Paramagnet Enhanced Nuclear Relaxation of H_2 in Organic Solvents and in $H_2@C_{60}$

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Abstract: We have measured the bimolecular contribution (*relaxivity*) R_1 (M^{-1} s^{-1}) to the spin−lattice relaxation rate for the protons of H_2 and $H_2@C_{60}$ dissolved in organic solvents in the presence of paramagnet nitroxide radicals. It is found that the relaxation effect of the paramagnets is enhanced 5-fold in $H_2@C_{60}$ compared to H_2 under the same conditions. ^{13}C relaxivity in C_{60} induced by nitroxide has also been measured. The resulting value of R_1 for ^{13}C is substantially smaller relative to the ^1H relaxation in $H_2@C_{60}$ than expected solely on the basis of the smaller magnetic moment of ^{13}C. The observed values of R_1 have been analyzed quantitatively using an outer-sphere model for bimolecular spin relaxation to extract an encounter distance, d, as the dependent variable. The resulting values of d for H_2 and $^{13}C_{60}$ are similar to the sum of the van der Waals radii for the radical and the corresponding molecule. The value of d for $^1H_2@C_{60}$ is substantially smaller than the corresponding van der Waals estimates, corresponding to larger than expected values of R_1. A possible explanation for the enhanced relaxivity is a contribution from hyperfine coupling. Based on the results reported here, it seems that not only is the hydrogen molecule in $H_2@C_{60}$ not insulated from magnetic contact with the outside world but also the interaction with paramagnets is even stronger than expected based on distance alone.

Introduction

The discovery that the fullerenes are able to encapsulate noble gas atoms[1] and hydrogen molecules[2] leads irresistibly to speculation about the extent to which endohedral molecules are able to sense the outside world through the carbon "skin" of the capsule. For example, selective, low O_2 sensitivity of the relaxation time of H_2 nuclei was used as supporting evidence for trapping of H_2 within an open-cage fullerene.[3] Furthermore, the first measurements by ^3He NMR of $He@C_{60}$ employed a relaxation reagent "because a very long T_1 was expected for ^3He inside fullerene molecules".[4]

In an effort to study quantitatively the accessibility of the interior of C_{60} to external agents, we have carried out a systematic investigation of the influence of nitroxides **1**−**4** (Chart 1) on the relaxation behavior of ^1H and ^{13}C nuclei in $H_2@C_{60}$.

Chart 1. Structures and Abbreviations of the Nitroxides Used as Relaxants
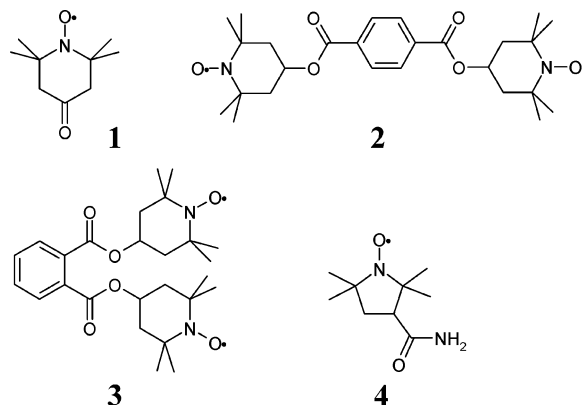
This work follows an earlier investigation of the relaxivity of some of the same nitroxides in solutions of small molecules[5] and a detailed comparison between the T_1's for encapsulated H_2 in $H_2@C_{60}$ and H_2 dissolved in solution.[6] The latter study probed the rotational behavior of encapsulated H_2. The present

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investigation probes the relative translational motions of the nitroxides and H_2 in the two environments.

Our methodology is similar to that which is being employed in a resurgence of interest in intermolecular relaxation using nitroxides and other stable paramagnetic species as contrast reagents in MRI,[7] NMR signal enhancers through dynamic nuclear polarization,[8] the use of O_2 and other paramagnetic molecules as site specific probes of macromolecular structure,[9,10] and applications of stable radicals as "spin catalysts".[11]

It should also be noted that despite extensive study of the effects of intermolecular interactions on the relaxation times of H_2 and its isotopomers in the gas, liquid, and solid phases,[12] and extensive measurements of paramagnetic catalysis of ortho−para conversion in H_2,[13] there seems to have been no previous report of paramagnetic effects on the relaxation of H_2 in ordinary organic solvents.
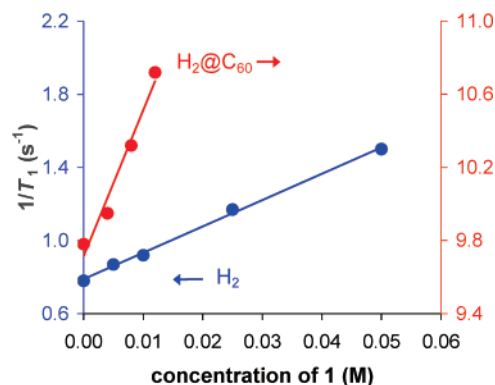
Experimental Section

Materials. 4-oxo-TEMPO (**1**) was purchased from Aldrich and used as received. The synthesis and properties of biradicals **2** and **3** were described previously.[5,14] 3-Carbamoyl-PROXYL (**4**) (Chart 1) and toluene-d_8 (D, 99.5%) were purchased from Cambridge Isotope Laboratories. H_2 (>99.99%) was obtained from AirGas.

Relaxivity Measurements. Solutions of nitroxides for H_2 relaxation measurements were bubbled with H_2 for 20 min in J-Young NMR tubes and then sealed. Solutions of $H_2@C_{60}$ were degassed by bubbling with Ar before sealing.[15]

^1H T_1 measurements were made at 500 MHz using standard inversion recovery techniques. ^{13}C T_1 measurements were carried out at 125 MHz using the Superfast Inversion Recovery (SUFIR) method.[16]

Diffusion Coefficients. Measurements of the diffusion coefficient of H_2 were carried out using the DOSY method at 500 MHz with a Bruker probe modified for pulsed field gradient experiments.[17] The standard Bruker protocol was used with the stebpgp1s pulse sequence (STE with bipolar gradient pulse pair, 1 spoil gradient). The gradient strength was incremented in 16 steps from 0.68 to 32 G/cm. A diffusion time, Δ, in the range 12.5−20 ms and a length of the diffusion gradient, δ, in the range 0.75−1.5 ms were used.

Calculations. Computation of relaxivity R_1 values using eq 1 was carried out using Mathematica and the complex arithmetic features of Microsoft Excel 97.

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Figure 1. Relaxation rates for H_2 and $H_2@C_{60}$ induced by **1** in toluene-d_8, 300 K.

Table 1. Relaxivities for Various Combinations of Paramagnets (*S*) and Nuclei (*I*)

paramagnet (*S*) /nucleus (*I*)	R_1 (M^{-1}s^{-1})^a			
	$^1H_2$	$^1H_2@C_{60}$	$^{13}C_{60}$	$^1H_6C_6{}^b$
1	14.5 ± 0.4	70 ± 10	2.7	68 ± 7^c
2	40 ± 5	170 ± 20		147 ± 8
3	40 ± 5	170 ± 20		160 ± 5

^{a} Unless otherwise indicated, in toluene-d_8, 300 K, 500 MHz (ν_{C13} = 125 MHz). ^{b}300 MHz, methanol-d_4, ref 5. ^{c}**4**.

Table 2. Diffusion Coefficients (*D*), Molecular Radii (*a*) and Minimum Spin Contact Radii (*r*m)

	10^9D^a			*a*		$r_m{}^b$
	(m^2/s$^-$)	ref		(Å)	ref	(Å)
$^1H_2$	14	this work		1.38^c	31	1.01
$^1H_2@C_{60}$	0.97 ± 0.04	29		5.0^d	32	4.41
$^{13}C_{60}$	0.97 ± 0.04	29		5.0^d	32	1.7
1 and **4**	1.6^f	18		3.4^e	33	1.5
$^1H_6C_6$	3.0^g	30		2.3^e	33	1.0

^{a} Unless otherwise indicated, toluene-d_8, 300 K. ^{b} See text for discussion of the distances r_m. ^{c} van der Waals radius, measured. ^{d} Lennard-Jones radius, computed. ^{e} van der Waals radius, estimated. ^{f} Estimated from measured values for **1** in ethanol corrected for differences in viscosity. ^{g}Methanol-d_4.

Results

The measured relaxation rates, $1/T_1$, of both H_2 and $H_2@C_{60}$ dissolved in toluene-d_8[5c] containing nitroxides are found to depend linearly on the concentration of the relaxant, [*S*], according to the relationship: $1/T_1 = 1/T_{1,0} + R_1[S]$, where $T_{1,0}$ is the relaxation time in the absence of paramagnetic relaxant[6] and the second-order relaxation coefficient, or *relaxivity*, is R_1 (M^{-1} s^{-1}). ^1H relaxation rates as a function of concentration for the mononitroxide **1** in toluene-d_8 at 300 K is shown in Figure 1. Similar plots were obtained for relaxation by biradicals **2** and **3**. ^{13}C relaxivity in C_{60} induced by **1** has also been measured. Values of R_1 obtained from least-squares fitting of the data for **1**, **2**, and **3** are presented in Table 1.

For comparison we also have included R_1 values measured previously[5] for protons in benzene relaxed by biradicals **2** and **3** and the related mononitroxide 3-carbamoyl-PROXYL, **4**, dissolved in methanol-d_4. The value of the diffusion coefficient, D_S, for **1** and **4** given in Table 2 was estimated from the published value[18] for **1** in ethanol after correction for differences in viscosity assuming Stokes−Einstein−Debye behavior.

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Data Analysis. Theoretical treatments of the relaxation of nuclei by intermolecular interactions between spins fall between two limits: the outer-sphere and the inner-sphere models. The translational, outer-sphere, ideal solution, or free diffusion model was pioneered by Torrey[19] in an attempt to use NMR relaxation as a tool to study diffusion and has been extended by Hubbard,[20] Freed,[21] and others.[22] The rotational, inner-sphere, or "sticking" model was first developed by Solomon[23] and Bloembergen[24] to explain relaxation of water protons by paramagnetic ions and applied by others[22,25] to investigate the structure of molecular complexes. The outer-sphere model is characterized by modulation of the inter-spin distance by relative diffusive motions of the two molecules. The inner-sphere model, on the other hand, as usually formulated, assumes the intermediacy of a transient complex between the two molecules in which the distance between the spins is fixed and the spin interaction is modulated by rotational motion of the complex.

Our starting point for the analysis of relaxivity in the present case will be the outer-sphere model in which the bimolecular contribution to $1/T_1$ is expressed[26] by

$$R_1 = (32\pi/405)\,\gamma_I^2\,\gamma_S^2\,\hbar^2 S(S+1)(N_A/1000\,dD)[j_2(\omega_S - \omega_I) + 3j_1(\omega_I) + 6j_2(\omega_S + \omega_I)] \quad (1)$$

In eq 1 d is usually defined as the distance of closest approach, $a_S + a_I$, of the centers of spherical molecules of radii a,[19] and D, their mutual diffusion coefficient $D = D_S + D_I$, where the subscripts S and I refer to the molecules containing the electron and nuclear spins, respectively. N_A is Avogadro's number, S is the electron spin, γ_S and γ_I are magnetogyric ratios of the electron and of the nucleus, respectively, and ω_S and ω_I are the respective Larmor frequencies in rad s^{-1}. The normalized spectral density functions appearing in eq 1 are

$$j_k(\omega) = \mathrm{Re}[(1 + s/4)/(1 + s + 4s^2/9 + s^3/9)] \qquad k = 1, 2 \quad (2)$$

where the complex parameter $s = [i\omega + 1/T_{Sk}]^{1/2}\,\tau^{1/2}$. $\tau = d^2/D$ may be interpreted as a translational correlation time for relative motion of the molecules. T_{Sk} is the longitudinal ($k = 1$) or transverse ($k = 2$) relaxation time of the paramagnet spin.

As can be seen, the model involves four adjustable parameters: the coefficient for relative diffusion, D, which expresses the dynamics of motion, a structural parameter, d, describing the distance of closest approach of the spins, and the longitudinal and transverse relaxation times of the paramagnetic species, T_{S1} and T_{S2}. The values of D may be independently measured[17] or estimated from published values under slightly different condi-

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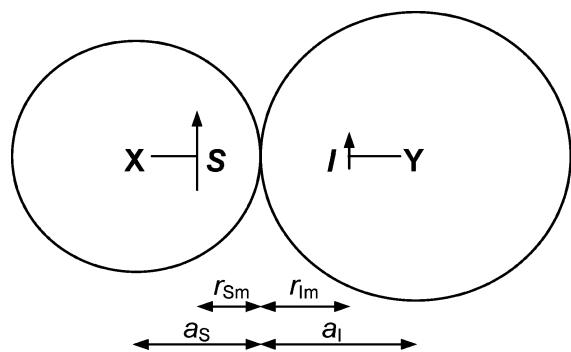(22) Banci, L.; Bertini, I.; Luchinat, C. *Nuclear and Electronic Relaxation*; VCH: Weinheim: Germany, 1991.
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Table 3. Data for Fitting of R_1 Values to d for Paramagnet (S)−Nucleus (I) Pairs[a]

I	S	R_1 (M^{-1} s^{-1})	$10^9[D_I + D_S]$ (m² s^{-1})	d (Å)	$[a_I + a_S]$ (Å)	$[r_{Im} + r_{Sm}]$ (Å)
^{1}H₂	1	14.5	15.6	3.6	4.8	2.5
^{1}H₂@C₆₀	1	70	2.6	3.6	8.4	5.9
^{13}C₆₀	1	2.7	2.6	6.1	8.4	3.2
^{1}H₆C₆	4	68[b]	4.6	2.6	4.8	2.5

[a] In toluene-d_8 except for ^{1}H₆C₆ where solvent was methanol-d_4. [b] Reference 5.
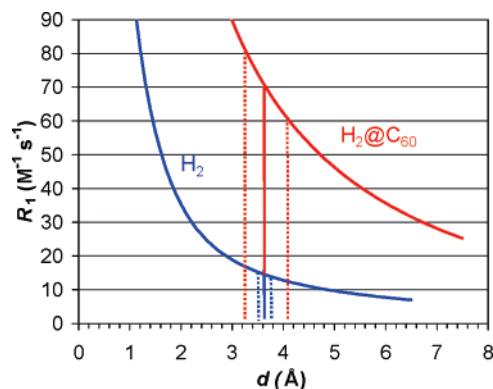
Figure 2. Calculated values of R_1 for H₂ and H₂@C₆₀ using values of D from Table 3. Vertical lines connect observed values of R_1 with the corresponding values of d. Solid lines indicate average values of R_1, and dotted lines, ranges of estimated error.

tions.[18] The values of $1/T_{S1}$ and $1/T_{S2}$ are of the order of 10^6 s^{-1} for **1** in toluene-d_8[10c] and may be ignored[10a] relative to the transition frequencies ω, all of which exceed 7×10^8 rad s^{-1} for the measurements presented here. We may therefore use eqs 1 and 2 with known values of D to compute R_1 for a range of values of d and determine the value of d which best fits the observed value of R_1. Alternatively, one could reformulate eq 1 in terms of the lifetime $\tau = d^2/D$ and extract this parameter rather than d from the computed values of R_1. We have chosen to derive d because it is expected to be more directly related to estimable structural parameters than is τ.

The values of the diffusion coefficients for each of the S and I species employed in the computations are given in Table 2, and the values of $D_I + D_S$ and best fit values of d are summarized in Table 3. Plots of R_1 vs d for H₂ and H₂@C₆₀ relaxed by **1** in toluene are shown in Figure 2.

Relaxation by Biradicals 2 and 3. As discussed in our study of solvent relaxivity,[5] it is expected that polyradicals will exhibit enhanced relaxivity because of the larger contribution of the average magnetic moment via the $S(S + 1)$ factor in eq 1. The situation is simplified for **2** and **3** because in both biradicals the singlet−triplet separation is much smaller[5b] than kT and the magnetic moment contribution is expected to be equivalent to twice that of the corresponding monoradical; i.e., they play the role of the monoradical at twice the concentration and, all else being equal, should be twice as effective as relaxants. Comparison of the values of R_1 in Table 1 shows that in all three examples the biradicals are between two and three times as effective as the monoradical. Since reliable values of D_S were not available for **2** and **3**, no attempt was made to estimate d for the corresponding S−I pairs. The increase of R_1 beyond the expected factor of 2 is, however, consistent with somewhat smaller values of D_S expected for these larger molecules, provided that the distance d is comparable to that for **1**.

Figure 3. Schematic representation of the van der Waals radii (a_S, a_I) and minimum distances (r_{Sm}, r_{Im}) for the paramagnetic (X–S) and nucleus containing (I–Y) molecules. See Table 3 for estimated values.

Discussion

The values of d determined for the sets of radicals, S, and nuclei, I, studied here are given in column 5 of Table 3. They fall within the range 2.6–6.1 Å as is expected for pairs of small- to medium-sized molecules. Given the relatively good precision with which R_1 and D have been measured or estimated, however, it would be desirable to compare the values of d with more refined estimates of the expected values. This is done below.

Interpretation of d Values. The distance d, as defined in eq 1, would be expected to hold only for interactions between atoms, where the spins of both species reside at the center of a sphere. Hubbard[27] and others[28] have considered the effect on R_1 of having the interacting spins sit away from the centers of mass of the corresponding molecules. The qualitative effect is to increase the relaxation rate relative to the value expected using values of the molecular radii in eq 1, or alternatively, to yield values of d which are smaller than the combined molecular radii, $a_I + a_S$, estimated from van der Waals radii. *This is true for all of the S–I pairs listed in Table 3.* Modifying eq 1 to take account of off-center placement of the spins has been undertaken by Hubbard[27] and improves somewhat the agreement between the observed and calculated intermolecular contribution to proton relaxation in liquid ethane.[26] We have attempted to estimate an upper limit to this effect on d by comparing the calculated value of d with the minimum distance, $r_{Im} + r_{Sm}$, that the two spins might approach each other during a bimolecular encounter. The relationship between this distance and the molecular radii is illustrated in Figure 3. Estimates of a and r_m are given in Table 2 and discussed below.

The values of r_m for the nuclear spins in H_2 and C_{60} are estimated from the location of the nucleus relative to the surface of a sphere defined by the van der Waals radius. For H_2 the distance is simply the measured van der Waals radius, 1.38 Å minus one-half the bond length, 0.37 Å, or a value of $r_{Im} = 1.01$ Å. For ^{13}C in C_{60} we have assumed that the thickness of the outer "skin" is defined by the one-half the radius of a carbon $2p$ orbital, estimated to be ca. 1.7 Å.[33a] Adding this value to the radius of C_{60}, 3.1 Å, determined by X-ray and electron

diffraction,[34] gives a value of 4.8 Å for the van der Waals radius, a, of C_{60} which is nearly the same as the Lennard–Jones radius, 5.0 Å, calculated for the interaction of two C_{60} molecules.[32]

Estimating r_m for $H_2@C_{60}$ is accomplished by a straightforward extension of the approximations used for H_2 and C_{60}. We assume an inner thickness of 1.7 Å for the carbon skeleton which limits the approach of the endohedral H_2 to the surface of the molecule to a minimum of 3.4 Å. Adding to this the 1.01 Å offset of the proton from the H_2 surface yields an estimate of $r_{Im} = 4.41$ Å. For the proton in C_6H_6 we have taken the value of r_{Im} to be the corresponding partial van der Waals radius for the H atom in an aromatic C–H bond, 1.0 Å.[33]

For the nitroxides, the van der Waals radius was estimated using the group increments recommended by Bondi[33a] and Edward[33b] and r_{Sm} was estimated by assuming that the electron spin is localized on the oxygen atom at a distance of ca. 1.5 Å from the surface of the molecule.[33a] We assumed that **1** and **4** are similar in size and location of the unpaired electron. Allowing for delocalization of the electron onto the nitrogen atom of the nitroxide would yield a somewhat larger value of r_{Sm} for **1** and **4**, moving the values of $r_{Im} + r_{Sm}$ closer to $a_I + a_S$, but making the deviation from the value of d for $^1H@C_{60}$ even larger.

Comparison of d with Distance Estimates. With the exception of $^1H_2@C_{60}$, all of the values of d derived from the outer-sphere model fall between the values expected for $a_S + a_I$ and the smaller values $r_{Sm} + r_{Im}$. For relaxation of $^1H_2$ and $^{13}C_{60}$ by **1** the distance is probably not significantly different from the sums of the van der Waals radii of the radical and diamagnetic molecule. For relaxation of the protons in benzene by **4**, on the other hand, d is nearly identical to the minimum distance $r_{Sm} + r_{Im}$.

The above observations might be restated as the following:

(a) $^1H_2$ and $^{13}C_{60}$ paired with **1** behave approximately as if the interacting spins were at the centers of spherical molecules, despite the fact that the ^{13}C atom is clearly on the surface of C_{60} and nowhere near the center.

(b) For $^1H_6C_6$ with **4**, and $^1H_2@C_{60}$ with **1**, the values of R_1 are close to, or, in the case of $^1H_2@C_{60}$, greater than, what is predicted by the outer-sphere model with dipole–dipole interactions. In the latter case, for example, the van der Waals estimate for d would predict a value of R_1 of 8 M^{-1} s^{-1}, compared to the observed value of 70! As a consequence, even using the closest conceivable contacts between the two species gives a value of R_1 smaller than that observed.

Comments on Case (a). The similarity between the value of d and the sum of the van der Waals radii implies that the electron and nuclear spins behave as if they resided at the centers of the corresponding molecules. This may be explained qualitatively by invoking rapid rotation of the two molecules during the translational encounter time, τ. For the $H_2/$**1** and $^{13}C_{60}/$**1** pairs the values of d and D for toluene-d_8 in Table 3 correspond to τ values of 8 and 143 ps, respectively. For comparison, the rotational correlation times, τ_{rot}, for H_2 and C_{60} in the same solvent, estimated from relaxation times,[6] were determined to be 0.20 and 2.1 ps, respectively, allowing for tens of rotations

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of the molecules while in the vicinity of the relaxant molecule. While, as Hubbard[27] has shown, this does not guarantee that the effective position of the nucleus will be at the center of rotation, the tendency would be to shift the average locations of the spins away from their minimum values relative to the relaxant.

Comments on Case (b). The above argument should, of course, also hold for the $^1H_6C_6$/**4** and $^1H_2@C_{60}$/**1** pairs. Why, then, are the values of R_1 for these pairs larger than expected from van der Waals contacts? The most obvious explanation is that one or more additional interactions and/or modulation processes contribute to relaxation in these cases. Two possibilities come readily to mind:

I. Formation of an inner-sphere-type complex that would hold the pairs together for a time longer than the translational correlation time τ, allowing for enhancement of the effects of the dipole−dipole interaction. This could be incorporated quantitatively by using the theory already developed by Solomon[23] and Bloembergen.[24]

II. Interaction of the S and I spins via contact hyperfine coupling. This might act either via an inner-sphere complex, as invoked to explain a variety of dynamic nuclear polarization experiments[35] and induced chemical shifts,[36] or be incorporated in the outer-sphere model via a through-space contact interaction.[20,26]

It appears to us that the intermediacy of an inner-sphere complex in case (b) is unlikely. A significant charge transfer attraction seems questionable because both molecules involved in each pair are good electron acceptors but poor electron donors. The intermediacy of a covalently bonded adduct would also seem to be ruled out by recent calculations[37] of C_{60} paired with a model nitroxide which indicate that adducts involving bonding through either the oxygen or nitrogen to C_{60} would be at least 1 eV higher in energy than the isolated molecules.

The presence of a distance-dependent contact interaction between C_{60} or benzene and nitroxide remains a possibility. This is supported qualitatively by the observation of small contact shifts in $^{13}C_{60}$ and benzene-d_6[38] and other aromatics[39] in the presence of a nitroxide. Properly modeling this effect would, however, introduce two additional adjustable parameters and would not be justified by the present data.

There remains the seeming contradiction between the especially large additional contribution to R_1 for $^1H_2@C_{60}$/**1** and the better agreement of R_1 for $^{13}C_{60}$/**1** with that expected from van der Waals radii. One possible explanation might be an enhancement of the contact interaction between the nitroxide and the endohedral H_2 *via* the p-orbitals of the C_{60} carbon shell. This would occur by spin polarization induced by the nitroxide on one side of the shell and transmission of the spin density onto the H_2 molecule embedded on the endohedral side of the p-orbital. In contrast, spin density on the ^{13}C would arise only from spin polarization and might be small compared with the direct effect. Such a "direct π- type interaction" has been invoked previously to explain ^{13}C contact shifts induced in aromatics by a nitroxide radical.[36b] It suggests that unusually large contact shifts might be observed in the NMR spectrum of $^1H_2@C_{60}$ in the presence of **1**. Those measurements, to our knowledge, have not yet been carried out.[40]

Summary and Conclusions

We have measured the bimolecular contribution, R_1, to the spin−lattice relaxation rate for the protons of H_2 and $H_2@C_{60}$ in the presence of monoradical **1** and biradicals **2** and **3** in toluene-d_8. It is found that the relaxation effect of the paramagnets is enhanced 5-fold in $H_2@C_{60}$ compared to H_2 under the same conditions. The relative relaxivities of **1**, **2**, and **3** are similar to those determined earlier for benzene protons relaxed by **2**, **3**, and the monoradical **4** whose structure is similar to that of **1**. Related measurements were carried out for $^{13}C_{60}$ relaxed by **1**. The resulting value of R_1 for ^{13}C is substantially smaller relative to the ^1H relaxation in $H_2@C_{60}$ than expected solely on the basis of the 16-fold decrease due to the smaller magnetic moment of ^{13}C.

The observed values of R_1 for **1** or **4** have been analyzed quantitatively using an outer-sphere model for bimolecular spin relaxation via the dipole−dipole interaction to extract an encounter distance, d, as the dependent variable. The resulting values of d for H_2 and $^{13}C_{60}$ are similar to the sum of the van der Waals radii for the radical and the corresponding molecule. That is, the spins behave approximately as if they resided at the centers of spheres. The values of d for $^1H_2@C_{60}$ and $^1H_6C_6$, however, are substantially smaller than the corresponding van der Waals estimates and are similar to, or even shorter than, reasonable estimates for the distance of closest approach of the spins, corresponding to larger than expected values of R_1. A possible explanation for the enhanced relaxivity in these cases is a contribution from hyperfine coupling between the unpaired electron and the proton modulated by the relative motions of the two molecules. This is consistent with the previously reported observation of small contact shifts induced in $^1H_6C_6$ by nitroxides and other stable radicals.[39] The corollary prediction of a shift in $^1H_2@C_{60}$ induced by **1** has yet to be tested.

Based on the results reported here it seems that not only is the hydrogen molecule in $H_2@C_{60}$ not insulated from magnetic contact with the outside world but also that the interaction with paramagnets is even stronger than expected based on distance alone.

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(40) We have found no detectable difference between the ^{13}C chemical shifts of C_{60} and $H_2@C_{60}$ relative to the solvent, toluene-d_8, in the presence of concentrations of **1** as high as 50 mM.