Dynamics of Methane Trapped in C_{60} Interstices

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Abstract

In order to understand the hindered rotational and vibrational dynamics of methane trapped in C_{60} interstices and to determine the structure around the interstitial site, we have carried out inelastic neutron scattering studies of the methane/C_{60} system. At temperatures of 20K and below, we observe inelastic peaks from rotational transitions of the CH_4. These transitions allow unambiguous assignment of the hindered rotational energy levels and a determination of the interaction potential. The appearance of two peaks for one of the $J = 0 \rightarrow 3$ transitions implies the existence of two distinct kinds of interstitial sites and the measured transition energies suggest a rotational barrier of about 26 and 16 meV for these sites. Time-dependent changes in peak heights indicate slow ($t_{1/2} \approx 2.6$ hrs) triplet→quintet nuclear spin conversion that necessarily accompanies the $J = 1 \rightarrow 0$ rotational relaxation. We also have observed a sharp inelastic peak at 9.3 meV, which corresponds to a local vibrational mode of CH_4 rattling in its cage at ~2.2 THz. Other peaks involving higher-energy vibrational excitations in CD_4/C_{60} correspond in energy to assigned peaks in the inelastic neutron scattering spectra of C_{60}, albeit sometimes with different intensities.

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I. INTRODUCTION

The trapping of atoms or molecules in porous media such as fullerenes, zeolites, graphite, and clays can endow the resulting material with remarkable new properties. Such systems have found use as catalysts, molecular sieves, gettering materials, and storage media. In the case of the fullerenes,[1] such trapping may yield new materials with exotic electrical properties; for instance, C_{60} doped with interstitial alkali atoms is a superconductor.[2] Thus, understanding the structural and dynamical aspects of trapping in these systems is of both fundamental and practical importance.

We have studied the dynamics of intercalation of rare gases into C_{60} interstices under pressure,[3-6] and by applying high temperature as well, we have recently succeeded in inserting methane into the octahedral interstitial sites.[7] The CH_4 molecule provides an effective probe of the crystal environment of these sites because its hindered rotational spectrum is sufficiently rich to provide detailed information about crystal forces, while its tetrahedral symmetry greatly simplifies analysis of the observed spectrum. The unique advantage of using neutron scattering methods to observe the CH_4 motion despite the more abundant carbon atoms is that the incoherent neutron-scattering cross section of the hydrogen is 16 times greater than the cross section for carbon. In this Article, we describe inelastic neutron-scattering spectroscopic studies of the dynamics of CH_4 molecules trapped in these sites. These studies provide information about the dynamics of CH_4 trapped in C_{60} interstices. These include the following: hindered rotation of CH_4 in C_{60}, the potential experienced by the CH_4 and the nature of the interstitial site, spin conversion of CH_4, the local vibrational mode of CH_4 in C_{60}, and changes of the vibrational spectra of C_{60} when CD_4 is trapped in the interstices.

II. EXPERIMENTAL DETAILS

The preparation of CH_4/C_{60} has been described earlier.[7] C_{60} (99.6% nominal purity) from commercial sources was heated under vacuum up to 500°C for several days in order to remove all solvents and occluded gases. The samples (≈ 1.5 g/run) were then wrapped in gold foil, loaded

into a high-pressure gas cell, and charged by cryopumping to fill the cell with either liquid CH_4 (Matheson high-purity grade) or liquid CD_4 (Cambridge Isotope Laboratory, 99% D). The cell was then sealed off and heated to 400°C in a tube furnace for up to 70 hrs in order to produce the CH_4/C_{60} or CD_4/C_{60}; at the end of the run, the cell was quenched in cold water. The pressure in the cell at 400°C was estimated to be between 1 and 2 kbar.

Weight gains following preparation of each of the samples showed that the resulting stoichiometries correspond to mole ratios of 0.91(8):1 and 0.87(8):1, for CH_4/C_{60} and CD_4/C_{60} respectively. These values are close to those expected for full site occupancy, especially if the absence of trapping sites on grain surfaces is taken into account. A CH_4/C_{60} sample monitored over several months showed no weight loss.

The inelastic neutron scattering spectra were collected with the Quasielastic Neutron Spectrometer (QENS) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory.[8] The 30 Hz pulsed source provides a broad range of useable wavelengths, and fixed final energy selection of the scattered neutrons using time-of-flight techniques yields the inelastic scattering law. The QENS spectrometer makes use of a time-correlated white beam of incident neutrons and operates by selecting a fixed final energy using the (002) reflection from graphite crystals in the scattered beam. The timing of the fixed energy scattered neutrons determines the neutron energy gain and loss by the time-of-flight of the incident neutron. The elastic resolution is 0.070 meV, and the inelastic resolution is approximately 3% of the energy transfer. The beam size at the sample position is 12.5 mm wide by 100 mm high. Three spectra were simultaneously collected at elastic momentum transfer values of 0.91, 1.88 and 2.41 Å^{-1}. Samples were placed in a 6 mm dia by 125 mm long aluminum sample tube and mounted on a He cryostat (for CH_4/C_{60} and CD_4/C_{60}) or a He refrigerator (for the C_{60} blank).

Data were collected at 1.5, 4.2, 12, 20 and 40K for CH_4/C_{60}, at 1.5K for CD_4/C_{60}, and at 12K for C_{60}. In addition, for CH_4/C_{60} at 40K, data were collected at three different angular settings of the detector banks with respect to the incident beam in order to measure the Q dependence of the quasielastic scattering. Typical collection times for CH_4/C_{60} were 4 hrs, with longer times of 15 and 30 hrs for the 1.5 and 4.2K runs, respectively. For CD_4/C_{60} and C_{60}, collection times were 60 and 35 hrs, respectively.

3

III. CRYSTAL STRUCTURE AND DYNAMICS OF PURE AND INTERCALATED C$_{60}$

Upon cooling, the pure C$_{60}$ crystal undergoes a first-order phase transition at 260K, and another, higher-order, phase transition at about 90K. Both transitions are intimately associated with molecular rotational reorientation, as has been determined by x-ray[9] and neutron diffraction,[3,10-12] differential scanning calorimetry,[9] and ^{13}C NMR spectroscopy.[13,14] These experiments include studies of temperature effects down to 5K and pressure effects up to 6 kbar. At ambient temperature and pressure, the C$_{60}$ molecule is effectively a sphere. The reorientational correlation time at 300K is about 9 ps, only slightly slower than that for freely rotating C$_{60}$ molecules, and the crystal adopts the face-centered cubic (fcc) Fm3m structure typical of a lattice of close-packed spheres. The first-order transition at 260K is characterized by the quenching of this nearly free rotation. The crystal symmetry is reduced to the simple cubic (sc) Pa3 space group.[3,9-12] The density increases by about 1%, but aside from this uniform contraction of the unit cell, there is no change in the centers of mass of the C$_{60}$ molecules. On the other hand, the reorientational correlation time increases by a factor of 30 to about 0.30 ns. The C$_{60}$ molecules become oriented with their three-fold axes aligned in the [111] crystal direction in either one of two orientations which differ from one another by a 60° rotation about the <111> axis. These two structural variants differ only in that the electron-rich interpentagonal double bonds point toward either the electron-poor pentagons or the electron-poor hexagons of neighboring C$_{60}$ molecules. The latter configuration, which we call the "secondary" configuration is about 1% smaller in volume and has a marginally (by 10.5 meV) higher energy. Observed motional narrowing of the NMR spectral lines is consistent with a C$_{60}$ molecule making frequent 60° hops between sites with relatively long site residence times.[13,14] As the temperature is further decreased from 260 to 90K, the relative populations of the "primary" and "secondary" orientations increases continuously from 1.7:1 to 5.1:1[10-12]; this is accompanied by a gradual contraction of the unit cell and a decrease in the hopping frequency. At 90K the system undergoes a glass transition with the reorientational correlation time increasing to about an hour.[13,14]

There are two kinds of interstitial sites in crystalline C$_{60}$: one is a tetrahedral site (two for each C$_{60}$) with an approximate radius of 1.1 Å, and the other is an octahedral site (one for each C$_{60}$) with an approximate radius of 2.1 Å. The channels connecting these sites are much smaller with a minimum radius of ~0.8 Å and a maximum radius of ~1.1 Å, depending on the orientations of the "locally-nonspherical" C$_{60}$ molecules. Molecular CH$_4$ is tetrahedral with an approximate

4

radius of 2.13 Å.[15] Thus we expect that CH_4 can only occupy the octahedral sites. The insertion of CH_4 also increases the room-temperature lattice constant from 14.153 to 14.179 Å and lowers the orientational ordering temperature from 260K in pure C_{60} to 241 and 235K for CH_4 and CD_4, respectively.[7] Below these temperatures, the rotational motion of the C_{60} molecules is again quenched, and the system transforms from the Fm3m structure to the Pa3 structure.[3]

The insertion of CH_4 into C_{60} is consistent with our studies of rare-gas insertion into C_{60} interstices, where we have found that at room temperature, He (radius 1.499 Å) is absorbed readily, Ne (1.572 Å) is intercalated on the time scale of hours (and then only into the octahedral sites), and Ar (1.878 Å) is not absorbed at all.[3,15] In addition, at elevated temperatures and high pressures, larger molecules like pentanes were shown to intercalate into C_{60} also, forming orthorhombic compounds that could be recovered at ambient conditions.[16] Subsequently, the heavy rare gases (Ar, Kr, and Xe) were successfully intercalated into C_{60} under similar conditions.[17] The key to the latter is now understood to result from thermally activated dynamics involving "paddle-wheel" rotations of the C_{60} molecules.[6]

Our initial studies of the CD_4/C_{60} system consisted of neutron-diffraction determinations of the structure and of ^{13}C and ^2H NMR studies of the molecular motion, both at a number of different sample temperatures.[7] The diffraction experiments at 296K show that the spectra are consistent with both the CD_4 and C_{60} molecules being spherically disordered (i.e., involving essentially free, uncorrelated rotation). As the temperature is lowered to 200K (below the orientational ordering temperatures for intercalated C_{60}), the C_{60} motion is found to be constrained to hopping between the two distinct orientations about the <111> direction; but the data do not allow an unambiguous choice between a freely rotating or positionally disordered CD_4. Finally at 15K, the CD_4 motion is frozen into the disordered model, but the large value of the atomic displacement parameters suggest that the CD_4 must still be undergoing large oscillations about its equilibrium position. The NMR data helps clarify this structural picture. The ^{13}C data show that the C_{60} molecule has ordered near 200K, while the corresponding ^2H NMR show that the CD_4 continues to be completely freely rotating, suggesting that the CD_4 orders at a much lower temperature. The ^{13}C spin-lattice relaxation time for the C_{60} molecules in CD_4/C_{60} has a value close to that predicted by the extrapolation shown by Tycko *et al.*[13] for pure C_{60} at the same magnetic field strength. Thus the trapped CD_4 molecule does not cause a

5

substantial change in the dynamics of the C_{60} molecule beyond slightly decreasing its orientational ordering temperature. Both the magnitudes of the correlation times and the difference in the temperature behavior imply that the rotational motions of CD_4 and C_{60} are not strongly coupled to each other.

The study of hindered rotation of CH_4 in solids using inelastic neutron scattering has been reviewed earlier.[18] In particular, studies have been carried out for methane trapped in rare gas matrices[19-21] and for solid methane II (where two of the eight sites in each unit cell are disordered and the methane molecules in these sites undergo hindered rotation).[22-24] The most relevant of these is the former because the methane substitutes for a rare-gas atom in a fcc lattice and has the same site symmetry as methane in C_{60} interstices. For the CH_4/rare-gas system, the neutron work was preceded by infrared spectroscopic studies which emphasized the vibration-rotation spectra,[25] hindered rotation,[25-27] nuclear spin conversion,[26-29] and the site structure.[27,28]

IV. RESULTS

In this Section, we present our results for methane trapped in C_{60} interstices. The topics are similar to those found earlier for the CH_4/rare-gas systems using infrared spectroscopic techniques. By using inelastic neutron scattering, we are able to learn about nuclear spin conversion, hindered rotation of methane, structure of the trapping site, and higher-energy excitations.

A. Spin Conversion in Methane

The population of the rotational states of CH_4 is governed by the total nuclear spin of the protons as was first pointed out by Wilson[30]; the rate of interconversion between these states was then addressed by Curl *et al.*[31] The $J = 0$ level consists of a nuclear spin quintet ($I = 2$), the $J = 1$ level of a triplet ($I = 1$), the $J = 2$ level of both singlet ($I = 0$) and triplet, and the $J = 3$ level of triplet and quintet spin states. On cooling the sample, thermal equilibration between most rotational levels is fast (even in the absence of paramagnetic neighbors), with the only exception being the slow transition for $J = 1 \rightarrow 0$ because of slow triplet$\rightarrow$quintet nuclear spin conversion ($t_{1/2} \approx 1.5$–2.5 hrs for CH_4 trapped in Ar matrices near 4–5K[26,29]). Although our samples are loaded into the sample tubes in the presence of air, the paramagnetic oxygen does not enter the lattice under ambient conditions[32] and equilibration between $J = 1$ and 0 levels is expected to be

6

slow. This is consistent with the observed slow drift of relative intensity in the associated peaks, indicating an approximate spin-conversion time $t_{1/2} \approx 2.6$ hrs.

B. Hindered Rotation of Methane Trapped in the C_{60} Octahedral Interstices

The theory of molecular rotation in crystals has a long history dating back to the early work of Pauling,[33] Devonshire,[34] and Cundy.[35] They introduced the concept of the crystal field potential, $V(\omega)$, where the rotational coordinates ω specify the orientation of the molecule relative to the crystal axes, to solve for the energy levels of the hindered rotor. In this case, quantum mechanical analysis of the hindered rotational motion is facilitated by the very high symmetry of the octahedral potential function.[36-38] Because the CH_4 carbon sits on a center of inversion in the fcc lattice, the molecular symmetry is effectively raised from tetrahedral to octahedral ($T_d \times i = O_h$). It follows that $V(\omega)$ is invariant with respect to a group, $\overline{O}$, of 24 rotations about axes fixed in the molecule, and a similar group, O, about axes fixed in the lattice. The hindered rotational states can thus be classified by the 25 irreducible representations, $\overline{\Gamma}\Gamma$, of a direct product of octahedral groups, $\overline{O} \times O$, where Γ is A_1, A_2, E, T_1, or T_2. As shown in the energy level diagram in Figure 1, the $J = 0$ and $J = 1$ levels with symmetries $\overline{A_1}A_1$ and $\overline{T_1}T_1$, respectively, are not split by the crystal field, but their energy separation in the crystal is lower than that in the gas phase. The $J = 2$ level, consisting of 25 degenerate states in the gas phase, splits into three levels: $\overline{T_2}T_2$, $\overline{E}E$, and the degenerate pair ($\overline{T_2}E$, $\overline{E}T_2$). Similarly, the 49 $J = 3$ free-rotor states split into six levels: $\overline{A_2}A_2$, $\overline{T_1}T_1$, $\overline{T_2}T_2$, and the degenerate pairs ($\overline{A_2}T_1$, $\overline{T_1}A_2$), ($\overline{A_2}T_2$, $\overline{T_2}A_2$), and ($\overline{T_1}T_2$, $\overline{T_2}T_1$).

In addition to these large energy-level splittings, one can expect further small splittings if we were to use the true space group symmetry $Pa3$ for the low temperature C_{60} structure, rather than the more symmetric $Fm3m$. The reduced crystal symmetry is associated with the fact that the fullerene host molecules have icosahedral rather than spherical symmetry. The effect of this symmetry reduction is to split each $\overline{\Gamma}\Gamma$ level into a pair of closely spaced sublevels, but these splittings are too small to be detected in our experiments (we will later show that a different feature observed in our data does result from the nonspherical "dimpled" structure of the C_{60} molecules).

The crystal-field potential can be represented by a linear combination of basis functions

with symmetry $\overline{A}_1 A_1$. There are only two such nonzero functions for $0 < J < 8$, so we adopt the familiar two-parameter model potential, $V(\omega) = B[\beta_4 V_4(\omega) + \beta_6 V_6(\omega)]$, where B is the CH_4 rotational constant, 5.24 cm^{-1} or 0.6496 meV, and β_4 and β_6 are dimensionless parameters chosen to give a best fit to the observed neutron scattering results. Test calculations including the next nonzero term, $\beta_8 V_8(\omega)$, gave a very small value for the coefficient β_8 and justified omitting this term.

We solved the rotational Schrödinger equation numerically to high accuracy for all low-lying energy levels over a dense grid of points covering the plausible regions of the (β_4, β_6) plane. The observed $J = 0 \leftrightarrow 1$ energy separation can be reproduced by any pair of (β_4, β_6) parameters lying on a line in one quadrant of this plane. The $\overline{A}_2 A_2$ energy level is the most sensitive to variations of the parameters along this line, so the final determination of parameter values was made by fitting as well to observed spectral peaks attributed to transitions to the $\overline{A}_2 A_2$ state, such as the $J = 0 \rightarrow 3$ $\overline{A}_1 A_1 \rightarrow \overline{A}_2 A_2$ transition. The $\overline{A}_2 A_2$ level is not split and appearance of a splitting at 1.73 and 1.91 meV implies that the methane must be trapped in two different kinds of sites. A fit to this doublet then resulted in two sets of potential parameters with (β_4, β_6) equal to ($-7.63, -3.40$) and ($-10.75, 0.40$) for what we will later call the "primary" and "secondary" sites, respectively, corresponding to the two structural configurations found for pure C_{60}.

Figure 1 shows energy levels for a representative cut through the (β_4, β_6) plane with $\beta_4 \approx 2.244\beta_6$. The pattern of levels on the left, corresponding to a crystal field dominated by a $V_4(\omega)$ term with a negative β_4 coefficient, is consistent with the experimental results (as noted below). Negative β_4 corresponds to the hydrogen atoms being repelled by nearest-neighbor C_{60} molecules. This result might have been anticipated from size considerations, where rough estimates suggest average radii of 2.13 and 2.1 Å, for the CH_4 and the octahedral hole, respectively. A more definitive test of the relative sizes and the sign of the potential is provided by the fact that the lattice expands from 14.153 to 14.179 Å with the insertion of CH_4. Thus, if one pictures the octahedral site as being the center of a cube with a C_{60} molecule in the center of each cube face, the methane molecule finds itself crowded in the site and has its lowest potential energy when oriented with its hydrogens pointing towards the cube corners.

Figure 2(a) shows the inelastic-neutron-scattering spectrum for CH_4/C_{60} at 4.2K as

8

collected on the intermediate angle detector bank ($Q_{elastic} = 1.88$ Å^{-1}). Figure 2(b) shows a calculated spectrum with all the transitions as assigned in Table 1. As mentioned earlier for C_{60}, the presence of two octahedral sites can be explained by the two different conformations of the C_{60} in the CH_4/C_{60} which, in pure C_{60}, involve rotations of the C_{60} about the <111> axis. Thus, this spectrum was calculated with the "primary" and "secondary" conformations of CH_4/C_{60} in a 2:1 ratio [the measured ratio was found to be roughly 1.8(3):1]. The effect of spin conversion was taken into account based on a data collection time of 30 hrs and the measured spin-conversion time $t_{1/2}$ of 2.6 hrs.

Unlike optical spectroscopy where there are selection rules for the allowed values of ΔJ, the only selection rule applicable here is nuclear spin conservation ($\Delta I = 0, \pm 1$). Thus, transitions $\overline{A} \leftrightarrow \overline{E}$ are forbidden, but all others are allowed. The absence of selection rules for ΔJ gives rise to a rich spectrum that provides a well-constrained assignment. The model has very little flexibility for the energy differences of the other transitions once the potential parameters have been chosen to fit the ± 0.61 meV and the 1.73 and 1.91 meV peaks. The peaks at ± 0.61 meV are assigned to the CH_4 rotational transitions $J = 0 \leftrightarrow 1$ and $J = 1 \leftrightarrow 2$ (which happen to be coincident). The broad peak at ≈ 1.22 meV is a doublet made up of contributions from the $J = 1 \rightarrow 3$ (1.12 meV) and $J = 0 \rightarrow 2$ (1.27 meV) transitions. When the data were initially being collected, the observed splitting appeared more pronounced and the peaks were more nearly equal in height. As a consequence of spin conversion during data collection, the population of the $J = 1$ level gradually decreased compared to that for the $J = 0$ level, and the low energy $J = 1 \rightarrow 3$ peak was then reduced to a shoulder on the $J = 0 \rightarrow 2$ transition. The two low-energy peaks at ~ 0.21 and 0.40 meV are assigned to the intramultiplet transition $J = 2 \rightarrow 2$ and the rotational transition $J = 1 \rightarrow 2$, respectively.

As discussed earlier, the $J = 0 \rightarrow 3$ transition should not be split, and peaks appearing at 1.71 and 1.93 meV result from the CH_4 occupying two different kinds of interstitial sites (see Section IV.C below). There should be a corresponding splitting of the $J = 1 \rightarrow 3$ transition. However, a 1.93 meV $J = 0 \rightarrow 3$ transition implies a $J = 1 \rightarrow 3$ at 1.30 meV which is most likely masked by the much stronger $J = 0 \rightarrow 2$ transition at 1.27 meV.

The observed $J = 0 \rightarrow 1$ transition energies for CH_4 in C_{60} are considerably smaller than the corresponding free-rotor energies for CH_4, and the hindered rotor energies for CH_4 in Ar, as

9

shown in Table 1. However, the relative sizes of the rotational barriers cannot be inferred from a comparison of the transition energies because the case of CH_4/C_{60} is different from the one for CH_4 in Ar. As can be seen in Figure 1, the former corresponds to the case where β_4 is negative, while CH_4 in Ar corresponds to the case where β_4 is positive. The relative insensitivity of the $J = 0 \rightarrow 1$ transition energy to the value of β_4 on the right-hand side of Figure 1 makes it more difficult to determine the crystal field potential when $\beta_4 > 0$. Thus, the several different sets of reported (β_4, β_6) parameters[19,21] for rare gas systems are in rather poor agreement with one another; although there is qualitative agreement in the choice of a large negative value of β_6 and a smaller positive value of β_4. For these systems Kataoka et al.[19] noted a shift to larger energies (i.e. lower barriers) in the $J = 0 \rightarrow 1$ transition as the size of the matrix increases from Ar, to Kr, to Xe; although as expected, the potential parameters could not be assigned unambiguously, and no rotational barriers were reported. Frayer and Ewing[26] obtain good fits to the $J = 0 \rightarrow 1$ rotational spacing deduced from rotation-vibration spectra of CH_4 in Ar, but the single measured transition did not provide enough information to allow a clear determination of the potential parameters.

In comparing these systems, one must recognize the qualitative differences in the various crystal environments alluded to earlier. In the case of CH_4-doped rare-gas matrices (Ar, Kr, and Xe), the CH_4 molecule is present as a substitutional impurity and occupies an octahedral site with twelve neighboring rare-gas atoms located at the centers of the cube edges. The CH_4 tends to orient itself with its hydrogens pointing toward cube faces. In contrast, for CH_4 in the C_{60} lattice, the CH_4 is surrounded by six nearest-neighbor C_{60} molecules and the CH_4 tends to orient itself with its hydrogens pointing toward the cube corners and the energy levels are quantitatively described by the left-hand side of Figure 1. The hindered rotational motion corresponds to localized librational motion with quantum tunneling through relatively high energy barriers. When the sign of the potential function is reversed (as in the case of the CH_4/Ar system), the deep potential wells for CH_4/C_{60} become high mountains surrounded by interconnected valleys. The hindered rotational motion of CH_4 in a rare-gas matrix then corresponds to a quantum flux through interconnected energy troughs passing over relatively low-energy barriers and avoiding the isolated high-energy peaks.

C. Structure of the Trapping Sites

Although we have treated the C_{60} molecules as spheres, the real structure of the C_{60} is icosahedral, and the surface of these spheres are deeply "dimpled" (by as much as 0.3 Å from the surface of the sphere) at the centers of the pentagonal and hexagonal faces.[6] Thus the crystal field experienced by the intercalated methanes is expected to depend on the orientations of the C_{60}. Given that the methane and the C_{60} are not strongly coupled to each other, the two different kinds of octahedral sites that produce the observed splittings in the $J = 0 \to 3$ transition must involve structural variants similar to those found for pure C_{60}.[10-12] The different orientations of the C_{60} about the <111> direction then provide the methane with octahedral sites with different local environments.

As mentioned earlier, the spectrum in Figure 2(b) is computed for a two-site model with (β_4, β_6) parameters of (-7.63,-3.40) and (-10.75,0.40) for the "primary" and "secondary" sites. These sites must correspond to the orientational variants of C_{60} with the interpentagon double bonds facing pentagons or hexagons of adjacent C_{60} molecules. With this choice of parameters, the "secondary" site energy for the $\overline{A}_2 A_2$ state of the CH_4 rotor is computed to lie 0.17 meV above that of the "primary" site energy with all other relevant levels remaining very nearly the same. This would explain the two transitions at 1.73 and 1.91 meV, without requiring other observable "splittings" arising from such a two-site model. Although local structures modify the crystal field of the two sites, both site potentials have 24 deep potential wells corresponding to methane oriented with its hydrogens pointing to the cube corners. In either site the molecule can hop from one well to another by successive 90° rotations about two-fold axes. The energy barrier for this hopping mechanism is computed to be 26 meV for the "primary" site, and about 16 meV for the "secondary" site.

We associate the "primary" site with the dominant orientation in pure C_{60}, but the measured ratio of the peak areas is only about 1.8(3):1 instead of the two-site ratio of 5.1:1 found at low temperatures for pure C_{60}.[10-12] Expansion of the lattice with the insertion of CH_4 or CD_4 will weaken the interactions between the C_{60} and lower the orientational-ordering temperatures in CH_4/C_{60} and CD_4/C_{60}, as has been observed.[7] It is also likely that this insertion will decrease the relative energy difference between the two configurations. These observations are consistent with the earlier rare-gas/C_{60} studies where the ordering temperature was found to be a function of cell

11

size only and where the ordering always occurs at pressures where the average lattice parameter is 14.042 Å, regardless of rare-gas identity.[3]

D. Higher-Energy Excitations

Figure 3 shows the energy transfer data over the energy range 0-35 meV for CH_4/C_{60}, CD_4/C_{60} and pure C_{60} (from top to bottom), all collected on the lower-resolution but higher-Q wide-angle detector bank ($Q_{elastic}$ = 2.41 Å^{-1}). The scattering from CH_4 dominates the CH_4/C_{60} data because of the strong incoherent scattering from the protons, and the prominent features can then be easily assigned to various rotational and vibrational transitions involving CH_4. For CD_4/C_{60}, the CD_4 transitions analogous to those from CH_4/C_{60} are affected by the appropriate isotope shifts and reduced in intensity by more than an order of magnitude. For CD_4, the rotational energy levels will be reduced by the lower rotational constant (2.62 cm^{-1} or 0.325 meV), and vibrational transitions involving the entire molecule will be shifted down in energy by $(m_{CH_4}/m_{CD_4})^{1/2}$ = 0.89. The data shown in the lower panel were collected in order to distinguish the C_{60} modes from those involving CD_4/C_{60}. The quartet of peaks between 2.5 and 6.5 meV is made up of the now well-known C_{60} librational peaks.[39]

It is interesting that this latter group of peaks is much stronger than would be expected in the top spectrum. The different pattern of intensities indicates that the stronger proton scattering must be contributing to the observed transitions. Thus, despite the weak coupling between the CH_4 and the C_{60}, the librational modes of the C_{60} molecules must couple with the trapped CH_4 to produce CH_4 vibrations that mimic the librational motion and contribute to the observed intensity. The different pattern of intensities follows from the different strengths for coupling the CH_4 modes to the C_{60} librational modes.

We assign the peak at 9.3 meV, shown in the top spectrum of Figure 3 to a local mode of CH_4 vibrating in the octahedral cage formed by the C_{60} molecules. This energy corresponds to a rattling frequency of 2.2 THz. A preliminary molecular dynamics simulation is in agreement with this assignment.[40,41] A closer examination of this peak shows that it is asymmetrically broadened, and we suspect that this broadening may actually result from the existence of the two different octahedral sites. We had hoped to observe the corresponding local mode for CD_4/C_{60} at the isotopically-shifted value of 8.3 meV, and although there appears to be some intensity in that

12

region of the spectrum, the scattering from CD_4 may just be too weak to produce a clear peak. Kataoka et al.[14] have assigned a broad peak at 11.8 meV (or a frequency of 2.8 THz) to the local mode of CH_4 in Ar. Given that the cage is larger in CH_4/C_{60} than in CH_4/Ar, the higher energy for the CH_4/Ar local mode is again consistent with the 9.3 meV found for CH_4/C_{60}. Clearly, the much sharper peak for CH_4/C_{60} arises from the greater mass disparity between C_{60} and CH_4. Jobic[42] found a peak at 9 meV for the local mode of CH_4 in the NaZSM-5 zeolite, a case where the adsorption occurs into pores which are somewhat larger than the methane (simulations indicate the free rotation of the methane[41]).

Figure 4 shows the vibrational spectra at higher energy transfers (up to 100 meV) for CH_4/C_{60}, CD_4C_{60} and pure C_{60}. Also shown are the positions and assignments for C_{60} based on the neutron measurements by Coulombeau et al.[43] and the theoretical work by Schettino et al.[44] (the broad feature near 95-100 meV is not assigned because the individual features cannot be resolved). The expected features are present in the measured spectrum for the C_{60} sample, although the data are noisy because the QENS instrument works best at small energy transfers. Nevertheless, the quality of the data is sufficient to demonstrate that the CD_4/C_{60} has the same features, although some of the intensities have changed remarkably. For example the peaks at 51 and 54 meV, corresponding to the H_u and H_g vibrational modes of C_{60}, respectively, reverse in relative intensity (but do not change in energy) on going from pure C_{60} to CD_4/C_{60}. The CH_4/C_{60} spectrum does not show any of the higher-energy vibrational features. This is likely due to the incoherent scattering from the methane hydrogens which washes out the C_{60} vibrational modes for the CH_4/C_{60} sample. A measurement on an instrument better suited for the higher energies, and with a higher incident flux, is required to obtain the C_{60} vibrational modes for this sample. From the perspective of the present study, the CD_4/C_{60} measurement suffices to demonstrate that the vibrational modes of the C_{60} are only perturbed slightly by the intercalation of the methane into the octahedral sites.

V. CONCLUSIONS

Rotational spectroscopy of CH_4 in C_{60} interstices provides evidence for the existence of two kinds of octahedral interstitial sites, which we believe correspond to the two C_{60} configurations found in the orientationally ordered C_{60}. The hindered rotational spectrum provides enough information for the crystal field potential of both sites to be determined. The higher

energy excitations for CD_4/C_{60} agree well in energy with assigned vibrational transitions in C_{60}, but the insertion of the methane changes the relative intensities of some of the transitions. Together with information on the spin conversion rates and the local vibrational mode, these studies provide detailed information about the trapping of CH_4 in such sites. We hope that this work will lead to molecular structure and dynamics calculations that can be tested against these results to provide a better understanding of trapping phenomena in solids, in much the same spirit as the work of Wilson[45] and others[46] on hindered internal rotation in gas-phase molecules four decades ago led to a better understanding of the role of structural conformation in more complex systems.

VI. ACKNOWLEDGEMENTS

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Table 1. Comparison of transition energies (in meV) for a CH_4 free rotor with rotational transitions of CH_4 in solid CH_4 II, matrix isolated Ar, and C_{60} interstices.[a]

Rotational Transition		Free Rotor	Solid CH_4 II	CH_4/Ar	CH_4/C_{60}
J=2→2	$\overline{E}E \to \overline{T}_2 T_2$	0	–	–	0.21
J=1→2	$\overline{T}_1 T_1 \to \overline{E}E$	2.62	–	–	0.40
J=0→1	$\overline{A}_1 A_1 \to \overline{T}_1 T_1$	1.31	1.06[22] 1.10[23] 1.08[22]	0.89[19,20] 0.90[20] 0.82[b]	0.61
J=1→2[c]	$\overline{T}_1 T_1 \to \overline{T}_2 E$	2.62	1.8[22]	1.10[b]	–
J=1→2	$\overline{T}_1 T_1 \to \overline{T}_2 T_2$	2.62	–	–	0.61
J=1→3	$\overline{T}_1 T_1 \to \overline{A}_2 A_2$	6.55	–	–	1.12 (1.30)[d]
J=0→2[c]	$\overline{A}_1 A_1 \to \overline{T}_2 E$	3.94	2.8[22]	2.14[21]	–
J=0→2	$\overline{A}_1 A_1 \to \overline{T}_2 T_2$	3.94	–	–	1.27
J=0→3	$\overline{A}_1 A_1 \to \overline{A}_2 A_2$	7.86	–	–	1.73 1.91[d]

[a]Transition energies and assignments for CH_4 in solid CH_4 II and for CH_4 isolated in an Ar matrix are from the references indicated.

[b]Hindered rotational energy levels deduced from the ν_3 or ν_4 vibration-rotation bands. Observed transition energies have been corrected for Coriolis coupling, a large correction for ν_4. These were obtained from the original spectra from Reference 26 with improved Coriolis coupling calculations from Reference 37.

[c]Unlike CH_4 in C_{60}, the J=2 ($\overline{T}_2 E$) hindered rotational level for CH_4 in Ar shifts to low energies.

[d]Expected and observed peaks arising from the "secondary" site.

18

FIGURE CAPTIONS

1. Hindered rotational levels for CH_4 in an octahedral field for $\beta_4 = 2.244\beta_6$. The energy zero is taken as the J = 0 level and the reduced energy W (above the ground rotational state) is given in units of the rotational constant for CH_4, B (= 5.24 cm^{-1} or 0.6496 meV). β_4 is the dimensionless coefficient of the dominant term in the crystal field potential. $\beta_4=0$ corresponds to methane in the gas phase. $\beta_4>0$ corresponds to the CH_4 hydrogens being repelled by the twelve nearest neighbor C_{60} molecules at the centers of the cube edges, as in the case of CH_4 in an Ar lattice. $\beta_4<0$ corresponds to the hydrogens being repelled by six nearest-neighbor C_{60} molecules located in the centers of the cube faces. The arrow along the abcissa marks the appropriate value of β_4 for CH_4 in a C_{60} lattice with the C_{60} molecules in the "primary" conformation (e.g. $\beta_4 = -7.63$).

2. Panel (a): Inelastic neutron scattering spectra of CH_4/C_{60} at 4.5K over the energy transfer range -1.5 to 2.5 meV. The data are shown by open circles, which are joined with solid lines. All transitions have been assigned [see Panel (b) and Table 1]. For comparison, similar data for C_{60} (solid line) show the elastic contribution. The inset shows in greater detail the region around the two J = 0→3 transitions. Panel (b): Calculated spectrum for both the "primary" and "secondary" conformations of CH_4/C_{60} in a 2:1 ratio, with the potential parameters $\beta_4 = -7.63$, $\beta_6 = -3.40$ and $\beta_4 = -10.75$, $\beta_6 = 0.40$, respectively, a data collection time of 30 hr, and a spin-conversion time $t_{1/2}$ equal to 2.6 hrs.

3. Inelastic neutron scattering spectra of (a) CH_4/C_{60} (1.5K), (b) CD_4/C_{60} (1.5K) and (c) pure C_{60} (12K) over the energy transfer range 0-35 meV. Note that the scale for the CH_4/C_{60} data is a factor of three larger.

4. Inelastic neutron scattering spectra with the same notation as Figure 3 [(a) CH_4/C_{60} (1.5K), (b) CD_4/C_{60} (1.5K) and (c) pure C_{60} (12K)], but over the energy transfer range 0-100 meV. Note that, as in Figure 3, the scale for the CH_4/C_{60} data is a factor of three larger. Assignments of vibrational peaks are from Reference 44.

19