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The Spin Chemistry and Magnetic Resonance of $H_2@C_{60}$. From the Pauli Principle to Trapping a Long Lived Nuclear Excited Spin State inside a Buckyball

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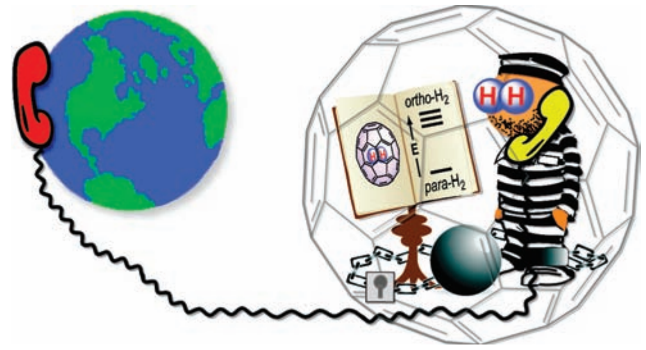

One of the early triumphs of quantum mechanics was Heisenberg's prediction, based on the Pauli principle and wave function symmetry arguments, that the simplest molecule, H_2, should exist as two distinct species—allotropes of elemental hydrogen. One allotrope, termed *para*-H_2 (pH_2), was predicted to be a lower energy species that could be visualized as rotating like a sphere and possessing antiparallel (↑↓) nuclear spins; the other allotrope, termed *ortho*-H_2 (oH_2), was predicted to be a higher energy state that could be visualized as rotating like a cartwheel and possessing parallel (↑↑) nuclear spins. This remarkable prediction was confirmed by the early 1930s, and pH_2 and oH_2 were not only separated and characterized but were also found to be stable almost indefinitely in the absence of paramagnetic "spin catalysts", such as molecular oxygen, or traces of paramagnetic impurities, such as metal ions.

The two allotropes of elemental hydrogen, pH_2 and oH_2, may be quantitatively incarcerated in C_{60} to form endofullerene guest@host complexes, symbolized as $pH_2@C_{60}$ and $oH_2@C_{60}$, respectively. How does the subtle difference in nuclear spin manifest itself when hydrogen allotropes are incarcerated in a buckyball? Can the incarcerated "guests" communicate with the outside world and vice versa? Can a paramagnetic spin catalyst in the outside world cause the interconversion of the allotropes and thereby effect a chemical transformation *inside* a buckyball? How close are the measurable properties of $H_2@C_{60}$ to those computed for the "quantum particle in a spherical box"? Are there any potential practical applications of this fascinating marriage of the simplest molecule, H_2, with one of the most beautiful of all molecules, C_{60}? How can one address such questions theoretically and experimentally?

A goal of our studies is to produce an understanding of how the H_2 guest molecules incarcerated in the host C_{60} can "communicate" with the chemical world surrounding it. This world includes both the "walls" of the incarcerating host (the carbon atom "bricks" that compose the wall) and the "outside" world beyond the atoms of the host walls, namely, the solvent molecules and selected paramagnetic molecules added to the solvent that will have special spin interactions with the H_2 inside the complex. In this Account, we describe the temperature dependence of the equilibrium of the interconversion of $oH_2@C_{60}$ and $pH_2@C_{60}$ and show how elemental dioxygen, O_2, a ground-state triplet, is an excellent paramagnetic spin catalyst for this interconversion. We then describe an exploration of the spin spectroscopy and spin chemistry of $H_2@C_{60}$. We find that $H_2@C_{60}$ and its isotopic analogs, $HD@C_{60}$ and $D_2@C_{60}$, provide a rich and fascinating platform on which to investigate spin spectroscopy and spin chemistry. Finally, we consider the potential extension of spin chemistry to another molecule with spin isomers, H_2O, and the potential applications of the use of $pH_2@C_{60}$ as a source of latent massive nuclear polarization.

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Introduction: Elemental Spin Chemistry of H_2, O_2, and C_{60}

Our research group has studied the spin chemistry of guest@host complexes of singlet and triplet radical pairs for several decades.[1] For example, photochemical production of a radical pair as a guest in a host system results in large magnetic field effects and magnetic isotope effects on the lifetimes and on the products of the reactions of the radical pairs. The existence[2] of the two molecular hydrogen *spin isomers*, *ortho*-H_2 (*o*H_2) and *para*-H_2 (*p*H_2), was also of interest. We were fascinated with the seminal reports of the endofullerenes,[3] structures for which atoms and molecules were incarcerated in fullerenes, and wondered about possible investigations of their photochemistry and spin chemistry. However, there was no obvious connection between H_2 and endofullerenes in our research portfolio of spin chemistry of guest@host systems. This situation changed after a conversation in 2005 with Professor Martin Saunders of Yale University, a pioneer[3a] in the synthesis and study of atoms and molecules in fullerenes. Professor Saunders pointed out the elegant synthesis of $H_2@C_{60}$ by Professors Koichi Komatsu and Yasujiro Murata of Kyoto University,[4] inspiring us to initiate what has turned out to be a very fruitful and productive collaboration to investigate the spin chemistry and magnetic spectroscopy of $H_2@C_{60}$, which began after a meeting with Professors Komatsu and Murata at the ACS Pacifichem meeting in December of 2005. This Account describes the progress we have made investigating the spin chemistry of $H_2@C_{60}$.

To supramolecular chemists, $H_2@C_{60}$ is an important example of a guest@host system. To spin and photochemists, $H_2@C_{60}$ provides a virtual gold mine of intriguing aspects for investigation. For example,[5,6] could the paramagnetic triplet "skin" of $H_2@{}^3C_{60}$ serve as a spin catalyst of the interconversion of *o*$H_2@C_{60}$ and *p*$H_2@C_{60}$? The latter interconversion would correspond to a chemical reaction, performed inside a buckyball! We did not expect, however, that another favorite element for photochemists, triplet molecular oxygen ($^3O_2$), and its lowest lying electronically excited state, singlet oxygen ($^1O_2$), would also play an important role in our investigations of the spin chemistry of $H_2@C_{60}$.

The Allotropes of H_2: *ortho*-H_2 and *para*-H_2

The word allotrope (Greek, *allos* = another and *tropos* = form) was coined to describe an element that exists as two or more distinct chemical substances. Two familiar allotropes with different compositions are oxygen (O_2) and ozone (O_3). Based on more recent work, we now know that there are a huge number of allotropes with the composition C_n, for which *n* may be almost any number. Two recent allotropes are C_{60} and C_{70}, members of the class of fullerenes.[7] Surprisingly, perhaps, there are two completely different substances that possess the diatomic composition H_2, namely the two allotropes *p*H_2 and *o*H_2. A difference between these allotropes is *a difference in spin stereochemistry*, that is, *in the relative orientation of their nuclear spins*! As shown in Figure 1, *o*H_2 has a parallel nuclear spin orientation (⇈) and *p*H_2 has an antiparallel nuclear spin orientation (⇅). For organic chemists, perhaps the most profound difference between these two substances is that *p*H_2 (⇅) is NMR "silent" and does not possess a ^{1}H NMR spectrum, whereas *o*H_2 (⇈) is NMR active and possesses the ^{1}H NMR spectrum. In the absence of a paramagnetic spin catalyst, these two spin isomers can be completely separated from one another and are stable for months at room temperature! However, there is another remarkable difference between *p*H_2 and *o*H_2 that is imposed by the Pauli principle: the rotational states of these two allotropes are intimately entangled with their rotational motion. Let us see how this works, since the history makes a fascinating chemical story in its own right.

Heisenberg's Prediction of the Allotropes of H_2 and the Nobel Prize. The Pauli Principle and the Quantum Mechanical Basis of the Two Spin Isomers of H_2

The citation of the Nobel Prize awarded to Werner Heisenberg in 1932 stated that he had "created quantum mechanics, the application of which led to the discovery of the two *allotropic forms of hydrogen*". Let us describe schematically (Figures 1 and 2) the quantum mechanical basis for the differences between *o*H_2 and *p*H_2 and then consider the implications of these differences for applications to both electron

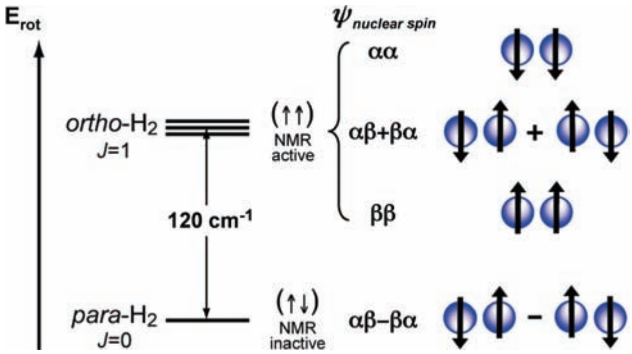


FIGURE 1. Energy diagram for the four lowest spin-rotational states of H_2. The Pauli principle requires that the lowest rotational state ($J = 0$, symmetrical wave function) possesses a singlet nuclear spin state (⇅) and that the first rotational state ($J = 1$, antisymmetrical wave function) possess a triplet nuclear spin state (⇈). *p*H_2 is 120 cm^{-1} (0.3 kcal/mol) lower in energy than *o*H_2.

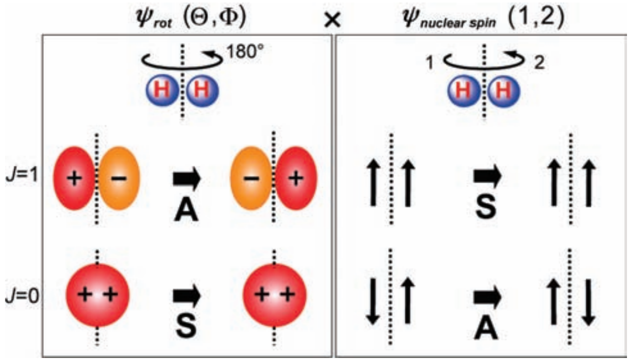


FIGURE 2. Schematic description of the effect on rotation about the H−H axis on the symmetry (A or S) of the rotational wave function (left) and the spin wave function (right) for the lowest energy pH_2 ($J = 0$) and oH_2 ($J = 1$) rotational states. A rotation about the H−H axis is S for $J = 0$ and A for $J = 1$ for the rotational wave function and is S for parallel (↑↑) triplet spin orientation and A for antiparallel (↑↓) singlet spin orientation.

and nuclear spin chemistry and electron and nuclear spin spectroscopy.

Heisenberg's prediction of the existence of the two allotropes of H_2 is based on the Pauli principle's very strict conditions on the acceptability of molecular wave functions under the exchange of indistinguishable fermion particles (e.g., electrons or protons): The overall total wave function of a molecule (Ψ_{total}) *must* change sign when two indistinguishable fermions are interchanged. In simple terms, $\Psi_{total}(1,2) = -\Psi_{total}(2,1)$ for the exchange of indistinguishable fermions 1 and 2. Figure 1 displays the lowest energy levels of pH_2 and oH_2 and two descriptions, one mathematical and one pictorial, of Ψ_{spin}, the nuclear spin wave functions. Without going into a detailed discussion, we can follow Heisenberg's argument for the existence of two allotropes by considering the symmetry restrictions imposed on Ψ_{total} by the molecular symmetry of H_2. The symmetry of the electronic (Ψ_{elect}) and vibrational (Ψ_{vib}) parts of Ψ_{total} are symmetrical (S) with respect to molecular symmetry operations such as a 180° rotation about the H−H axis. Therefore, if a change in sign of Ψ_{total} is to occur, the change must result from the symmetry properties of the spin (Ψ_{spin}) and rotational (Ψ_{rot}) parts of Ψ_{total}. Let us see how to visualize the symmetries of these two wave functions of H_2 and how these symmetries behave upon the symmetry operation of a rotation about the molecular axis of H_2.

Consider Figure 2, which displays schematically the symmetry (S or A) of the spin (Ψ_{spin}) and rotational (Ψ_{rot}) wave functions as the result of 180° rotation about the H−H axis. Since the symmetry of Ψ_{rot} is of the same form as that of simple atomic orbitals, we conclude (1) that for the lowest rotational level ($J = 0$), the rotational wave function, $\Psi_{rot}^{J=0}$, possesses S symmetry, the same as that of an atomic s-orbital and (2) that the symmetry of $\Psi_{rot}^{J=1}$ for the first excited rotational level ($J = 1$) possesses A symmetry, the same as that of an atomic p-orbital.

The symmetries of the nuclear spin functions are a bit more complicated (Figure 1) but can be deduced from the schematic representations shown in Figure 2. A 180° rotation about the H−H axis causes $\Psi_{spin}^{pH_2}$ to change sign (A symmetry), but for the same rotation $\Psi_{spin}^{oH_2}$ does not change sign (S symmetry).

According to the Pauli principle, for a 180° rotation of H_2, $\Psi_{total}(1,2) = -\Psi_{total}(2,1)$, where the labels refer to two indistinguishable protons 1 and 2. We conclude that $\Psi_{rot}^{J=0} = S$, $\Psi_{rot}^{J=1} = A$, $\Psi_{spin}^{pH_2} = A$, and $\Psi_{spin}^{oH_2} = S$. From these symmetry considerations, we are forced to conclude that the only acceptable wave functions for H_2 are the following combinations: (1) $\Psi_{rot}^{J=0} = S$ *only* when $\Psi_{spin}^{pH_2} = A$; (2) $\Psi_{rot}^{J=1} = A$ *only* when $\Psi_{spin}^{oH_2} = S$. For example, pH_2 must be in the $J = 0$ *ground state* rotational level and oH_2 must be in the $J = 1$ *excited* rotational level! Thus, the allotropic isomerism of H_2 is due to *a difference in both spin orientation and in rotational properties!* We shall see how this remarkable marriage of rotation and spin for H_2 molecules as the result of the Pauli principle has a profound implication for its spin chemistry and magnetic spectroscopy of H_2 and of $H_2@C_{60}$. But first, let us review briefly the remarkable synthesis of $H_2@C_{60}$.

Synthesis of $H_2@C_{60}$ (and $HD@C_{60}$ and $D_2@C_{60}$)

The synthesis[4] of $H_2@C_{60}$ is outlined schematically in Figure 3. The synthetic approach has been termed a "molecular surgery strategy" that employs the following steps: (1) creating a hole on the C_{60} surface by a cage opening; (2) increasing the size of the hole until its size allows insertion of H_2 at high pressure and temperature and (3) closing the hole to regenerate the C_{60} fullerene host with an incarcerated H_2 guest. $HD@C_{60}$ and $D_2@C_{60}$ were synthesized by an analogous method in which HD or D_2 is substituted for H_2 in the inclusion step.

Experimental ^1H NMR Investigations of H_2 and $H_2@C_{60}$. Spin−Lattice Relaxation and Paramagnet Relaxivity of H_2 and $H_2@C_{60}$

Incarceration of H_2 inside C_{60} influences the NMR properties of H_2. For example, the chemical shift of H_2 in organic solvents is typically found at approximately +4.5 ppm, whereas the chemical shift of $H_2@C_{60}$ is found at much higher fields, approximately −1.3 ppm, "to the right of TMS".

Spin−lattice relaxation of magnetic nuclei in an external magnetic field is characterized by a relaxation time, T_1 (rate constant $k_1 = 1/T_1$). Since the value of T_1 for H_2 is related to

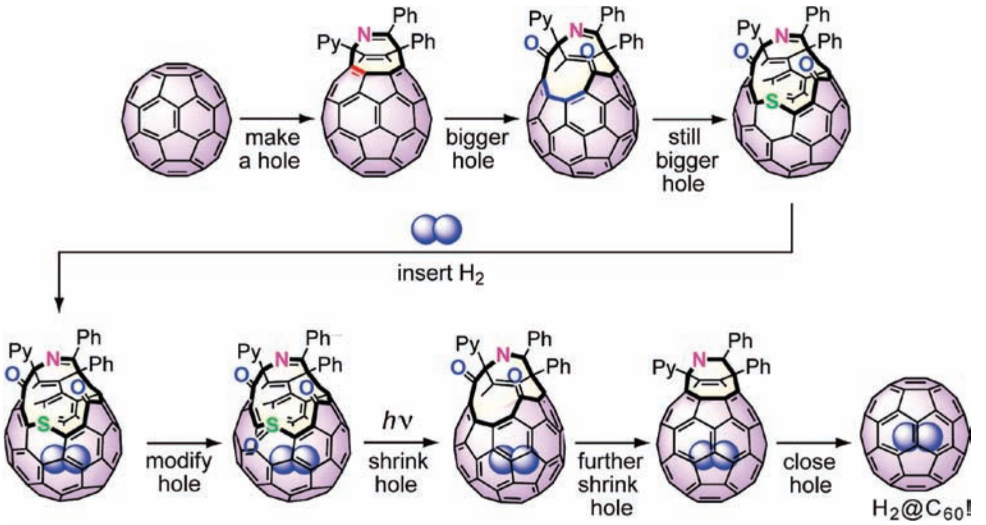


FIGURE 3. An example of molecular surgery: the synthesis of $H_2@C_{60}$. Starting with C_{60}, the surgery starts with the opening of the buckyball followed by creation of larger holes until the hole is large enough for the insertion of H_2 at high temperature and pressure. Upon return to room temperature and atmospheric pressure, the H_2 is incarcerated and stable inside the fullerene. The surgery is completed by closing the hole and regenerating C_{60}.

its molecular motion and the mechanism of spin−spin and other magnetic interactions, it was of interest to make a comparative investigation of T_1 of both H_2 and $H_2@C_{60}$. A systematic comparison of the nuclear spin−lattice relaxation of H_2 and $H_2@C_{60}$ was conducted[8] in various solvents in order to explore and compare the effects on T_1 of the interactions of an H_2 molecule transiently incarcerated within the walls of a solvent cavity with those for an H_2 molecule incarcerated within the cavity of a buckyball, C_{60}.

In a variety of perdeuterated organic solvents (chloroform-d_1, toluene-d_8, 1,2-dichlorobenzene-d_4, 1,1,2,2-tetrachloroethane-d_2), the value of T_1 of H_2 is $\sim$1 s, whereas the value of T_1 of $H_2@C_{60}$ is $\sim$0.1 s, an order of magnitude shorter for the incarcerated guest. Furthermore, both relaxation times exhibit a temperature-dependent maximum at ca. 260 K. These results were analyzed assuming that for both H_2 and $H_2@C_{60}$, the dominant relaxation mechanism at high temperature is due to the intramolecular spin-rotation interaction and at low temperature the intramolecular dipole−dipole interaction between the nuclear spins. This analysis made it possible to estimate the characteristic correlation time for reorientation of H_2 in both media. It is found that, at the same temperature, H_2 reorients itself about an order of magnitude faster in solution than as a guest in $H_2@C_{60}$, as might be expected for a very small molecule tumbling in the "soft" solvent cage, compared with the closed confines of the "hard" walls of C_{60}. In addition, in both media the reorientation correlation time is at least an order of magnitude *slower* than the rate of free rotation calculated from the thermally averaged rotation frequency of the isolated molecule. Thus, in a simplistic interpretation, the incarcerated H_2 "feels" the walls of the C_{60} cage to a greater extent than in a solvent but is still undergoing rapid reorientation relative to the motion of the cage. In both cases, the rotation of H_2 is slowed relative to its motion as an isolated molecule.

Proton and ^{13}C NMR of $H_2@C_{60}$ and some of its derivatives have also been studied in the solid state over a range of temperatures and magnetic fields.[9] Among the fascinating results obtained from ^{13}C and ^1H relaxation times and other measurements are several that are particularly relevant to our discussion: (1) at low temperatures, the presence of the endohedral H_2 molecule reduces substantially the barrier to rotational jumps of C_{60} in the solid, (2) measurement of ^1H T_1's over a much larger temperature range than is possible in liquids reveals not only substantial rotational motion of the trapped H_2 molecule at even the lowest temperatures but leads to the conclusion that the thermal motion of the cage, which is minimal in the solid, must contribute to the substantially longer T_1's observed in solution, and (3) probing the $^1H-^1H$ dipolar interaction reveals a weak interaction between ^1H spins in H_2 molecules trapped in cages on neighboring sites. Solid-state NMR clearly has much to contribute to understanding the structure and dynamics of trapped H_2, the C_{60} cage, and the interaction between them.

Relaxivity is the quantitative term applied to the ability of a paramagnetic species, PM, such as $^3O_2$ or a nitroxide, to enhance the spin relaxation of a nuclear spin beyond the relaxation induced by the surrounding lattice. From a measurement of the value of the observed total spin relaxation rate constant, R_1, as a function of [PM], a value of the bimo-

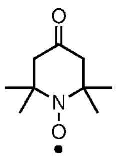
TABLE 1. Representative Comparisons of Rate Constants for H_2 and $H_2@C_{60}$:[a] (1) Relaxation Rate Constants (k_1); (2) Relaxivities (k_{RX}); and (3) pH_2-oH_2 Conversion Rate Constants (k_{po})

dynamic process	relaxation rate constants, k_1 (s^{-1}) [T_1 (s)]	"uncatalyzed" pH_2-oH_2 conversion rate constants, k_{po} (s^{-1}) [T_{po} (s)]	relaxivity, k_{RX} ($M^{-1}s^{-1}$)	conversion rate constants, k_{po} ($M^{-1}s^{-1}$)	k_{RX}/k_{po}
H_2	0.83 [1.21]	10^{-4} [10,000] (~ 3 h)	14.5	8.3×10^{-2}	270
$H_2@C_{60}$	12.20 [0.082]	10^{-6} [6.5×10^5] (~7.5 days)	70	4×10^{-5}	1.7×10^6

[a] Unless otherwise indicated, measurements have been carried out at $T = 300$ K, at a field of 11.7 T (500 MHz).

lecular rate constant for relaxivity, k_{RX} can be evaluated. Such measurements are completely analogous to the "Stern–Volmer" plots so familiar to photochemists for the extraction of rate constants from the dependence of some parameter on the concentration of a quencher/reagent. Relaxivity can be considered as spin catalysis of spin–lattice relaxation for which a single molecule, PM, in the lattice is particularly effective in causing relaxation.

In toluene-d_8 for nitroxide **1** as a PM, the values of k_{RX} for H_2 and $H_2@C_{60}$ are ~14 and ~70 M^{-1} s^{-1}, respectively (Table 1).[8b] From these results, the average distance of encounter between the paramagnet and the nuclei of H_2 is computed to be approximately the sum of the van der Waals radii of the two molecules for H_2 in solution. However, for $H_2@C_{60}$, the distance is much smaller. We conclude that H_2 in C_{60} is *less* shielded than expected from the magnetic field of **1**, less than is free H_2. This remarkable result is consistent either with the formation of a complex between **1** and $H_2@C_{60}$ or with a special mechanism for magnetic communication between the electron and nuclear spins that is more effective than the dipole–dipole coupling. But perhaps the most striking finding is that the indirect communication of the paramagnet (a form of superexchange) with the incarcerated guest ($H_2@C_{60}$) through collisions with the guest walls is *more* effective, as measured by k_{RX}, than is the direct collisional communication between the paramagnet and the free guest H_2.



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Running a Chemical Reaction between H_2 Allotropes inside a Buckyball. Spin Conversion of H_2 and $H_2@C_{60}$ by Spin Catalysis with Elemental $^3O_2$

Let us now consider the conversion of pH_2 to oH_2 and of oH_2 to pH_2. The conversion is strongly forbidden because of the lack of any available mechanism for mixing of the nuclear spin states. As a result, in the absence of a paramagnetic "spin catalyst", the interconversion is extremely slow. Paramagnetic spin catalysis of the pH_2 to oH_2 and oH_2 to pH_2 conversion arises from the difference in magnetic field of the paramagnet that is experienced by the two nuclear spins of H_2. The effectiveness of a paramagnetic spin catalyst may be characterized by the conversion rate constants, k_{po} and k_{op}, respectively, for the pH_2 to oH_2 and oH_2 to pH_2 conversion. The paramagnetic spin catalysis of the conversion of the H_2 allotropes is related to the relaxivity contribution to T_1 arising from fluctuating fields due to collisions with the paramagnet that determines the rate constant for relaxivity, k_{RX} described above. Therefore, we set forth to measure both k_{RX} and the rate constant for pH_2 to oH_2 conversion, k_{po}, for H_2 using the same paramagnetic relaxant, solvent, and temperature.

To determine the value of k_{po} in solution, an enriched sample of pH_2 is required. A sample of hydrogen enriched in pH_2 is readily prepared[2] by passing nH_2 (defined as the equilibrium mixture of H_2 at a given temperature and corresponding to a 25%/75% mixture of pH_2 and oH_2 at room temperature) through a porous catalyst containing paramagnetic sites. Activated charcoal is such a spin catalyst that causes conversion at low temperatures at a convenient rate, which allows the achievement of equilibrium and enrichment in the lower energy pH_2 (Figure 1). When rapidly returned to room temperature in the absence of a spin catalyst, the enriched pH_2 is stable for months or longer!

The percent of pH_2 relative to oH_2 at equilibrium depends strongly on the temperature in the range of 20–150 K (Figure 4). At a conveniently available temperature, 77 K, that of boiling liquid nitrogen, the equilibrium mixture corresponds to 50% pH_2 and 50% oH_2.

The strategy for the enrichment in $pH_2@C_{60}$, a solid at room temperature, needs to be modified from that for H_2, a gas at room temperature. Our strategy for the enrichment has the following components:[10a] (1) development of a paramagnetic spin catalyst that can catalyze the conversion of $oH_2@C_{60}$ to $pH_2@C_{60}$ at 77 K (or lower) and that can then be removed at 77 K or can be removed *rapidly* to prevent back conversion as the sample is returned to room temperature; (2) development of a means of dispersing the $H_2@C_{60}$ molecules so

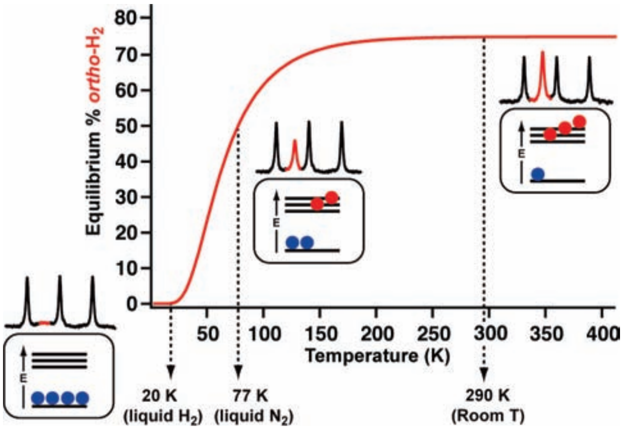

FIGURE 4. The percent oH_2 in equilibrium mixtures of oH_2 and pH_2 plotted versus temperature. The expected relative distributions of the two forms in the $J = 0$ and $J = 1$ rotational states as functions of temperature are shown schematically, with the lower level corresponding to $J = 0$. The expected ^1H NMR of a mixture of H_2 (red signal) and HD (black signal) at high and low temperature is shown (*vide infra*).

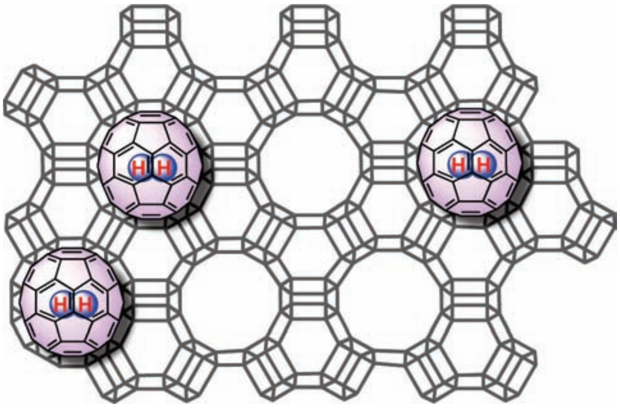

FIGURE 5. Schematic of the molecular dispersion of H_2@C_{60} on external surface of the zeolite NaY (modified from ref 10b).

that each molecule can come into contact with the spin catalyst at low temperature; (3) development of an analytic method to quantify the relative percent of pH_2@C_{60} and oH_2@C_{60} in a sample.

Elemental oxygen, $^3O_2$, was selected as the paramagnetic spin catalyst for the conversion since it is a liquid at 77 K. In addition, the high volatility of $^3O_2$ allows the paramagnetic catalyst to be easily removed from the sample at 77 K by simply applying a vacuum. Intimate contact between $^3O_2$ and each H_2@C_{60} molecule is required for effective spin catalysis. This intimate contact was achieved by dispersing the H_2@C_{60} onto the external surface of a zeolite whose external porous structure allows only one H_2@C_{60} molecule to occupy each external pore (Figure 5). The zeolite NaY meets these requirements with external pores that are ~8 Å in diameter, very close to the diameter computed for the van der Waals size of C_{60}.

^1H NMR analysis was selected as a convenient analytical method for monitoring the interconversion of oH_2@C_{60} and pH_2@C_{60}. The NMR measurement takes advantage of the fact that singlet, diamagnetic pH_2 is "NMR silent" (does not possess any net nuclear spin and therefore does not produce an NMR signal), whereas triplet, paramagnetic oH_2 is "NMR active". Thus, the ^1H NMR signal arises exclusively from oH_2 (which possesses a net nuclear spin of 1 and therefore produces an NMR signal). The accuracy of the ^1H NMR was improved markedly by designing an internal standard for ^1H NMR analysis that would be as similar as possible to H_2@C_{60}, have a chemical shift close to that of H_2@C_{60}, and yet is not converted to a new material at 77 K in the presence of a paramagnetic spin catalyst. With these considerations in mind, it occurred to us that HD@C_{60} would be an outstanding internal standard. Since H and D are *distinguishable* particles, HD is not required to follow the Pauli principle, that is, a quantum mechanically enforced coupling of nuclear spins with rotational levels. Thus, upon cooling and warming, HD achieves an equilibrium between its rotational states very rapidly. This means that the ^1H NMR signal will be the same at room temperature for a HD@C_{60} sample upon cooling to 77 K and then returning to room temperature.

We note that the ^1H NMR of HD@C_{60} is a triplet due to spin–spin coupling with D, which has a spin of 1. Fortunately, as shown in the ^1H NMR of HD@C_{60} (black curves, Figure 4), each of its three signals is resolved from that of H_2@C_{60} (red curves, Figure 4). Importantly, as discussed above, since HD is not subject to the Pauli restrictions of H_2, the ^1H NMR intensity of HD will be proportional to the number of HD@C_{60} molecules at all temperatures; however, the ^1H intensity of the signal from H_2@C_{60} will be proportional to the number of oH_2@C_{60} only. Furthermore, it would be expected that the physical properties of H_2@C_{60} and HD@C_{60} are sufficiently similar so that the ratio of the two species should not change during the adsorption/extraction on/from the zeolite or the enrichment process. Thus, if the experiment works as designed, at the time of NMR analysis, the signal of the extracted HD@C_{60} will be exactly the same before and after the treatment of the sample with the paramagnetic catalyst, $^3O_2$, at 77 K; however, because of its slow conversion in the absence of the removed spin catalyst, the H_2@C_{60} should show a significant decrease in the ^1H NMR signal due to the decrease in the relative amount of oH_2 in the equilibrium mixture as the result of the treatment. Therefore, comparison of the NMR signal intensities for H_2@C_{60} and HD@C_{60} at various times will provide a quantitative measure of the change in the percentage of oH_2@C_{60} in the sample.

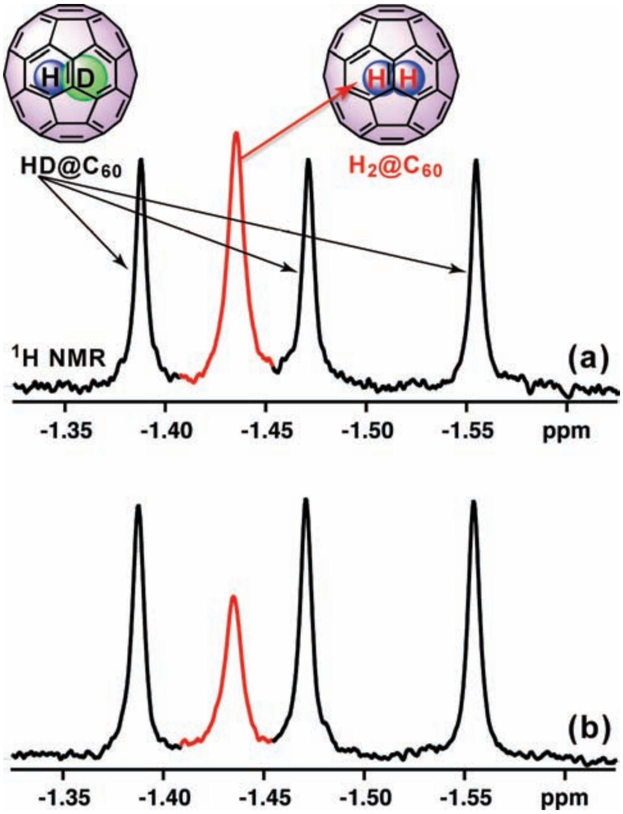

FIGURE 6. Comparison of the ^1H NMR spectrum of a mixture of $H_2@C_{60}$ and $HD@C_{60}$ in 1,2-dichlorobenzene-d_4 before (a) and after (b) treatment with liquid oxygen at 77 K.

Running a Chemical Reaction Inside a Buckyball. Conversion of the Allotropes of H_2 by Spin Catalysis

In a typical conversion experiment, a mixture of $[H_2@C_{60}]@NaY$ and $[HD@C_{60}]@NaY$ was cooled to 77 K on a vacuum line, and gaseous oxygen was added and allowed to liquefy until the $H_2@C_{60}@NaY$ and $[HD@C_{60}]@NaY$ complexes were completely immersed in liquid $^3O_2$. The sample was kept at 77 K for approximately 30 min and then the oxygen spin catalyst was removed by applying a vacuum for approximately 30 min at 77 K. The $[H_2@C_{60}]@NaY$ and $[HD@C_{60}]@NaY$ mixture was then treated with CS_2 at room temperature to extract $H_2@C_{60}$ and $HD@C_{60}$ from the zeolite. The ^1H NMR of the extracted endofullerenes was then taken. Figure 6 shows a comparison of the ^1H NMR spectra of the sample before adsorption on the external surface of NaY (a) and after the conversion and extraction procedure (b) described above. An obvious decrease in the intensity of the ^1H signal for the $oH_2@C_{60}$ relative to that of $HD@C_{60}$ is apparent. Quantitative integration of the signal indicates that the percent oH_2 has dropped from 75% to ~50% as expected (Figure 6) if equilibrium was achieved and no significant change in the *o*-*p* ratio occurred upon passing from 77 K to room temperature.

Figure 6 demonstrates that the composition of the mixture of pH_2 and oH_2 nuclear spin states has been altered by the procedure, that is, a persistent *excited* nuclear spin state has been synthesized while the molecule of H_2 remains trapped inside C_{60}. The rate of return to the room temperature equilibrium of the sample, estimated to be at least 7.5 days, was too slow to measure conveniently. The half-life for conversion was somewhat faster ~100 h (~4 days) in $^3O_2$ saturated (~1 mM) 1,2-dichlorobenzene-d_4 solution, demonstrating that $^3O_2$ is a spin catalyst for both the $oH_2@C_{60}$ to $pH_2@C_{60}$ conversion at 77 K and for the $pH_2@C_{60}$ to $oH_2@C_{60}$ conversion at room temperature.

Because the rate of $pH_2@C_{60}$ to $oH_2@C_{60}$ conversion is very slow at room temperature, once prepared, enriched $pH_2@C_{60}$ is a convenient *reagent* with the potential for studying, qualitatively and quantitatively, the spin chemistry of $pH_2@C_{60}$ and for serving as a device for examining extremely small magnetic effects. For example, the rate constant, k_{po}, for the conversion of $pH_2@C_{60}$ to $oH_2@C_{60}$ can be measured systematically using various paramagnetic spin catalysts. The measurements are the same as those described above for relaxivity. A Stern–Volmer plot with TEMPO (**1**) as a paramagnet (in the absence of O_2) yields a rate constant $k_{po} = 4 \times 10^{-5}\ M^{-1}\ s^{-1}$ (Table 1) for the $pH_2@C_{60}$ to $oH_2@C_{60}$ conversion. A comparison of the rate constants for H_2 and $H_2@C_{60}$ relaxation (k_{RX}) and the conversion (k_{po}) of both $pH_2@C_{60}$ to $oH_2@C_{60}$ and pH_2 to oH_2 at room temperature is given in Table 1. A salient feature of the results is that k_{RX} with a nitroxide spin catalyst, **1**, is ~5 times larger for $H_2@C_{60}$ than for H_2 under the same conditions. However, the value of k_{po} is ~2000 times smaller for $pH_2@C_{60}$ than for pH_2! These effects suggest that the magnetic field gradient needed for pH_2–oH_2 conversion is markedly reduced when the surrounding solvent molecules are replaced by the nearly spherical C_{60} cage. Thus, being incarcerated protects the guest from the fluctuating magnetic assaults of the outside world.

Photophysics and Spin Properties of O_2

Unlike nearly all organic molecules, the ground electronic state of O_2 is a triplet, T_0, and its first electronic excited state is a singlet, S_1. It has been found that the rate of the electronic intersystem crossing (ISC) process $S_1 \rightarrow T_0$ of $^1O_2$ depends strongly on the vibrations of the solvent, with high-frequency vibrations being most effective. For example,[11a] with H_2O as solvent, the lifetime of $^1O_2$ is 3 μs, whereas in D_2O as solvent, the lifetime of $^1O_2$ is increased to 68 μs. For

TABLE 2. Singlet Oxygen Quenching Rate Constants[11b]

quencher	k_q ($M^{-1}s^{-1}$)	solvent
C_{60}	3.8×10^4	CS_2
$H_2@C_{60}$	1.5×10^5	CS_2
$D_2@C_{60}$	4.9×10^4	CS_2
H_2	8.1×10^4	CCl_4
D_2	2.4×10^3	CCl_4

CS_2 or CCl_4 solvents,[11a] which possess only low-frequency vibrations, the lifetime of S_1 is more than 50 000 μs. In these solvents, the rate constants for quenching of S_1 by selected molecules can be measured. In CCl_4, the rate constant for quenching (k_q) of $^1O_2$ by H_2 is 8.1×10^4 M^{-1} s^{-1} whereas the rate constant for quenching by D_2 is 2.4×10^3 M^{-1} s^{-1}. Thus, there is a factor of difference of 34 in the rate constants for quenching, with H_2 being a much better quencher of $^1O_2$ than D_2.

We have seen that the guest H_2 in $H_2@C_{60}$ can communicate with $^3O_2$ in the solvent through measurement of $^3O_2$ spin-catalyzed relaxivity (k_{RX}) and spin conversion (k_{po}). We now ask whether the electronically excited $^1O_2$ in the outside world can communicate with the incarcerated guest H_2 in $H_2@C_{60}$. This question can be answered directly by comparing the rate constant, k_q, for deactivation (quenching) of $^1O_2$ by $H_2@C_{60}$ and C_{60}. We employed[11b] both a steady-state chemiluminescence method and a time-resolved method to produce $^1O_2$. Table 2 shows that the value of k_q for $H_2@C_{60}$ is larger than that for C_{60}. Furthermore, $D_2@C_{60}$ is a less effective quencher than $H_2@C_{60}$ but still is a slightly better quencher than empty C_{60}. Since quenching of the $^1O_2(S_1)$ state by electronic energy transfer to form $^3C_{60}(T_0)$ is energetically forbidden, we conclude that the quenching effects of C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$ all arise from vibrational energy transfer involving the electronic ground states of the quenchers, the same effect proposed to account for vibrational quenching of $^1O_2$ by solvents.

From Table 2, we note the remarkable result that the "incarcerated" $H_2@C_{60}$ ($k_q = 1.5 \times 10^5$ M^{-1} s^{-1}) is a better quencher of $^1O_2$ than is "free" H_2 ($k_q = 8.1 \times 10^4$ M^{-1} s^{-1}). We suspect that the reason for the more effective quenching of $H_2@C_{60}$ relative to H_2 is the formation of an exciplex between $^1O_2$ and $H_2@C_{60}$. The exciplex provides a relatively long duration of contact for exploring electronic-vibrational interactions between $^1O_2$ and $H_2@C_{60}$ compared to the very short time of contact between $^1O_2$ and H_2. H_2 is a very light rapidly diffusing quantum particle that probably does not form an exciplex with $^1O_2$.

Making the Walls of C_{60} a Paramagnetic Spin catalyst

Absorption of a photon by ground-state $C_{60}(S_0)$ produces an excited singlet state, $C_{60}(S_1)$, that crosses to the lowest triplet state, $C_{60}(T_1)$, in less than a nanosecond. As a result, for $H_2@C_{60}(S_0)$, the "prison walls" provided by the host C_{60} may be rapidly switched from diamagnetic to paramagnetic by the absorption of a photon to form $H_2@C_{60}(T_1)$. For $H_2@C_{60}(T_1)$, the guest will experience the paramagnetism of the triplet host. We can ask how do the allotropes of the guest H_2 molecules interact with paramagnetic walls of the host and how can we experimentally study such interactions. The possible interactions may be investigated by exploring changes in the magnetic properties of the guest H_2 (e.g., the rate of conversion of the guest allotropes) or magnetic properties of the host, C_{60} (e.g., changes in the properties of the host C_{60}). The interactions of the triplet walls of $H_2@C_{60}$ with the guest were examined by laser flash photolysis and measurement of the triplet−triplet absorption of C_{60} and $H_2@C_{60}$. However, to date,[11b] no differences have been found in the spectra or the lifetimes (110 μs) of the triplet−triplet absorption of C_{60} or $H_2@C_{60}$. $^3C_{60}$ is unusual in that it possesses a triplet electron spin resonance (ESR) spectrum that is readily observed by time-resolved (TR) ESR in fluid solutions.[12] TR ESR experiments of C_{60} and $H_2@C_{60}$ were readily observed in benzene, toluene, or methyl cyclohexane at 285 K. However, again no differences were found in the ESR spectra or the decay kinetics of C_{60} or $H_2@C_{60}$. The effect of the triplet paramagnetism on the incarcerated guest was investigated by measuring the rate of conversion of pH_2 to oH_2 during photoexcitation of $H_2@C_{60}$ and comparing this rate with that for unirradiated $H_2@C_{60}$. The conversion rates were experimentally indistinguishable. Although it is likely that the T_1 state can act as spin catalyst, its short lifetime (110 μs) makes it inefficient, because the paramagnetic effect is "on" for only a very short time.

Thus, the interaction between the guest H_2 and the paramagnetic walls of the host $^3C_{60}$ is too weak to be determined by triplet lifetime or ESR measurements, which directly measure the properties of the paramagnetic walls. Further work will be required to see if the paramagnetism of the walls can be used in the spin chemistry of $H_2@C_{60}$. We are also examining the influence of covalently attached nitroxides and external Xe on the rate of $pH_2@C_{60}$ to $oH_2@C_{60}$ conversion. Xe may appear to be an odd choice for a spin catalyst since it is diamagnetic. However, Xe both is very polarizable and possesses a strong degree of spin−orbit coupling; as a result, collisions of Xe with $pH_2@C_{60}$ may be catalyzed by using the indirect paramagnetism of spin−orbit coupling during collisions.

Theoretical and Spectroscopic Considerations

The synthesis and availability of $H_2@C_{60}$ has stimulated a number of theoretical and spectroscopic investigations. The low mass and tight confinement of H_2 in $H_2@C_{60}$ are expected to cause the guest molecule to exhibit quantization of all of its degrees of freedom, including translations. In addition we have the added feature that the Pauli exclusion principle plays a fundamental role in controlling the guest's dynamical behavior through pH_2 and oH_2. From the theoretical standpoint, the guest is the simplest molecule, exhaustively investigated by quantum mechanics computations. The host is a buckyball, whose structure approaches spherical symmetry that in itself provides a means of detailed quantum mechanical computations despite its complexity. A particularly fascinating aspect for theoretical and experimental investigation is the issue of the nature of the rotations and translations of the guest. Of particular interest for understanding the spin chemistry of $H_2@C_{60}$ is the evaluation of the interaction between the rotational and translational motions of H_2 within the confines of a C_{60} cage. This amounts to determining to what extent the motion of the H_2 in C_{60} can be described as a rigid rotor moving translationally as a particle in a spherical box or behaving as a spherical harmonic oscillator. The related question "Does H_2 Rotate Freely inside Fullerenes?" was answered[13] as cautiously affirmative on the basis of *ab initio* calculations. It was found that although the distortions of hydrogen and the carbon cage relative to the free components should be negligible, the C_{60} cage does introduce a small asymmetry in the interaction potential between H_2 and the walls that would be expected to exert a torque on the rotating molecule sufficient to induce transitions between the rotational states. More recent five-dimensional quantum calculations[14] have documented the importance of translation−rotation coupling in $H_2@C_{60}$. Very recent infrared[15] spectroscopy and inelastic neutron scattering[16] (measurements on $H_2@C_{60}$ and related open fullerenes) are now making it possible to test the computational results[17] and refine the potential used to describe the interaction between H_2 and the interior of the C_{60} cage. Both infrared and neutron scattering results provide evidence for a strong quantization of translational motion and for translational−rotational interactions. The infrared method probes vibrational states and the translational and rotational energy levels are inferred from the fine structure of the spectra. Inelastic neutron scattering has a characteristic energy scale that is closely matched to the rotational and translational splittings of the guest H_2. Furthermore, the selection rules for the inelastic neutron scattering allow for changes in the nuclear spin states, providing a probe for the transitions between the H_2 allotropes. It is clear that a very fruitful interaction between theory and experiment in endofullerene chemistry is in place.

Beyond the Hydrogen Allotropes: *ortho*-Water (oH_2O) and *para*-Water (pH_2O)

One of the most interesting systems possessing two indistinguishable spin isomers beyond H_2 is the $pH_2O(\uparrow\downarrow)/oH_2O(\uparrow\uparrow)$ spin duet.[18] It is interesting that this system, which is obviously of fundamental importance, has not been investigated with the intensity of the pH_2/oH_2 spin duet. As for H_2, the relative amounts of gaseous $pH_2O(\uparrow\downarrow)/oH_2O(\uparrow\uparrow)$ are 25% to 75% at room temperature. The pH_2O isomer is lower in energy[19] than the oH_2O isomer by about 40 cm^{-1}, so at equilibrium the pH_2O isomer will be strongly favored at temperatures below 10 K. There are literature reports[20] of the enrichment of pH_2O in the gas phase through absorption methods at room temperature. As was the case for spin isomers of H_2, it is a challenge to separate and investigate the properties of the spin isomers of H_2O. Although $H_2O@C_{60}$ is currently an unknown species, examples of $H_2O@openC_{60}$ are known.[21] It will be an exciting area of research to investigate the possibility of producing enriched $pH_2O@openC_{60}$ and to investigate the ^1H NMR properties of this fascinating system.

Conclusion

The stories of the prediction of the existence of two spin allotropes of H_2 and the discovery of C_{60} and the fullerenes provide two fascinating and delightful tales that cross scientific disciplines and possess a wide appeal. For H_2, the appeal may be in the surprise that the simple and well-known mother of all molecules could possess subtle, unexpected, and important spin characteristics that enrich its chemistry and spectroscopy. For C_{60} the appeal may be in the intrinsic beauty of the structure and the remarkable ability to synthesize a huge number of derivatives with ease. The synthesis of $H_2@C_{60}$ brought a marriage of the chemistry and spectroscopy of these two elements into a single supramolecular guest@host complex. Spin chemistry (relaxation, relaxivity, and spin allotrope interconversion) of the $H_2@C_{60}$ complex provides a playground for exploring communication with the outside world of the incarcerated guest in the crowded cell of the host. The fact that the skin of the host can be made paramagnetic by absorption of a photon or addition of an electron adds still another dimension of exciting possibilities for spin chemistry.

Spin chemistry in turn is dependent on and related to fundamental issues such as the translational, rotational, and vibrational motions of the guest. These motions may be examined by NMR and IR spectroscopy and neutron scattering. Results of these experiments can be compared with high-level computations of the details of the motion of the guest in the host.

These days researchers may find it necessary to suggest possible applications of findings, even as fundamental as those reported here. We can suggest some "Holy Grails" whose possible existence justifies these studies because of the potential for extraordinary payoff applications. One such Holy Grail is the possibility of controlling the spin selectivity of the catalyzed conversion of $pH_2@C_{60}$ into $oH_2@C_{60}$ (and the reverse) so that a strong nuclear spin polarization is produced. The fact that such a polarization would enhance NMR signals at room temperature by orders of magnitude is well established[22] for the reactions of pH_2 itself with double bonds. If successful, such spin selective conversion could find use in MRI imaging systems. Furthermore, fullerenes have found a place in a number of important medical applications.[23] As an extension of these ideas, a second Holy Grail would be to find ways to make useful quantities of pH_2O. Pure pH_2O does not possess a NMR spectrum, and its selective and controlled conversion into oH_2O is a profoundly fascinating and challenging direction for current and future research. Stay tuned.

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FOOTNOTES

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