signaling pathways that delay reproduction and increase somatic endurance could adaptively retard organismal decline. When exercised in the adult, such mechanisms could secondarily extend life. Another notion is that developmental timing mechanisms that determine a species' life plan may somehow influence the life span. Perhaps the great natural variation in animal life spans is determined by such global temporal regulators.

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CHEMISTRY

Nuclear Spin Conversion in Molecules

Jon T. Hougen and Takeshi Oka

Molecules with identical nuclei having nonzero spin can exist in different states called nuclear spin modifications by most researchers and nuclear spin isomers by some. Once prepared in a particular state, the arrangement of spins can in principle convert to another arrangement. The concept of nuclear spin modifications in molecules (*1*) is intriguing to chemists because interconversion between different spin states is often slow enough to be considered negligible for many purposes. This in turn allows one to treat different spin modifications as though they were different molecules both in terms of spectroscopy and collision dynamics. In addition, these spin modifications are associated one-to-one with different rotational levels in the molecule. In fact, however, the interconversion rates are not zero, so the scientific questions become: How can these extremely slow rates be measured, and how can these rates be explained by theory? On page 1938 of this issue, Sun *et al.* (*2*) present answers to both of these questions in the case of the ethylene molecule.
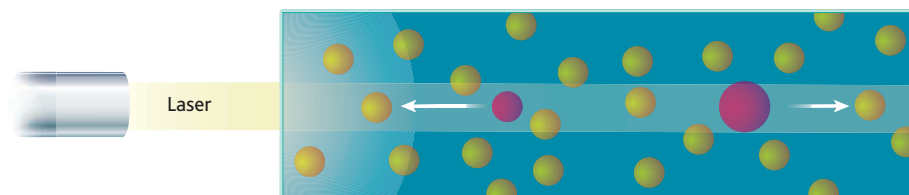
In the case of hydrogen, it is well known that rotational levels with even and odd *J* quantum number belong to the *para* (where the nuclear spins are aligned in opposite directions and *I* = 0) and *ortho* (the spins are parallel and *I* = 1) nuclear spin modifications, respectively (*I* is the total nuclear spin angular momentum of the two H nuclei). Furthermore, nearly pure *para*-H_2 can be readily prepared by cooling hydrogen to low temperature on a paramagnetic catalyst

as initially shown by Bonhoeffer and Harteck in 1929 (*3*). Once prepared, a *para*-H_2 sample can be preserved for months at room temperature in a glass container without converting to *ortho*-H_2. This remarkable stability of a single spin modification was ascribed by Wigner to the smallness of the nuclear spin interaction term that mixes *ortho* and *para* states (*4*).

Spin modifications are relevant also for polyatomic molecules with two or more identical and equivalent nuclei. Thus, for example, H_2O, H_2CO, etc., have *ortho* (*I* = 1) and *para* (*I* = 0) species; NH_3, CH_3F, etc.,

Getting the drift. Laser light tuned slightly below resonance excites a molecule moving away from the laser (red sphere on the right) and increases its size. The molecule is slowed down by collisions with buffer gas because of its larger size. A molecule in the same level moving toward the laser (red sphere on the left), however, is not excited and keeps moving with the normal speed. This causes a net drift toward the laser of molecules with selected spin modification. The increase of the molecular size is greatly exaggerated for clarity. [Adapted from (*8*)]

have *ortho* (*I* = 3/2) and *para* (*I* = 1/2) species; and CH_4 has *ortho* (*I* = 1), *meta* (*I* = 2), and *para* (*I* = 0) species. More complicated molecules such as C_2H_4 have more than three spin modifications, and their symmetry is used to label different spin modifications, as reported by Sun *et al.* (*2*). Polyatomic molecules have faster interconversion rates than H_2, not because their magnetic interactions are larger but because their rotational levels are closer. This is particularly true for spherical-top molecules in which levels are clustered and some levels with different spin modifications are very close. Thus, Ozier *et al.* observed a spectrum between *ortho* and

para CH_4, by shifting an *ortho* level close to a *para* level with a magnetic field, and determined the small mixing term (*5*). For a heavy spherical top like SF_6 with very high rotational level (*J* = 53), the levels are so close that Bordé and colleagues naturally observed transitions between different spin species (*6*).

The theory for spin conversion in polyatomic molecules by collision was first formulated by Curl *et al.*, who enumerated mixing terms in the spirit of Wigner's theory—that is, choosing those nuclear spin interaction terms that are invariant with respect to exchange of the entire sets of nuclear coordinates but are not invariant to exchange of spin coordinates alone (*7*). They identified levels belonging to different spin modifications that are accidentally close and surmised that interconversion occurs through those pairs of levels. The validity of the theory of Curl *et al.* has been demonstrated by a series of beautiful experiments by Chapovsky and his collaborators since 1980. They introduced the method of light-induced drift developed in the former Soviet Union (see the figure) and succeeded in separating *ortho* and *para* species of CH_3F, the first such separation since H_2 and D_2 were separated several decades ago. [Readers are referred to an excellent review by Chapovsky and Hermans (*8*) for more details of history, experiments, and theory of the field.] This is the technique used by Sun *et al.* in their studies.

The exciting aspect of the experiment by Takagi and colleagues. (*2*) is that ethylene, C_2H_4, has symmetry with higher dimension than that of other molecules so far studied,

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and there are four nuclear spin modifications with different symmetry. This has allowed them to demonstrate yet another subtlety of the interconversion. Because the parity (the symmetry of the wave functions with respect to an inversion in space) is rigorous in atomic and molecular physics, the parity selection rule, unlike the *ortho*/*para* selection rule, should not be violated in these experiments. In other words, the nuclear spin interaction considered by Wigner and enumerated by Curl *et al*. may mix different spin species but cannot mix parity. This is clearly demonstrated in figure 2 of Sun *et al*. (*2*). Figure 2A (*2*) shows that there is an interconversion between the B_{2u} and B_{3u} species, and figure 2B shows that there is no interconversion between the B_{2u} and A_g species. The symbols g and u represent symmetric and antisymmetric states with respect to the molecule-fixed inversion operation, i.e., interchange of two pairs of H nuclei and inversion of space. However, all rotational functions are g with respect to this operation, and thus it turns out for a planar molecule like ethylene that g and u nuclear spin functions are associated with rotational–nuclear-spin wave functions of + and – parity. Thus, $B_{2u} \leftrightarrow B_{3u}$ conversion in ethylene is parity allowed but $B_{2u} \leftrightarrow A_g$ is parity forbidden, as indeed shown in figure 2 of Sun *et al*. (*2*).

This leaves an interesting problem to be solved. The authors should be able to determine the magnitude of the interaction term from the observed interconversion rate. In order to do this, the authors need to locate a pair or pairs of levels with the B_{2u} and B_{3u} symmetry that are accidentally or systematically (*9*) close through which the conversion proceeds. They also need to estimate collision cross sections that are temperature dependent. Experimentally, it will be interesting to measure the temperature dependence of the conversion rate. Also measuring the conversion rate caused by other gases will be interesting, especially paramagnetic gases such as oxygen. It is well known that *para*-H_2 converts to *ortho*-H_2 much faster in the presence of O_2. The mechanism of such conversion must be different from that considered by Curl *et al*.

Which other molecules will be interesting to study? Benzene, C_6H_6, has spin modifications with six different symmetries: A_{1g}, A_{2g}, E_{2g}, B_{1u}, B_{2u}, and E_{1u}. Here also, the molecule is planar, so one might expect that the parity selection rule will be equivalent to g $\leftrightarrow$ g and u $\leftrightarrow$ u. Because rotational levels in this symmetric-top molecule with $K = 6n$ (where $n \neq 0$) systematically consist of very nearly degenerate B_{1u}-B_{2u} nuclear spin pairs, rotational levels with quantum number $K = 6n + 3$ consist of very nearly degenerate A_{1g}-A_{2g} nuclear spin pairs, and the E nuclear spin functions do not cluster, one can further speculate (*9*) that conversion rates within the nuclear spin A species or within the B species will be much faster than rates between A and E or between B and E species. Ethane, C_2H_6, has spin modifications with seven different symmetries

A_1, A_4, E_1, E_2, E_3, E_4, and G. Because the molecular symmetry group of ethane does not have any element corresponding exactly to inversion in space, the connection between symmetry species and parity is more complicated than for the planar molecules mentioned above. One can thus wonder if permutation-inversion symmetry species together with systematic level clustering will in the end provide a more unified way of discussing allowed nuclear spin conversions than parity together with accidental degeneracies does. In any case, a study of nuclear spin conversion rates in other highly symmetric molecules will almost certainly reveal further subtleties of the mechanism. However, the experiments will become more challenging as one goes to heavier molecules because of the larger rotational partition function.

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GEOCHEMISTRY

# A Tale of Early Earth Told in Zircons

Yuri Amelin

No rock or mineral record has been preserved from Earth's "dark age"—the mysterious time after accretion of the planet about 4560 million years ago. Thanks to a continuous effort to find the oldest pieces of our planet, however, the duration of this unknown era is becoming shorter and shorter. Following the development of modern isotopic dating, the extent of the dark age was established at about 800 to 1000 million years by the discovery of exceptionally old rocks in western Greenland (*1*). The discovery of still older grains of zircon (zirconium silicate, a common if not very abundant component of crustal rocks, and an extraordinarily resilient mineral) in archean sedimentary rocks in Western Australia reduced the dark age to 400 to 300 million years (*2*, *3*) and recently to less than 200 million years (*4*), a mere 5% of Earth's life span. That this was an eventful time is clear from studies of the Moon and Mars, where internally driven magmatism and differentiation ceased quickly or slowed down. We know that the processes that shaped further evolution of these bodies—large-scale mantle differentiation and formation of the primary crust—were occurring within the first few hundred million years.

On page 1947 of this issue, Harrison *et al*. (*5*) report their use of some of the oldest known zircons to explore the prehistory of the source rocks of these minerals. Their approach relies on the slow radioactive decay of the rare isotope ^{176}Lu to ^{176}Hf (half-life 37 billion years). This decay process increases the ratio of ^{176}Hf to other isotopes of hafnium, usually expressed as ^{176}Hf/^{177}Hf. The rate of growth of the ^{176}Hf/^{177}Hf ratio is proportional to the Lu/Hf ratio. In geochemical studies, the ^{176}Hf/^{177}Hf ratio in a mineral or rock is expressed as a deviation from this ratio in bulk silicate earth (thought to be broadly similar in composition to, and determined from, chondritic meteorites). This deviation is measured in parts per 10,000 and is denoted as $\varepsilon_{Hf}(T)$, where T is time. When primitive mantle differentiates to form continental crust (a cover of less dense aluminum- and silicon-rich rocks) and depleted mantle (the more dense and refractory magnesium- and iron-rich residue left after extraction of crust-forming melts), the depleted mantle acquires a Lu/Hf ratio several times that found in crustal rocks. As a result, the ^{176}Hf/^{177}Hf ratio in the mantle grows faster than in the crust and $\varepsilon_{Hf}(T)$ becomes positive, whereas the complemen-

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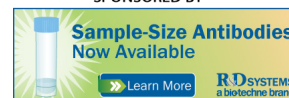
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