Comparative NMR Properties of H$_2$ and HD in Toluene-d_8 and in H$_2$/HD@C$_{60}$[†]

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Spin−lattice relaxation times, T_1, have been measured from 200−340 K for the protons in H$_2$ and HD molecules dissolved in toluene-d_8 and incarcerated in C$_{60}$. It is found that HD relaxes more slowly than H$_2$ in both environments and at all temperatures, as expected from the smaller values of the spin-rotation and dipole−dipole coupling in HD compared to H$_2$. More detailed analysis using models developed to describe relaxation in both condensed media and the gas phase indicates that transitions among the rotational states of H$_2$ occur at a rate similar to those of HD in both toluene-d_8 solution and in C$_{60}$, in contrast to the situation in gas phase collisions between hydrogen and He or Ar, where the lifetimes of rotational states of HD are markedly shorter than those for H$_2$. Measurements of the relative ^{1}H chemical shifts of H$_2$ and HD, the coupling constant J_{HD}, and the widths of the HD peaks at various temperatures revealed only small effects with insufficient accuracy to warrant more detailed interpretation.

Introduction

In a previous communication[1] we compared the proton spin−lattice relaxation time, T_1, for H$_2$ in several organic solvents with that in H$_2$@C$_{60}$ dissolved in the same solvents. The results were analyzed assuming the relaxation to be due primarily to the spin−rotation and dipole−dipole interactions at high and low temperatures, respectively. Using this asymptotic model, it was concluded that, at both high and low temperatures H$_2$ in toluene-d_8 reorients itself ca. 10 times faster than in H$_2$@C$_{60}$ dissolved in the same solvent. We were, however, unable to achieve a quantitative fit to the T_1 data over the full temperature range of 200−330 K using either the Hubbard theory[2] for relaxation in liquids or the Schwinger−Bloembergen theory[3] of relaxation in slowly equilibrating rotational states of H$_2$, which has been used with modifications[4] to describe relaxation in the gas phase. An empirical fit of the temperature dependence of a similar set of measurements of T_1 for H$_2$ in various organic solvents[5] required four parameters, including two activation energies. Earlier measurements of T_1 for H$_2$ in D$_2$O[6] yielded an estimate of the reorientation correlation time at each of several temperatures but employed the assumption of a fixed ratio of the correlation times for dipole−dipole and spin−rotation contributions to T_1.

In an attempt to understand the temperature dependence of T_1 in these media and to further elaborate the dynamic behavior of H$_2$ in C$_{60}$, we measured the values of T_1 for the proton in HD in toluene-d_8 and in HD@C$_{60}$ dissolved in toluene-d_8 for comparison with the values for H$_2$ under the same conditions. The use of HD as a relaxation probe allows for examining

changes in the following properties relative to H$_2$: (1) the magnetic parameters[7] responsible for T_1 differ significantly from those for H$_2$, (2) the difference in moments of inertia between the two molecules leads to a different rotational energy spectrum and rotational state populations,[8] and (3) the increase in mass of HD and the shift of center of mass relative to the location of the proton via the motion of HD as a "loaded sphere",[9] changes to some extent the average position of the proton in HD relative to H$_2$ in the solvent or C$_{60}$ cages and affects the interaction of the molecule with the surrounding medium.

As will be seen, (1) the difference in magnetic parameters makes possible an additional test of the applicability of the analysis of the dynamics of reorientation for HD using the Hubbard theory for relaxation in liquids[2] than was possible with H$_2$ alone. (2) The rotational energy differences may be used to assess the applicability of a gas phase model, which requires averaging over rotational states.[10,11] (3) The mass and center of mass differences, on the other hand, give rise theoretically,[9a] to changes in the average location of the protons in the two molecules within the solvent cage[9b] or relative to the π-electrons of the C$_{60}$ capsule, which could, in principle, manifest itself in a detectable difference in chemical shift between HD and H$_2$ in the two environments.

We have already made use of a fourth difference[12] between HD and H$_2$, the absence of *ortho* and *para* isomers in the former, by employing HD and HD@C$_{60}$ as intensity standards for studies of the p-H$_2$−o-H$_2$ conversion in H$_2$ and H$_2$@C$_{60}$. Although the proton T_1 of pure HD (or HD as an impurity in H$_2$ or D$_2$) gas,[13a,14] liquid,[13b,15] and solid[13c,15,16] has been reported, we are not aware of a previous determination of T_1 for HD in organic media. The detection of both H$_2$ and HD peaks in the same sample and the resolution of the HD coupling constant, J_{HD}, also makes it possible to measure J_{HD} and the ^{1}H chemical shift difference between the two species in the two media over a range of temperatures as a probe of the changes of these parameters compared to experimental[17] and theoretical[18] determinations for H$_2$ and HD in the gas phase.
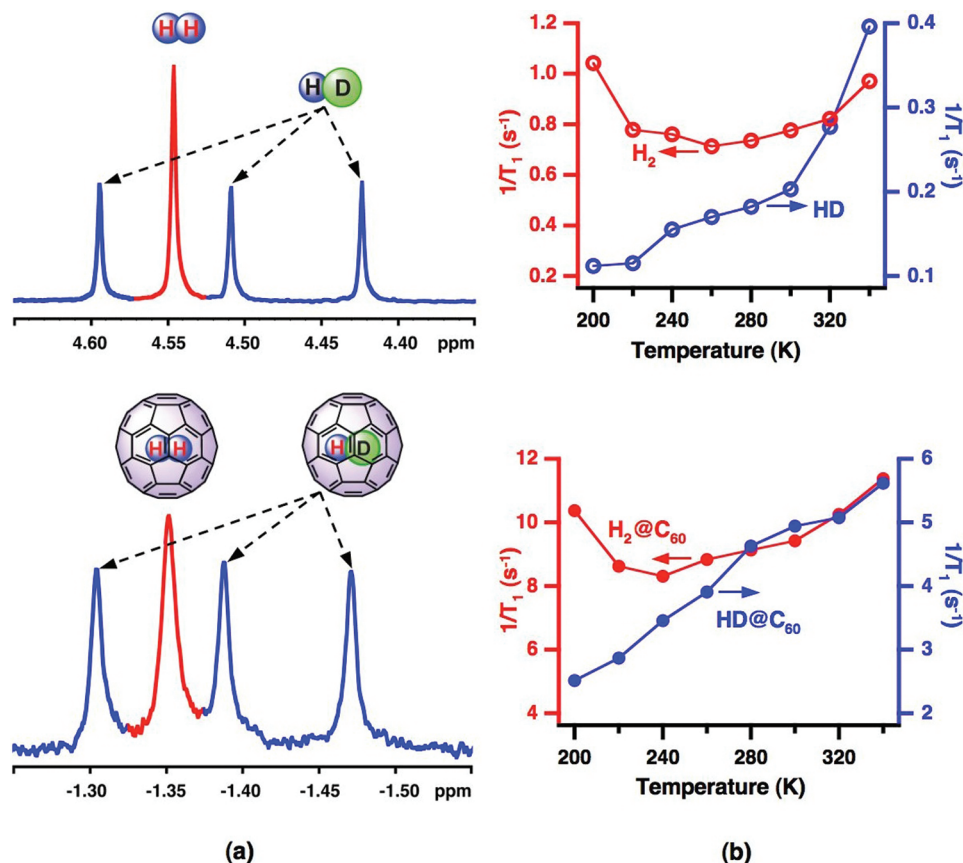
Figure 1. ^{1}H NMR spectra (a) and relaxation rates ($1/T_1$) (b) of toluene-d_8 solution of a H_2/HD mixture (top) and a toluene-d_8 solution of H_2/HD@C$_{60}$ mixture (bottom). Estimated errors in relaxation rates are within the width of the symbols on the plots.

Experimental Section

Materials. Calcium hydride (CaH$_2$) powder, reagent grade, was purchased from Sigma Aldrich with 90−95% purity. Deuterium oxide (D$_2$O) D, 99.9% and toluene-d_8 D, 99.5% were obtained from Cambridge Isotope Laboratories, Inc. Mixtures of H$_2$@C$_{60}$ and HD@C$_{60}$ were synthesized by Komatsu and co-workers.[19] Argon gas was purchased from TechAir.

Sample Preparation. CaH$_2$ was carefully loaded into a round-bottom flask and the apparatus to generate H$_2$+HD gas was assembled and purged with argon for 5 min. Approximately five drops of D$_2$O was carefully added dropwise with a plastic syringe into the round-bottom flask. Mixtures of the HD and H$_2$ gas generated were bubbled directly into a Wilmad, "J. Young Valve" NMR tube containing 600 μL toluene-d_8 that was purged with argon prior to the addition of the HD/H$_2$ mixture.

In a separate J. Young tube, 2 mg of H$_2$@C$_{60}$+HD@C$_{60}$ mixture was dissolved in 600 μL toluene-d_8. The resulting purple solution was bubbled with argon for 5 min prior to measurements.

NMR Measurements. T_1 measurements were taken between 200 and 340 K with temperature increments of 20 K. Spectra were obtained on a Bruker DMX-500 NMR spectrometer. The operating frequency for ^{1}H was 500.13 MHz. For the spin−lattice relaxation time, T_1, at each temperature, the sample was allowed to equilibrate for 15 min or until the shimming, as monitored by the lock-signal, was stable prior to data acquisition. The 90° pulse was recalibrated at each temperature. T_1 measurements were performed using the inverse-recovery pulse sequence: relaxation delay → π → τ → $\pi/2$ → acquire, with 13 values for the variable delay τ, in the ranges 0.001−2.5 s and 0.001−20 s for H$_2$/HD@C$_{60}$ and H$_2$/HD, respectively. A recycle delay

between pulses of 2.5 s was used for H$_2$/HD@C$_{60}$ and 25 s for H$_2$/HD. T_1 values were calculated for the H$_2$ peak and each of the peaks of the HD triplet (Figure 1) assuming first-order recovery. The digital resolution was 0.18 Hz/point. The standard deviations for fitting the H$_2$ and the HD data were not significantly different, which we take to imply that any nonexponential contribution to HD relaxation is undetectable in our data, which is consistent with an insignificant contribution from ^{2}H−^{1}H cross-relaxation.[9,10]

Results & Discussion

A. Spin−Lattice Relaxation Times. Figure 1a shows a typical spectrum of the H$_2$/HD mixture. Figure 1b shows the values of the relaxation rate, $1/T_1$, for H$_2$ and HD in toluene-d_8 and in C$_{60}$ over the temperature range 200−340 K. The values for H$_2$ in the H$_2$/HD mixture in both environments are indistinguishable from those reported previously.[1] The values of T_1 determined for each of the three lines of HD were the same within experimental error, and only the average value is shown in the figure. The value of the relaxation rate for HD is consistently smaller than that for H$_2$. As observed previously, H$_2$ relaxation in both media as a function of temperature passes through a shallow minimum,[1,5] whereas the relaxation rate for HD increases monotonically with temperature.

The above observations support the qualitative idea that relaxation of ^{1}H in HD is dominated by the spin−rotation interaction over the entire temperature range studied. This is in contrast to H$_2$, where the dipole−dipole interaction between the protons becomes of greater importance than the spin−rotation interaction at low temperatures. The observations for HD are consistent with the 6-fold decrease in the magnitude of the ^{2}H

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magnetogyric ratio, which greatly reduces the dipole−dipole interaction. As expected, the spin−rotation interaction becomes increasingly effective at high temperature. The substantial enhancement of the relaxation rate of HD in the C_{60} cage parallels that observed for H_2 and may be similarly attributed to the reduced mobility of the incarcerated hydrogen molecule.

B1. Theoretical Analysis of T_1's. The qualitative behavior of the relative ^{1}H relaxation times of H_2 and HD is as expected for the change in the magnitude of the magnetic parameters in the two isotopomers. But what of the quantitative picture? For more than 50 years, the relaxation times of ^{1}H and ^{2}H in H_2 and its isotopomers have been employed as a tool to extract information about the dynamics of molecular hydrogen in a variety of environments. The theoretical models have been able to exploit knowledge of the magnitudes and anisotropies of the parameters describing the spin−rotation, nuclear spin dipole−dipole, and, in the case of ^{2}H, nuclear quadrupole interaction, obtained from pioneering molecular beam resonance measurements carried out even before the modern era of NMR.[7,20]

As in our previous report,[1] the starting place for a more quantitative interpretation of the T_1's will be the assumption that only intramolecular interactions contribute to T_1, leaving the interesting field of intermolecular relaxivity[21] of HD relative to H_2 to other studies.[22] It is also assumed that the modulation of these interactions is related primarily to the rotational degrees of freedom of the molecule through changes in orientation or rotational angular momentum. Within this approximation, the theoretical challenge then becomes deciding how to describe the way the intramolecular interactions are affected by the dynamics of the hydrogen molecule. Two limiting models have been employed, which might be called, after Gordon,[23] the "J-diffusion" and "m-diffusion" models, where J and m are the quantum numbers for the principal value of the rotational angular momentum and its z-component, respectively. In the former model, it is assumed that collisions produce transitions among all of the molecular rotational states on a time scale suitable for inducing the nuclear spin state transitions required for spin−lattice relaxation. Such collisions also are implicit in the Hubbard theory[2] for relaxation in liquids. That model seems to be especially appropriate for heavy molecules with closely spaced rotational states or, possibly, small molecules in a strongly interacting medium. It gives rise to separate correlation times for rotational angular momentum and reorientation, although, as Hubbard has shown,[2] for large molecules these may be related. We employed this model to analyze our earlier work on H_2 relaxation[1] and for the sake of completeness will apply it to the current results.

At the other extreme is the m-diffusion model first proposed by Schwinger and Bloembergen[3] to describe intramolecular relaxation of H_2 in the gas phase. It assumes that the total angular momentum, J, is preserved for a time that is too long to contribute to T_1, relaxation occurring instead via more rapid reorientation of the vector J among the values of its m components. Changes in J do occur sufficiently rapidly, however, to yield a single relaxation time that is averaged over the thermally accessible values of J. While it might seem unlikely that a model developed to describe relaxation in the gas phase would be applicable to H_2 in condensed media, we are encouraged to apply it to the current results by recent spectroscopic studies, which show that the translation−rotation states of H_2 in H_2@C_{60}[24] and an open fullerene cage[25] are well-resolved. These results are similar to the observation some time ago that the rotational Raman spectrum of H_2 in liquid water[26a] and ice[26b] and neutron scattering of H_2 in ice[26c] exhibit well-

resolved peaks with widths corresponding to rotational state lifetimes on the order of picoseconds. Studies of sound propagation in hydrogen gas also attest to the relative ineffectiveness of collisions in bringing about changes in J,[27] although the number of collisions required is smaller for HD interacting with the noble gases.[28]

B2. J-Diffusion/Hubbard Model. We have applied both of the above models to the analysis of the T_1 measurements for H_2 and HD. In applying the J-diffusion model, we have used the formulation of Hubbard to separately estimate the correlation times for the dipole−dipole interaction, $\tau_{\text{dip,HY}}$, and spin−rotation interaction, $\tau_{\text{sr,HY}}$, (Y = H or D) over the entire temperature range studied. The observed spin−lattice relaxation rate, $1/T_{1,HY}$, is related to these two correlation times by eq 1

$$T_{1,HY}^{-1} = \frac{2\langle J^2 \rangle_{HY} C_{HY}^2}{3}\tau_{\text{sr,HY}} + \omega_{HY}^2 \tau_{\text{dip,HY}}$$

$$\langle J^2 \rangle_{HY} = 2I_{HY}k_B T/\hbar^2 \qquad \omega_{HY}^2 = \frac{4\kappa_{HY}\gamma_H^2\gamma_Y^2\hbar^2}{3r_{HY}^6}I_Y(I_Y + 1)$$

$$\kappa_{HH} = 3/2; \qquad \kappa_{HD} = 1$$

$$(1)$$

As eq 1 shows, each contribution to the relaxation rate may be expressed as the product of a factor involving the temperature-averaged square of the angular momentum, J, using the moment of inertia, I_{HY}, the nuclear spin angular momentum, I_Y, an angular frequency factor, C_{HY} or ω_{HY}, and the appropriate correlation time, $\tau_{\text{sr,HY}}$ or $\tau_{\text{dip,HY}}$. Equation 1 is derived on the assumption that the observation frequency, $\omega_0 = 3.1 \times 10^9$ rad s^{-1} (at 500 MHz) is much smaller than $1/\tau$. Using the known molecular constants[7] for H_2 and HD, the coefficients multiplying each of the four varieties of τ can be readily calculated (rad^2 s^{-2}): $C_{HH}^2 = 0.51 \times 10^{12}$; $C_{HD}^2 = 0.29 \times 10^{12}$; $\omega_{HH}^2 = 5.20 \times 10^{12}$; $\omega_{HD}^2 = 0.22 \times 10^{12}$. When written this way, it becomes clear that T_1's on the order of 1 s yield correlation times on the order of 1 ps, assuring that $\omega_0\tau$ is much less than 1.

The challenge is how to employ eq 1 to use *two* observables, $T_{1,HH}$ and $T_{1,HD}$, at each temperature, to calculate *four* correlation times. In order to accomplish this, we have assumed, somewhat in the spirit of the J-diffusion approximation, that the corresponding correlation times are the same for H_2 and HD at a given temperature. This would hold if the reorientation depends primarily on the potential energy of interaction between hydrogen and the medium, which should be nearly the same for the two isotopomers, but is insensitive to the translational or rotational kinetic energy of the molecule. The values of τ_{sr} and τ_{dip} can be obtained in this way by straightforward algebraic manipulation of eq 1 for H_2 and HD at each temperature. The values obtained are shown in Figure 2 for the toluene-d_8 and C_{60} environments. The qualitative features of this analysis may be summarized as follows: (1) Both correlation times are an order of magnitude longer for HY in C_{60} than in toluene-d_8, consistent with our earlier analysis.[1] It is consistent with our earlier proposed model in which the rotation of HY is slowed by some degree of interaction with the slowly rotating C_{60} cage. (2) The angular momentum correlation time, τ_{sr}, is generally longer than that for reorientation, τ_{dip}, at all temperatures. This is qualitatively consistent with m-diffusion-type behavior.

B3. m-Diffusion/Johnson−Waugh−Bloom−Oppenheim. In applying the m-diffusion model, we have used the extension by Johnson and Waugh[10] of the original model to include HD. Their formulation also incorporates separate correlation times
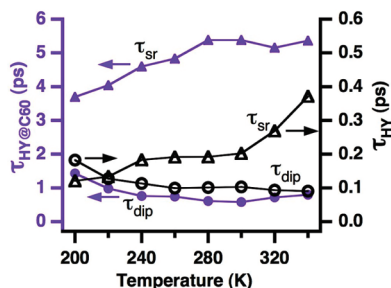
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Figure 2. Correlation times for spin−rotation interaction, τ_{sr}, (triangles) and dipole−dipole interaction, τ_{dip}, (circles) for HY in toluene (open symbols) and HY@C$_{60}$ (filled symbols) from the Hubbard model. See text for details.
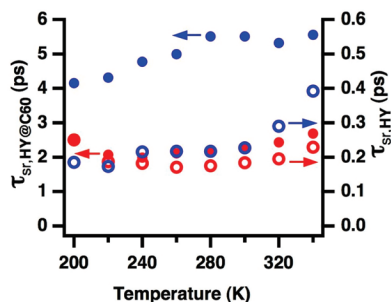

Figure 3. Spin−rotation correlation time, τ_{sr}, for HY in toluene (open circles) or in C$_{60}$ (filled circles) for H$_2$ (red) and HD (blue) from the *m*-diffusion model. See text for details.

for the dipole−dipole and spin−rotation contributions to T_1, which in principle depend on the rotational state, J. The observed T_1 in this case represents a Boltzmann average over thermally accessible states with populations p_J.

$$T_{1,HY}^{-1} = \sum_J p_J T_{1J,HY}^{-1}$$

$$T_{1J,HY}^{-1} = \frac{2J(J+1)C_{HY}^2}{3}\tau_{srJ,HY} + \frac{J(J+1)}{[(2J-1)(2J+3)]}\omega_{HY}^2\tau_{dipJ,HY}$$

(2)

We have estimated values of the thermally averaged dipole−dipole correlation time, τ_{sr}, separately for H$_2$ and HD by using the relation in eq 3 between τ_{dip} and τ_{sr} derived by Bloom and Oppenheim[11] for relaxation of H$_2$ at low pressures. If it is further assumed that the *J*-dependence of either τ_{dip} or τ_{sr} is weak,

$$\frac{\tau_{dipJ}}{\tau_{srJ}} = \frac{(2J-1)(2J+3)}{3(4J^2+4J-7)}$$

(3)

it possible to compare a single approximate correlation time, which we choose to be τ_{sr}, for HD and for H$_2$ in both environments. The values of τ_{sr} at each experimental temperature are shown in Figure 3. There is a striking qualitative similarity between the values and temperature dependence of the correlation times shown in Figures 2 and 3. As with the Hubbard model, there is a distinctly longer correlation time for either isotopomer in C$_{60}$ compared to toluene-d_8. Also revealed, however, is the additional information that HD has a somewhat longer τ_{sr} than H$_2$ in the same environment, the difference being somewhat greater in C$_{60}$ than toluene-d_8. This is opposite to the effect observed for noble gas collisions in the gas phase (*vide infra*). The relatively small differences between the values
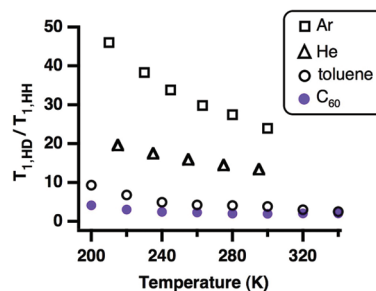

Figure 4. Comparison of T_{1HD}/T_{1H2} in toluene-d_8, C$_{60}$, and in Ar and He buffer gas. See text for details.

of τ_{sr} for HD and H$_2$ is roughly consistent with the assumption used in applying the *J*-diffusion model that the corresponding correlation times are the same for both species.

C. Comparison with Noble Gas Collision Data. There have been a number of studies of the effects of noble gas collisions on the relaxation times of nuclei in all three of the hydrogen isotopomers. The principal goal of these studies has been to characterize the anisotropic part of the intermolecular potential, which brings about changes in the rotation of the hydrogen molecule.[4] Of relevance to the present study are measurements of the proton relaxation times of H$_2$−He,[14c] HD−He,[14a] H$_2$−Ar,[14d] and HD−Ar[14b] mixtures over a range of temperatures and gas densities. The most significant qualitative difference between these results and those reported here is the much longer T_1 of HD compared to H$_2$ at the same temperature and collision gas density. The qualitative explanation for at least a portion[14a] of this effect is the fact that HD can readily undergo $\Delta J = \pm 1$ rotational transitions, whereas *ortho*-H$_2$ is restricted to $\Delta J = \pm 2$ transitions.[9a] An additional, perhaps more important effect is that the lower symmetry of HD compared to H$_2$ allows it to probe a wider range of anisotropy of the interaction potential.[14a] This leads to significant shortening of the lifetimes of HD spin states, corresponding to τ_{sr} and τ_{dip} in eqs 1 or 2, with consequent decrease in the relaxation rate. The ratios of T_1's for HD and H$_2$ in the gas phase are compared with those in toluene-d_8 and C$_{60}$ in Figure 4. The gas phase data shown in Figure 4 were obtained in the high-density region where the spin state lifetime is short compared to the larmor frequency. In this region, T_1 increases linearly, that is, $1/T_1$ varies inversely, with density because of the decreased lifetime of the spin states as the probability of collision with a gas molecule increases. We have therefore shown the ratio of the T_1's at the same density. It is clear that, at all temperatures in all media, $T_{1,HD}$ is longer than $T_{1,H2}$ and that the ratio increases as the temperature decreases, as is expected for a relative increase in the contribution of dipolar relaxation in H$_2$ at lower temperatures. It is also notable that the ratio for HY@C$_{60}$ (Y = H or D) varies less than for the other conditions, changing only 2-fold over the entire temperature range studied. A qualitative explanation for this would be a shorter correlation time for H$_2$ rotation in the condensed media, which compensates somewhat for the weaker magnetic interactions in HD compared to H$_2$.

One possible explanation for the striking difference in behavior of the relative relaxation rates of HD and H$_2$ in the gas and condensed phases is shown in Figure 5. We have compared on a semilog scale the actual values of $1/T_1$ in the condensed phase to those in the gas phase at a molecular density, 209 amagat (amg), corresponding to liquid toluene at 300 K. The most striking results are (1) the similarity of the relaxation rates of HD in C$_{60}$ to those induced by collisions with He or Ar, (2) the substantially slower relaxation of both HD and H$_2$
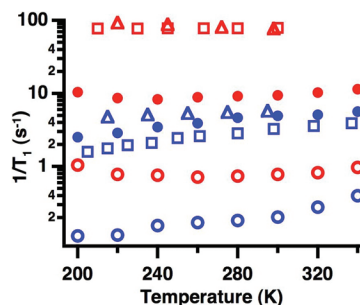
Figure 5. Relaxation rates, $1/T_1$, (log scale) for H₂ (red) and HD (blue) in toluene (open circles), C_{60} (filled circles), Ar at 209 amg (open squares), and He at 209 amg (open triangles). See text for details.

in toluene-d_8 compared to the gas phase, and (3) the substantially slower relaxation of H₂ in C_{60} compared to the gas phase. Result 1 could be explained by invoking $\Delta J = \pm 1$ transitions for HD with similar rates in C_{60} and in collisions with He or Ar atoms, and result 2 is consistent with more rapid reorientation of both HD and H₂ in toluene-d_8 compared to collisions with He or Ar. Result 3, however, requires the surprising conclusion that the rotational states of H₂ in C_{60} have a significantly shorter lifetime than in collisions with the noble gases at similar densities. This suggests a significant enhancement of the rate of $\Delta J = \pm 2$ transitions or of transitions among the *m*-states of a given *J*-state. We suggest that this result may be related to the rotation—translation coupling predicted[29] and observed spectroscopically[24,25] and thermochemically[30] for H₂@C₆₀ and other endo-H₂ fullerenes.

D. Other Measurements. In addition to determining the relaxation times in HD and H₂, we have measured three additional NMR parameters over the range of temperatures studied: (1) the chemical shift difference between HD and H₂ in solution and in C_{60}, (2) the magnitude of J_{HD}, and (3) the widths of the H₂ and HD peaks. As discussed below, in all cases we have detected only small, but possibly significant, effects of encapsulation on these parameters.

D1. Chemical Shift Comparison. The ¹H chemical shift of HD relative to H₂ was measured as a function of temperature over the range 200–340 K in toluene-d_8 and in C_{60} (See Figure SI1, Supporting Information). In both environments, the chemical shift difference decreased monotonically with increasing temperature, by about 2.5 parts per billion (ppb) in toluene-d_8 and 3 ppb in C_{60}. At each temperature, the chemical shift difference was 1–2 ppb smaller in C_{60} compared to toluene-d_8. The difference is also several percent smaller than observed and calculated for H₂/HD in the gas phase[18,31] and has a similar temperature dependence. Such effects have been termed a "site effect" as applied to the density dependence of the NMR isotope shift in hydrogen[18c] and may be related to the shift in the center of mass in HD.[9]

D2. ¹H—²H Spin—Spin Coupling. The value of the spin—spin coupling parameter, J_{HD}, measured as one-half the frequency separation of the outer lines of the HD triplet, was also determined in the two environments (see Figure SI2, Supporting Information) over a range of temperatures. It was found that J_{HD} is independent of temperature, but is consistently smaller by about 2% in C_{60} than in toluene-d_8. Furthermore, J_{HD} in both media is smaller by ca. 1–2% than observed in the gas phase.[17a] It is interesting to note that the smaller value of J_{HD} in the condensed media is consistent with the report that J_{HD} decreases on going from the gas to liquid phases[18b] and is supported by calculations predicting a *decrease* in J_{HD} with small decreases bond length, although dramatic reductions in J_{HD} have also been observed in Os—HD complexes where the HD bond order is markedly decreased.[32]

D3. Linewidth Comparison. The spectra shown in Figure 1 display noticeably narrower lines for HD than for H₂. It has also been noted previously[33] that the ¹H NMR lines of HD in an open fullerene cage are noticeably narrower than those of H₂, suggesting to the authors that the difference in relaxation times may be due to the larger dipole—dipole interaction in the latter. This is fully consistent with the observation reported here that the T_1 of HD is longer than the T_1 for H₂ at all temperatures. In the case of HD, however, there is the potential for an additional contribution to the line width from "scalar relaxation of the second-kind" via quadrupole relaxation of the ²H ($I = 1$) nucleus.[34] This line width contribution, which produces effects similar to chemical exchange, has been detected previously in gas-phase HD as a slight decrease in the value of J_{HD} arising from incipient collapse of the spin—spin triplet.[35] A more detailed analysis of the phenomenon, also predicts selective broadening of the outer lines of the multiplet. The latter effect is well-documented[34] for the related example of the contribution of ¹⁴N quadrupole relaxation to the appearance of the multiplet in ¹⁴NH₃.

In an initial effort to assess whether the above effects can be observed in our samples, we have estimated the magnitude of any broadening of the HD peaks beyond the contributions from processes reflected in T_1 and magnetic field inhomogeneity. The former contribution to the line width was assumed to be the same as $1/T_1$. The latter was estimated from the observed line width for H₂ by subtracting the calculated T_1 contribution, assuming that any additional broadening arises from field inhomogeneity and is the same for H₂ and HD. Figure SI3 (see Supporting Information) shows the values of the residual line width for each of the three peaks for HD in solution and in C_{60} over a range of temperatures. As can be seen from the figure, there seems to be a trend toward a residual line width of ca. 0.5 Hz for HD in C_{60} but not in toluene-d_8. If the excess broadening arises from relaxation of ²H, this would correspond to a ²H T_1 on the order of 3 s. This is, in fact, strikingly similar to the value of T_1 for ²H measured in preliminary experiments on D₂@C₆₀.[36] We were, however, unable to detect a statistically significant difference between the intensities of the middle and outer lines of the HD triplet, which would have indicated selective broadening due to quadrupole relaxation of the ²H nucleus. Furthermore, the expected decrease in measured J_{HD} due to incipient collapse of the multiplet would be expected to be greatest at low temperatures, where slowed rotation of the HD molecule should give rise to faster relaxation of the ²H nucleus by the quadrupole mechanism. As described above, however, it is observed that J_{HD} is independent of T over the range studied.

Summary and Conclusions

The values of T_1 have been measured from 200–340 K for the protons in H₂ and HD molecules dissolved in toluene-d_8 and incarcerated in C_{60} dissolved in toluene-d_8. The qualitative observations are that HD relaxes more slowly than H₂ in all media and at all temperatures. This is to be expected based on the somewhat smaller value of the spin—rotation interaction and the much smaller dipole—dipole coupling in HD compared to H₂. In an effort to develop a more detailed picture of the dynamics of molecular hydrogen in solution and C_{60}, the data were analyzed in three ways:

(A) Correlation times for angular momentum and orientation were estimated using a model developed by Hubbard[2] and Gordon[23] and others that invokes a classical average of the rotational angular momentum, *J*, to treat the spin—rotation

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contribution to T_1, and diffusional reorientation to describe the dipole−dipole contribution. By assuming that the correlation times for angular momentum, τ_{sr}, and orientation, τ_{dip}, are similar for H_2 and HD, it is possible to extract the values of these parameters from the T_1 data in toluene-d_8 and C_{60} at each temperature. The results confirm our previous conclusions[1] for H_2 alone, based on the assumption that the spin−rotation mechanism dominates at high temperature and the dipole−dipole mechanism at low temperature. In brief, Figure 2, shows both correlation times are substantially shorter for HY in toluene-d_8 than in C_{60} and that τ_{sr} is somewhat longer than τ_{dip} at all temperatures.

(B) An *m*-diffusion model in which the magnitude of J changes less rapidly than its *m* orientational components, has been used to relate the observed T_1 to a thermal average of J-dependent T_1's. It is also assumed that a J-dependent relation exists between the correlation times for the spin−rotation interaction, τ_{sr}, and the dipole−dipole correlation time, τ_{dip}, as proposed by Bloom and Oppenheim.[11] It is further assumed that τ_{sr} depends only weakly on the value of J. Under this assumption, the population weighted average T_1 then depends on a single correlation time, chosen to be τ_{sr}, at each temperature. As shown in Figure 3, in both media the correlation time for H_2 is shorter than for HD, implying faster redistribution among the rotational substates in the former than the latter. The difference is greater for HY@C_{60} than in solution.

(C) The ratios of T_1's for HD and H_2 in condensed media are compared with those resulting from collisions with He or Ar atoms in the gas phase (Figure 4). The measured values in condensed media are also compared with those estimated for gas phase collisions at the same molecular density as liquid toluene (Figure 5). It is found that the relaxation rates for both HD and H_2 in toluene-d_8 are much slower than in the gas phase, which would be consistent with shorter collision times in toluene compared to He or Ar at the same density. Surprisingly, however, the relaxation times of H_2 and HD in C_{60} are similar to that estimated for HD in a He or Ar. This suggests that the relaxation time of H_2 in C_{60} is shortened relative to what it would be if only $\Delta J = \pm 2$ rotational transitions were allowed, as in the gas phase.

The qualitative picture that emerges from the above analyses is that *transitions among the rotational states of H_2 occur at a rate similar to those of HD in both toluene-d_8 solution and in C_{60}.* This is in sharp contrast to the situation for transitions occurring as a result of collisions with He or Ar in the gas phase, where the lifetimes of the rotational states of HD are considerably shorter than those for H_2. The gas phase result is consistent with the expectation that HD can readily undergo $\Delta J = \pm 1$ transitions, whereas *ortho*-H_2 transitions are restricted to $\Delta J = \pm 2$. We suggest that this contrast may be related to the rotation−translation coupling of H_2 incarcerated in C_{60}, an explanation that is beginning to be revealed by both theoretical and experimental studies. The results for HY in toluene-d_8 also suggest a similar, though possibly less easily defined, shortening of the rotational state lifetimes of H_2 in solution.

Measurements of the relative ^1H chemical shifts of H_2 and HD, the value of J_{HD}, and the widths of the HD peaks at various temperatures revealed only small effects with insufficient accuracy to warrant more detailed interpretation in this report. Measurements with higher spectrometer resolution, direct measurement of transverse relaxation times, T_2, and determination of T_1's and other parameters for ^2H in HD and D_2 in the environments studied here, using instrumentation not readily available in the present study, would, however, clearly be of value in rounding out the description of the dynamics of H_2 in solution and in the fullerenes and should provide a better test of the theoretical models used in the present work. It would also be of interest to extend solid-state NMR relaxation studies of H_2@fullerenes[37] to the corresponding HD compounds. Of particular interest should be the ability to probe more effectively at very low temperatures the role of the $J = 0$ ground rotational state, which, in principle, cannot contribute to either the spin−rotation or dipole−dipole interaction.[13a]

Supporting Information Available: Graphs resulting from measurements of (1) the chemical shift difference between HD and H_2 in solution and inside C_{60}, (2) the magnitude of J_{HD} spin−spin coupling, and (3) linewidths of the H_2 and HD peaks. This material is available free of charge via the Internet at http://pubs.acs.org.

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