

Breaking Up Is Hard to Do Without an Electron

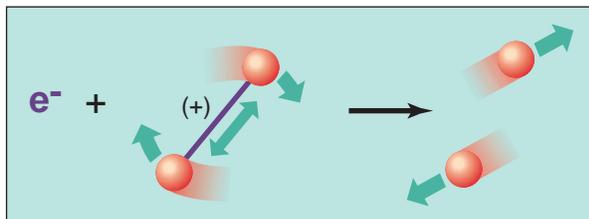
Steven L. Guberman

Experience tells us that when a very small mass collides with a much larger mass, the motion of the large mass is hardly altered. But at the molecular level, the process of dissociative recombination (DR) appears at first glance to deviate from our experience. In DR, an electron is captured by a molecular ion, causing the molecule to fragment (see the first figure). Yet the mass of an electron is 2000 times smaller than that of a hydrogen atom. How does the electron accomplish such a feat? Answers to this question were discussed in a symposium on “The Dissociative Recombination of Molecules with Electrons” at the American Chemical Society national meeting, 26 to 30 August 2001, in Chicago.

DR can proceed through several mechanisms. The basic mechanism, direct DR, was first proposed by Bates (1) over 50 years ago (1), shortly after the first apparent DR experiment was reported (2). In direct DR, the incoming electron does not interact with the massive nuclei; it is the interaction with the ion's electrons that leads to dissociation. A bond in the ion breaks if the incoming electron excites a bonding electron and falls into an antibonding orbital. The capture of an electron into a dissociative neutral state is most likely when the wave functions of the ion and the dissociative state have high overlap. Such high overlap occurs if the dissociative curve crosses the ion curve vibrational level between its end points at low electron energies (see panel A in the second figure). This overlap is sensitive to the vibrational state of the ion (see panel B).

Indirect recombination (3) is similar to the direct process except that the electron is first captured into a neutral excited bound state (called a Rydberg state). The bound state interacts with the dissociative state and “leaks” into it, leading to dissociation. For some molecules, the dissociative curve does not cross the ion curve for any vibrational state; indirect recombination alone may then have a nonnegligible rate constant (4). The vibrating or dissociating neutral molecule can also autoionize, that is, expel an electron. All these processes interfere with each other, adding to the complexity of DR.

This sensitivity of the rate constant to

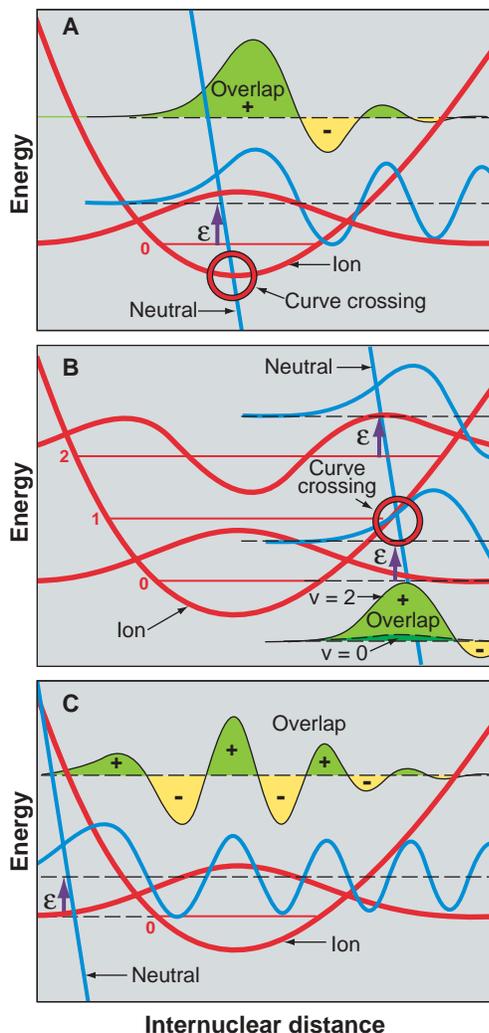


Dissociative recombination. An electron (e^-) is captured by a molecular ion, which breaks up into neutral fragments. The motion of the rotating and vibrating diatomic ion and of the fragments is shown with green arrows.

the vibrational state of the ion has been a serious problem in experimental studies. There is a long history of disagreement between rate constants measured by experiments with different techniques for

generating ions. Experimental results have also often disagreed with those predicted by theory. One source of disagreement has been the poorly defined electronic, vibrational, and rotational states of the ions in the experiments. The longstanding disagreement over the DR rate constant of H_3^+ continues this tradition.

H_3^+ is of great astrophysical importance because its DR rate determines the densities of many astronomical species (E. Herbst, Ohio State University; T. Oka, University of Chicago). The most recent microwave afterglow experiment (R. Plásil and J. Glosik, Charles University) gives a rate constant of less than $3 \times 10^{-9} \text{ cm}^3/\text{s}$, compared with values determined in storage ring experiments of $1.0 \times 10^{-7} \text{ cm}^3/\text{s}$ (5) and $1.15 \times 10^{-7} \text{ cm}^3/\text{s}$ (6). Storage rings merge high energy beams of electrons and ions and detect the neutral products arising from DR. However, a recent study (7) found that the H_3^+ in



DR rate dependence on the relative positions of potential curves.

The potential curve and vibrational wave functions and levels (v) for the ion are shown in red. The curves and wave functions for the neutral dissociative state are shown in blue. The curves and wave functions for the ion and dissociative state vibrational wave functions, is filled in with green for positive overlap and yellow for negative overlap. The total overlap is the sum of the yellow and green areas. The crossing point of the ion and dissociative neutral curves is denoted with a red circle. The ordinates for the wave functions and overlap are not shown. (A) Direct recombination for capture of an electron of energy ϵ by the $v = 0$ state. The capture is favorable and the rate constant can be high because the overlap of the red and blue wave functions is high. (B) The dissociative and ion curves cross beyond the outer classical turning point (where the vibrational level intersects the potential curve on the large internuclear distance side) of the $v = 0$ state and the vibrational overlap (dark green) and hence the rate constant is low for $v = 0$ at energy ϵ . For the same electron energy, overlap is high for an ion in the $v = 2$ state and a high rate constant is likely. (C) The dissociative curve does not cross the low ion vibrational states. Because of cancellation, the sum of the overlap areas is very small and the direct DR rate constant is very small.

The author is at the Institute for Scientific Research, Lexington, MA 02420, USA. E-mail: slg@sci.org

these experiments is highly rotationally excited (D. Zajfman, Weizmann Institute). Preliminary results (M. Larsson, Stockholm University) indicate that when cooler conditions are used in the ion source, the rate constant is lowered.

For H_3^+ , a slice through the potential surfaces resembles the curves of panel C. For these curves, direct recombination from the lowest vibrational level has a low rate constant, and indirect recombination can play a dominant role. Rotational excitation may lead to an increase in vibrational overlap and a higher rate coefficient. The magnitude of the effect depends on the relative shapes of the potential surfaces. In the rings, the ions are held for up to 40 s before measurements, allowing for vibrational relaxation. However, calculations (8) of the lifetimes of 62 rotationally excited levels in the lowest vibrational level show that half have lifetimes exceeding 500 s. A better understanding of the ion sources is needed to determine how the rotational population varies with source conditions.

In the most stable arrangement, the atoms in H_3^+ form an equilateral triangle. During electron capture (or in a bound Rydberg state), the atomic motion can distort the triangle, causing the potential surface to split into two surfaces connected by a nonzero coupling. An innovative theoretical approach using hyperspherical coordinates has been introduced in which this Jahn-Teller coupling drives the DR of H_3^+ (9). Including indirect recombination but neglecting autoionization and ion rotation gives an upper bound rate constant of $1.2 \times 10^{-8} \text{ cm}^3/\text{s}$. This value is about an order of magnitude below the experimentally determined value for rotationally excited H_3^+ , but still above the afterglow upper limit.

For most ions, we do not yet know what happens after electron capture. Are the products neutral or negatively and positively charged species or both? Which bonds are most likely to break? Can we develop general rules that describe the result of electron capture by polyatomic ions or will the results be unique for each ion? Considerable progress in product identification has been made with spectroscopic techniques for product detection (R. Johnson, University of Pittsburgh; N. G. Adams, University of Georgia).

Experimental studies of the DR of H_3^+ (10), H_2O^+ (11), NH_2^+ (12), and CH_2^+ (13) show that the three-body channel, that is, DR to three product atoms, accounts for 75, 73, 66, and 63%, respectively, of the product branching at electron energies near 0 eV. These numbers are surprisingly close even though the potential surfaces differ. It has been suggested (14) that the higher the energy release, the higher the three-body fraction. However, for H_3^+ , the

three-body percentage is only 35% near 5 eV electron energy. Studies at higher electron energies supplemented with measurements of the angular dependence of the branching percentages are needed.

Using flowing afterglows, recombination of ions as large as the phenanthrene cation ($C_{14}H_{10}^+$) has been reported (B. R. Rowe and C. Rebrion-Rowe, Université de Rennes). Its recombination rate constant is high, $1.7 \times 10^{-6} \text{ cm}^3/\text{s}$. These measurements detect the concentrations of the ions and electrons, not the fragments. It is possible that the rate constant does not apply to DR but instead to electron capture in which energy is deposited into internal modes of the neutral. Studies are beginning on the capture of electrons by multi-charged species including the ions of insulin (T. Tanabe, High Energy Accelerator Research Organization, KEK).

Although H_2^+ is the smallest molecular ion, the mysteries of its DR are only just being revealed. Interference effects due to dissociation on multiple pathways have been explored in theoretical (A. Orel, University of California) and experimental studies (15). For H_2^+ (D. Zajfman, Weizmann Institute), experiments show that the rate constant for superelastic collisions can exceed the DR rate constant, as found theoretically for N_2^+ (16). In superelastic collisions, an excited ion captures an electron

that is emitted before DR can occur. The ion is left in a lower energy state and the deexcitation energy is imparted to the product electron, which has more total energy than the reactant electron.

For those involved in DR research, this is an exciting time. New theoretical methods and experiments are shedding light on basic features even though more than 50 years have passed since the first proposed mechanism. There is much left to learn about this fundamental process and surprises are likely.

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PERSPECTIVES: NUCLEAR MAGNETIC RESONANCE

Multidimensional Symmetry in a Three-Dimensional World

Warren S. Warren

When placed in a strong magnetic field, the spinning motion (angular momentum) of some nuclei, such as the hydrogen atom, gives rise to two energy levels or spin states. Nuclear magnetic resonance (NMR) exploits the fact that the energy level spacings are a sensitive function of the intramolecular bonds (chemical shifts and scalar couplings). They are also sensitive to intramolecular structure (dipolar interactions) but these interactions have historically been viewed mostly as a nuisance to be eliminated.

In recent years, however, the perspective has changed. For example, dipolar interactions in liquids have been used to im-

prove protein structural determinations and enhance image contrast. Along the way, there have been some surprises. The newest such surprise is reported by Baugh *et al.* on page 1505 of this issue (1).

Baugh *et al.* show that large intermolecular dipolar interactions can be observed for hydrogen molecules in nanometer-scale voids in amorphous silicon. Rapid diffusional averaging over all positions in these tiny cavities reduces the spin system to an astonishing effective symmetry: Each of the ~1200 hydrogen atoms in a typical void has exactly the same dipolar coupling to the hydrogen atoms in all other molecules. The results permit direct determination of the size and orientation of the voids and help to understand intermolecular dipolar effects in more conventional samples.

Half a century ago, the NMR community thought it understood dipolar cou-

The author is in the Department of Chemistry and Center for Molecular and Biomolecular Imaging, Princeton University, Princeton, NJ 08544, USA. E-mail: wwarren@princeton.edu