_j) contained in $\mathcal{L}^2(S)$. Then $\mathcal{L}(S_j) \cap \mathcal{L}(S)$ already constitutes a *partial* local packing of S_j while the others of $\mathcal{L}(S_j)$ are exactly those additional neighbors belonging to the second layer of $\mathcal{L}^2(S)$. Thus, the *restriction* of the extension (see Fig. 1), $\mathcal{L}(S) \subset \mathcal{L}^2(S)$, to that of $\mathcal{L}(S_j)$ is an extension from the partial one, $\mathcal{L}(S_j) \cap \mathcal{L}(S)$, to a full-fledged local packing.

Herbst and Lee²¹ have found from model calculations on dark interstellar clouds (see Fig. 4) that although the breakup into neutral reaction products in DR of polyatomic ions is more substantial than previously believed, a general branching fraction of 0.30 for the single H atom channel is still sufficient to give molecular abundances in excellent agreement with observations. However, if this branching fraction is lowered to 0.05, a larger change in predicted abundances occurs. Such low branching was indeed measured for CH_5^+ , but so far this is the

exception rather than the rule, at least as far as the storage ring results are concerned.

5. Conclusions and Outlook

This article has focussed almost exclusively on the use of ion storage rings for the study of dissociative recombination of positively charged molecular ions with electrons. It is pertinent at this point to recall that ion storage rings by no means are confined to the study of this particular molecular process. Dissociative excitation has already been mentioned in passing, with a reference given to a recent review of the topic.³³ But there are also other aspects of molecular physics that can be addressed by means of the storage ring technology, as discussed in a recent article by Zajfman,²² and as witnessed by publications on electron impact detachment of negative molecular ions,^{23,24} laser photodetachment spectroscopy of fullerenes,²⁵ and laser photofragment spectroscopy.²⁶

Dissociative recombination of the simplest ion, H_2^+ and its isotopomers, is beginning to be well understood. Yet, discrepancies between experiment and theory still remain. They will most probably be cleared up within the next couple of years. A good understanding of DR of HeH^+ is also emerging, although there are still large discrepancies between experiment and theory for some of the isotopomers.

The importance of HeH^+ lies in fact that it is the simplest is to recombine the (tunneling mode). The primary actors of the modern corporation are shareholders, the board of directors, and managers. These three entities can be found in companies in developed countries, although variant forms of organization exist in some countries. Shareholders have all the rights related to property rights.

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