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 1.2×10^{-8} cm^3/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, Universite de Rennes). Its recombination rate constant is high, 1.7×10^{-6} cm^3/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 multicharged 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 improve 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-

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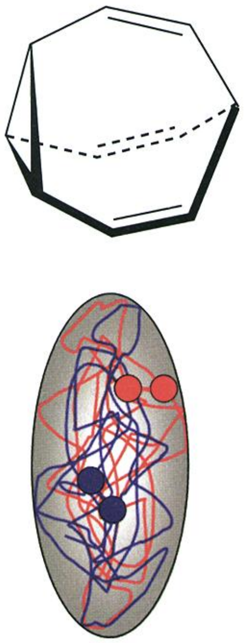
plings well. Observable NMR signals (magnetization) correspond to "flipping" one spin at a time. A dipolar coupling between two spins converts magnetization into unobservable, two-spin correlations. The same dipolar coupling can later convert these two-spin correlations back into magnetization, but this newly created magnetization tends to cancel the original signal. The net effect, in solids, is a broad NMR line that completely masks chemical shifts and scalar couplings. Over the past 50 years, methods have been developed to remove these couplings in solid state NMR, either by sample rotation or by multiple-pulse sequences (*2*).

In liquids and gases, the coupling process is short-circuited (*3*). Diffusion can reorient the internuclear vector between nearby spins in picoseconds, changing the sign of the coupling. As a result, magnetization cancellation is far less effective. Dipolar linewidths in liquid-phase experiments are typically five orders of magnitude smaller than in solids, allowing observation of chemical shifts and scalar couplings that can be used to unravel molecular structure.

The picture got a little more complicated with the advent of NMR in liquid crystal solvents (*4*), where hindered rotation causes intramolecular (but not intermolecular) couplings to partially survive motional averaging. A similar effect is now used to improve structural assignments in proteins (*5*, *6*). Residual dipolar couplings (first in liquid crystals, now also in liquids and gases) provide information about alignment, molecular structure, and sometimes dynamics.

Sometimes the dynamics lead to a very high apparent symmetry. The most dramatic example (until now) was the fluxional molecule bullvalene, $C_{10}H_{10}$ (see the figure). This molecule rearranges so rapidly that there are no permanent carbon-carbon bonds (*7*). If each of the carbon atoms were assigned a number between 1 and 10, then 1,209,600 distinct configurations would be possible; the molecule rearranges fast enough to sample essentially all these configurations on an NMR time scale. As a consequence, not only do all hydrogens have the same chemical shift, the dipolar coupling between each pair of hydrogen spins is also identical (*8*). The molecule thus has an apparent symmetry that should only be possible in 9-dimensional space.

The system studied by Baugh *et al.* is in effect a much larger version of bullvalene. In their growth method for hydrogenated amorphous silicon films, hydrogen molecules are trapped in elongated nanovoids that are aligned perpendicular to the film surface. The pressure inside the voids is about 1.1 kbar at room temperature, corresponding to about 600 molecules per void. On an NMR time scale (milliseconds), each hydrogen molecule freely samples most of the void and has the same average dipolar interaction *D* with every other molecule. This extremely high symmetry permits direct calculation of the effects of many pulse sequences (*9*).



Symmetry champions for dipolar interactions in NMR. (Top) The old champion, bullvalene, rearranges so fast that each of the 10 protons has the same dipolar coupling to each other proton. **(Bottom)** In the new champion, hydrogen molecules in nanocavities sample the entire cavity on an NMR time scale so that each of the 1000 or more spins has the same coupling to each other spin.

Aligning the voids along the magnetic field makes *D* negative, just as aligning two bar magnets end to end makes them attract; aligning the voids perpendicular to the magnetic field makes *D* positive, just as aligning two bar magnets side by side makes them repel. The magnitude of the effect enables the authors to measure the void shape and size (typically about 1.5 nm wide and 4.6 nm long).

The study also provides the first example of a rapidly diffusing system where a mean-field picture (in which nuclear spins are replaced with the local average magnetization) fails to describe intermolecular dipolar effects. About two decades ago (*10*), it was noticed that samples with very large magnetization density (first solid or liquid ^{3}He, later room-temperature solutions in large fields) displayed multiple echoes in inhomogeneous fields from a two-pulse sequence. So-called "CRAZED sequences" produced peaks with all of the experimental properties of intermolecular multiple-quantum coherences [simultaneous flips of multiple spins separated by a macroscopic distance (10 to 1000 μm)] (*11–14*). The first treatment of these effects used the dipolar demagnetizing field (*11*) (the "classical" or "mean-field" treatment). Later, a density matrix analysis (the "quantum" or "coupled-spin" treatment) (*11–15*) was developed that explicitly retained the dipolar couplings to generate intermolecular multiple-quantum coherences.

The relation between these two seemingly vastly different treatments was once controversial. Jeener and co-workers (*16*) and my own group (*15*, *17*) have, under different sets of assumptions, found conditions under which the two treatments give the same answer and have shown that these conditions are well satisfied in normal liquids and gases. The two treatments are currently used interchangeably by researchers exploring dipolar effects in spectroscopy and imaging.

Baugh *et al.* have now found a system with rapid diffusion where the two approaches do not give the same answer. They measure dipolar field effects that are several hundred times larger than a mean-field picture would predict and do not depend on field strength as the mean-field treatment does. Both of these results are consistent with a coupled-spin approach. The difference between the two treatments arises because the hydrogen molecules are always close enough to interact strongly. The effect will decrease as the nanovoid size increases. In contrast, a mean-field effect would depend only on void shape and orientation, not size.

Dipolar effects, far from being a nuisance, now provide a valuable probe of molecular and material structure. Baugh *et al.*'s study takes dipolar applications into a new and exciting size domain.

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