

# Classical Gas

## Dissociative Recombination of Molecular Ions

By Mats Larsson and Ann E. Orel.

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In the early years after World War II, both experimental and theoretical research pointed to the importance of a new electron–ion recombination process, upsetting conventional thinking. Experience with radar gained at the famed MIT Radiation Laboratory during the war led to experiments with gases exposed to microwaves. Of particular interest was the ionization of these gases and the mechanism by which the ionization disappeared when the field was turned off (the afterglow period). At the same time, theorists were trying to explain the existence of a layer of ionization in the Earth's upper atmosphere. It was known that this layer arose from solar photoionization. But what was removing the electrons? Without an efficient removal mechanism, the observed concentration of electrons could not be explained. The experimentalists were stymied by the conventional wisdom that only atoms existed in the ionized gas. Atomic recombination is too slow to account for electron capture during the afterglow. The theorists were led to the possibility that in the ionosphere, the electron removal mechanism could be electron–molecular-ion recombination but they were stymied by the need to explain how a relatively tiny electron could cause a massive molecular ion to fall apart. In 1950, Sir David Bates,<sup>[1]</sup> in what he considered to be his single most important contribution, introduced the fundamental mechanism for dissociative recombination (DR) and a new interpretation of the laboratory results and atmospheric observations was put on a firm footing. In Bates' mechanism, referred to as direct DR, an electron ( $e^-$ ) is captured by a molecular ion ( $AB^+$ ) leading to dissociation [Eq. (1)]:



Today, it is well known that DR is an important process in the interstellar medium, in the ionospheres of moons and planets, in laboratory experiments, in the divertors of fusion devices and wherever there are moderate- to low-temperature plasmas. While there have been a few reviews of DR in the literature, there has been no book that collected in a critical manner the history of DR research. This need has now been met with the publication of "Dissociative Recombination of Molecular Ions" by Larsson and Orel. Prof. Mats Larsson is the director of the CRYRING storage ring facility in Stockholm and Prof. Ann Orel is a theorist at the University of California at Davis.

The text starts with the early ionospheric research of 1902 and concludes in the summer of 2007. Covering over a century of research is an operose task demonstrated by the 56 pages of references. The first chapter includes a good overview of the early research with the details of more recent developments left for later chapters. While several reviews of DR are mentioned, one of the best critical histories<sup>[2]</sup> of the early work is omitted. Much attention is paid to identifying who is first with a new experimental technique or theoretical approach. There is some disorganization in this connection. In Chapter 1, the first ab initio calculation is incorrectly attributed to the important 1971 paper of Nielsen and Berry<sup>[3]</sup> on  $H_2^+$ . However, in Chapter 4, the first calculation is correctly identified as that of Bauer and Wu,<sup>[4]</sup> also on  $H_2^+$ , performed fifteen years earlier. In Chapter 1, the authors state that by the end of the 1960s, "No ab initio calculations had been performed." However, calculations were reported by Warke<sup>[5]</sup> in 1966 and those of Wilkins<sup>[6]</sup> and Dubrovsky et al.<sup>[7]</sup> in the 1960s are reported in Chapter 4.

Most of the experimental studies of DR have employed stationary and flow-

ing afterglows and single-pass and multipass merged beams. These methods are reviewed in Chapter 2. In the merged-beam methods, DR takes place at the intersection of an electron beam with an ion beam. Simultaneous detection of the neutral DR products allows for the determination of cross sections and rate coefficients. However, as the authors point out, the determination of these quantities is not so easy. The authors provide a valuable review of how the uncertainty in the relative electron–ion energy is determined by the uncertainties in the electron energy, in the ion energy and in the value of and the uncertainty in the angle of intersection of the two beams. The relative energy cannot reach zero unless the two beams are exactly aligned at an intersection angle of zero. One of the equations [Eq. (2.4)] expressing the relative energy is incorrect.<sup>[8]</sup> However the discussion is not affected.

The electron beam in the merged beam experiments is formed by using an electric field to extract it from a thermionic cathode. The electric field along the beam direction leads to a compression of the electron energy distribution in the beam direction but not in directions orthogonal to the beam. The result is a flattened pancake-like electron energy distribution. The explanation of the origin of this flattening effect is not included in most experimental papers and its inclusion here is most appropriate and valuable. The need to reduce the electron temperature in the perpendicular direction in order to increase the resolution in the measured cross section is also discussed. Using magnetic expansion of the electron beam, the perpendicular temperature has been reduced to 2 meV at CRYRING and to 0.5 meV at the Test Storage Ring in Heidelberg.

In the multipass storage ring experiments, the circulating molecular ions merge with the electron beam in a small section called the electron cooler where DR takes place. The electrons are de-

merged from the ion beam at the cooler exit. During merging and demerging, the electron beam is not collinear with the ion beam and the relative energies of the two beams differ from that in the colinear region. In order to account for this effect, a toroidal correction is applied. Indeed, as the authors point out, without the toroidal correction, a nonzero value is obtained for a spin-forbidden product channel in the DR of  $\text{NO}^+$ . Unfortunately, this effect is the subject of only a brief discussion, but it needs much more detailed discussion. The correction is applied in many storage ring measurements but also receives very little discussion in the literature.

Most of the storage ring DR experiments to date have used magnetic fields to confine the ions and electrons. The field places a severe constraint upon the maximum ion mass that can be stored in the ring. Electrostatic storage rings in which an electric field is used to confine the ions have no restriction on molecular mass, allowing for studies of heavy ions. In addition, the electrostatic rings are much smaller than the magnetic rings and much less expensive to build and operate. However, a disadvantage is that it is difficult to operate these rings at the low relative energies that are common in the magnetic rings. With the exception of two electrostatic rings currently in operation, most are still in their infancy. The brief discussion is a valuable addition to the book.

The discussion of the stationary and flowing microwave afterglow methods is quite good considering that both methods are outside of the areas of expertise of the authors. The early experiments on stationary afterglows were hampered by not having mass spectrometers to identify the recombining ions. The authors review the important analysis of Johnson<sup>[9]</sup> in which it was shown that the electron temperature may not always be uniform throughout the stationary afterglow leading to errors in the deduced electron temperature dependence of the rate coefficient. This is followed by a review of the flowing afterglow technique which is used for most current afterglow measurements. One page is devoted to shock tube studies

The coverage of theoretical techniques begins appropriately with a discussion of the important DR mechanisms: direct, indirect through ground and excited core Rydberg states and the case in which the dissociative state of the direct mechanism does not cross the ion. The latter situation was for many years thought to lead to low DR rate constants. However, it is now known that in certain cases, the indirect mechanism based upon Born-Oppenheimer breakdown coupling can lead to moderate to high DR rate constants.

The most powerful and widely used method for calculating DR cross sections and rate coefficients is the multichannel quantum defect theory (MQDT) approach and this approach is summarized in the text. MQDT easily allows for interference between direct and indirect DR and is able to treat whole Rydberg series, avoiding the problem of having to account for individual Rydberg states, one at a time. The latter problem occurs in the non-MQDT scattering theory approach and leads to a very cumbersome and less powerful procedure which is now rarely used for the calculation of cross sections and rate constants. Nevertheless, the scattering theory approach does allow one to assess the angular distribution of the DR products.<sup>[10]</sup> The scattering approach is introduced by first presenting the reader with a Jost function without giving it an adequate introduction. The discussion is not likely to be meaningful to those who do not have a working knowledge of scattering theory.

There is a misleading statement that the MQDT method "...provides no information about the final state distribution of products." In the case where there are multiple noninteracting dissociative routes, the cross section along each route can be easily calculated giving the final state distribution. For cases where the states have avoided crossings, the vibrational dissociative wave functions can be calculated using coupled equations and the final state distribution can also be determined using MQDT.

A discussion of the complex Kohn and R matrix methods is also included. The complex Kohn method has been used by one of the authors (Orel) to calculate

potential energy curves and electronic widths. There is only passing reference to the use of bound state methods for the calculation of electronic widths.

One of the authors (Orel) has pioneered the use of wave packet methods for the study of DR. These methods have mostly been used for high electron energy ( $>1$  eV) DR in which a closure condition over ion vibrational states is satisfied. Only direct DR has been studied with wave packets since Rydberg states have not yet been included, due to difficulties in solving the scattering equations. Probably the most important application of wave packet methods has been the calculation of the DR of  $\text{HD}^+$  leading to  $\text{H}^+ + \text{D}^-$  (and  $\text{H}^- + \text{D}^+$ ) in which interference of different pathways leads to oscillations in the cross section.<sup>[11]</sup>

Surprisingly, the single most important expression in DR theory does not appear in the book. While the expression for the total cross section in terms of S and T matrices does appear, the simple expression for the direct cross section in terms of the electronic width and ion and neutral vibrational wave functions is absent. The expression allows for a quantitative understanding of the balance between dissociation and autoionization in the absence of Rydberg states. For many molecular ions, the expression describes the "background" DR (i.e. DR without the Rydberg states) present in many DR cross sections.

Additional methods not discussed in detail are the use of quantum chemical approaches for determining potential curves and the recent use of hyperspherical coordinates to describe DR of polyatomics. The latter method has been successfully applied to several polyatomics and would have been worthy of detailed discussion.

The introductory chapters are followed by chapters on the DR of  $\text{H}_2^+$ , diatomic hydride ions, other diatomic ions,  $\text{H}_3^+$ , and polyatomic ions. For many molecular ions, there is qualitative agreement between experimental cross sections measured at different storage rings but not quantitative agreement. Differing ion rotational distributions and differing electron beam parallel and perpendicular temperatures at different rings make a quantitative comparison

rather difficult. The resolution of these issues is needed in order to compare theoretical and experimental cross sections. However, there is qualitative agreement between theory and experimental cross sections for several molecular ions.

Most of the discussion of diatomic hydride ions is centered on  $\text{HeH}^+$ . This ion was initially thought to have a slow recombination rate constant due to the lack of a favorable crossing between ion and dissociative states. Indeed, the initial flowing afterglow experiment found a low rate coefficient. However, theoretical calculations<sup>[12]</sup> showed that DR could occur with a non-negligible rate constant if electron capture occurs by breakdown of the Born–Oppenheimer approximation, that is, by the interaction of the incoming electron with the nuclear motion. This mechanism also plays a role in the DR of polyatomic ions. Among the other rare gas hydrides, two flowing afterglow experiments found no recombination for  $\text{KrH}^+$  but a third found a rate of  $2 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  at 250 K. The single storage ring experiment on  $\text{ArH}^+$  could not detect recombination at low electron energies. The reviews of the  $\text{CH}^+$  and  $\text{OH}^+$  studies are quite comprehensive.

The case of  $\text{LiH}^+$  is rather important. At first glance,  $\text{LiH}^+$  appears similar to  $\text{HeH}^+$  as there is no crossing of the ion by a neutral state potential curve. In contrast to  $\text{HeH}^+$ , the energetics are such that there is a much higher density of Rydberg states above the ion at low electron energies and some of these Rydberg states have asymptotes below the ion  $v=0$  level. Interactions between the Rydberg states lead to a rather high DR rate with the single storage ring experiment reporting a value of  $4 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  in agreement with recent theoretical calculations. As for  $\text{HeH}^+$ , the results show that DR can occur with a high rate constant in the absence of a curve crossing of the ion by a neutral state.

The discussion of the atmospheric ions  $\text{O}_2^+$ ,  $\text{N}_2^+$  and  $\text{NO}^+$  includes tables summarizing experimentally derived rate coefficients and the applicable electron temperatures. For  $\text{N}_2^+$ , theoretical results by this writer are included. However, the first theoretical rate constant listed is

misleading since it only applies to DR along a single potential curve and was not intended to represent the total DR rate constant from  $v=0$ . The remaining six are total rate constants along multiple potential curves.<sup>[13]</sup>

The discussion of the long meandering history of  $\text{H}_3^+$  DR is excellent. The discussion is not a simple recitation of experiments and results, but a highly critical analysis of past research. The criticism is especially sharp and deserved for several afterglow experiments (in the period 1987–1990) which had reported values for the DR rate constant at room temperature of  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , a value that is about four orders of magnitude smaller than the currently accepted value. These low values may have been due to a bias that arose from the early theoretical prediction that the rate constant is low. (The prediction was based upon one-dimensional potential curves which showed no crossing of the lowest vibrational states with a dissociative curve.) This value was used in astrophysical models even though the measurement was never fully documented. When the value was withdrawn by the experimenters in 1993, a reason was never offered.

More recent theory has shown that the cross section is large and agrees with storage ring cross section measurements with some discrepancies at low energies. The authors suggest that another theoretical study is needed to confirm these results. Calculations from excited rovibrational levels are needed to help understand some of the afterglow results.

The discussion of  $\text{H}_2\text{O}^+$  DR focuses upon the kinematic considerations needed to deduce the quantum yields of the products obtained with zero energy electrons. The detection of DR products is limited to those resulting from breakup in the plane parallel to the plane of the detector. Missing from the discussion is whether or not breakup at other orientations could yield different quantum yields. The discussion focuses entirely upon the CRYRING results and no comparison is provided to flowing afterglow results<sup>[14]</sup> which found very different yields.

A detailed discussion of the DR of ions important in astrophysical models ( $\text{HCO}^+$ ,  $\text{HCS}^+$ ,  $\text{N}_2\text{H}^+$ ,  $\text{HCNH}^+$ ,  $\text{HCN}^+$ ,  $\text{HNC}^+$ ,

$\text{H}_3\text{O}^+$  and  $\text{CO}_2^+$ ) is included. A table summarizes results for other polyatomic ions not discussed in the text. The largest ions studied in storage rings have five heavy atoms. Heavier species have been studied in afterglows.

Cluster ions are known to have rate coefficients that are often  $> 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ . However, the authors point out that after years of experiments it is still not understood why these rate coefficients are so high. This generalization may apply only to low-energy DR. For example, the DR cross section for  $\text{NO-NO}^+$  is below that for  $\text{NO}^+$  above 0.2 eV.<sup>[15]</sup> Experimental measurements at electron energies above 0 eV may help in understanding the mechanism.

The remainder of the book describes the DR of hydrocarbon ions, and related processes including dissociative excitation and ionization, ion pair production, and dissociative attachment to negative ions and neutrals. A brief closing chapter describes applications.

In spite of a few problems, this book provides a valuable and comprehensive view of the current state of DR research. The reader might also want to consult the review article by Florescu-Mitchell and Mitchell<sup>[16]</sup> and the CRYRING web site listing experimental DR results, <http://mol.physto.se/DRdatabase>. This book is a must-buy not only for those interested in DR, but also for those who study planetary atmospheres, the interstellar medium and other moderate to low temperature plasmas where DR plays a central role.

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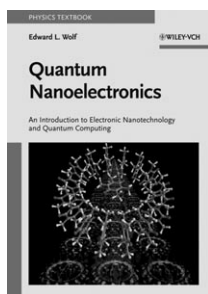
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## Quantum Nanoelectronics— An Introduction to Electronic Nanotechnology and Quantum Computing

By E. L. Wolf.

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Moore's law states that the number of transistors that can be placed on a circuit doubles every two years, but this is, in fact, an empirical observation of industrial relevance, not a law of nature. And, in its essence, it is quite an optimistic observation, with the size of electronic devices shrinking quickly, we are coming closer and closer to the point where quantum effects will rule their functioning. Quantum physics can be staggeringly different from its classical version, and some known concepts will have to be dropped, while new ones can be introduced. Whether this will be a smooth transition or whether we "will face an abrupt collision with the future", to cite A. Toffler, remains to be seen.



Whatever the case, this shift will also change the knowledge required to develop working devices and compete in electronics and related areas. At least basic notions of quantum mechanics and how it can be used for practical purposes will be needed at both R&D and decision-making levels, for the development of new devices and the concomitant managing activity.

While this is common knowledge for physicists, and the transition has already begun at the fundamental level, there will be soon the need to teach the basics of quantum electronics to a wider audience, with a more applicative and entrepreneurial approach. And this knowledge will soon need to reach synthetic chemists too, whose role is becoming increasingly important, as the size of the devices shrinks.

This is where the book "Quantum Nanoelectronics" by E. L. Wolf comes into play. Indeed, as stated by the author, the book presumes only elementary college physics and should be accessible to most readers with a very generic formation in scientific or technical disciplines. This choice of readership is, of course, both a point of strength and a limit of the book.

First of all it confers a pretty unique layout to the text, with about 40% of the book devoted to an introductory part about basic quantum mechanics and solid-state physics. All these concepts are approached with simplicity and an applicative mindset, illustrating the fundamental results more than the conceptual background of the quantum world. Examples of applications of the concepts to devices are often provided, sometimes with their commercial success or expected performance. The second part of the book provides an overview of the tools of the trade of a nanoscientist, covering the most common building blocks of nanodevices and the applicable fabrication methods of nanoelectronic systems. The practical explanation of how all this becomes very relevant for industrial and technological purposes is contained in the third part, which covers a broad spectrum of systems of current interest in nanotechnology. In particular, the nano-equivalents of diodes and transistors are discussed in

some detail, as well photovoltaic solar cells and quantum information devices.

All this affords a nice overview of this lively and rapidly evolving technological scenario. It can be an interesting and stimulating read to anybody who, having a higher education, wants to have an idea of how nanotechnology can alter the way we perceive and design electronic devices. In particular there is a motivating attention to what does not work or still remains to be done. The reader will promptly discover that, far from the hype of journalists and fiction writers, the nanoworld is promising, but suffers from a still limited control and understanding of what we can do.

And here, come the drawbacks of this book layout. As the reader is not intended to have a strong scientific background in the fundamentals of physics and chemistry, the book also offers limited tools to go beyond what is explained. Given the large collection of examples afforded, several important details (and sometimes not-so-details) are necessarily skipped, referencing the interested reader to the original papers. Only a few introductory articles are cited at the end of each chapter, even when excellent ones exist. This strategy could prove stimulating for a good student, a scientist or a very committed reader, but I somewhat feel the original papers will likely be inaccessibly complicated for a reader with a thin fundamental background. As the devil often is in the detail, this might prove an important drawback.

Moreover the discussion on some advanced subjects, like quantum computation and graphene, necessarily becomes so vague that the reader will likely fail to grasp the true fundamental importance of such topics. Thus, as a side effect, the book contents can sometime appear like a collection of technological possibilities, while a feeling of the fundamental scientific importance of the subjects treated is not fully conveyed.

Eventually chemists and materials scientists should notice that the fabrication part mostly covers physical methods. Chemical bottom-up fabrication methods, which are acquiring more and more importance in the field, are largely over-