Coherent Quasielastic Neutron Scattering Study of the Rotational Dynamics of C_{60} in the Orientationally Disordered Phase

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Coherent quasielastic neutron scattering has been used to investigate the character of the rotational dynamics in the high-temperature solid phase of C_{60}. The observed scattering can be described by a model in which each molecule undergoes rotational diffusion which is uncorrelated with the motions of adjacent molecules. The rotational diffusion constant D_R is $(1.4\pm0.4)\times10^{10}$ s^{-1} at 260 K and $(2.8\pm0.8)\times10^{10}$ s^{-1} at 520 K. The temperature dependence of D_R is consistent with a thermally activated process having an activation energy of 35 ± 15 meV.

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C_{60} (buckminsterfullerene) forms a mostly orientationally ordered [1] simple cubic phase belonging to the space group $Pa\bar{3}$ [2] below ~255 K. Near this temperature it undergoes a transition [3] to a face-centered-cubic phase which is an excellent example of a broad class of molecular solids, sometimes termed "plastic crystals," which exhibit rapid molecular reorientations [4,5]. Quasielastic neutron scattering is capable of determining both the time scale of reorientations and, more importantly, the detailed nature of the reorientations [6]. Here we present such a study of the rotational dynamics of C_{60} in the orientationally disordered, high-temperature phase and show that the observed scattering is well described by a model in which there are no intermolecular correlations, and each molecule reorients completely randomly, as opposed to jump rotations between a specific set of sites.

The sample consisted of ~2.5 g of powdered C_{60} of which 1.5 g were prepared at the University of Pennsylvania and 1.0 g at Exxon, using standard methods [7,8]. After the chromatographic separation of C_{60} from the C_{60}-C_{70} extract, great care was taken to remove the solvent, since neutrons are ~15 times more sensitive to hydrogen than to carbon. Prompt gamma activation analysis [9] showed a hydrogen content of 0.008 ± 0.002 atom per C atom for the Exxon sample and 0.0057 ± 0.0011 atom per C atom for the Penn sample. Scattering from the H in the residual solvent was observed in our experiments, but does not affect our conclusions.

The neutron scattering results were obtained using triple-axis spectrometers at the Neutron Beam Split-Core Reactor (NBSR) at NIST. For scattering vectors, Q, below about 4.0 Å^{-1}, the neutrons were monochromated and analyzed using the (002) reflection of pyrolytic graphite. Collimators having angular spreads of 10′-20′-20′-20′ were placed before and after both crystals, resulting in a measured energy resolution of 0.50 meV full width at half maximum (FWHM) at the elastic position. To reach larger values of Q a shorter wavelength was necessary. In order to maintain a relatively good energy resolution, the Cu (220) reflection was chosen to monochromate the beam and the graphite (004) reflection was used to analyze the energy of the scattered neutrons. Combined with collimations of 40′-40′-40′-40′ , this resulted in a measured resolution of 1.2 meV FWHM. For measurements in the fixed final energy configuration, the data were corrected for the separately measured second-order contamination of the incident beam. Data collected in the fixed initial energy configuration were corrected for variations in the final energy resolution volume. All of the data were also corrected for detailed balance and were then fitted by the sum of a delta function and a Lorentzian, each convoluted with the Gaussian instrumental resolution function, plus a linear background. Care was taken to avoid Bragg reflections.

Quasielastic neutron scattering spectra obtained at 260 K, just above the orientational order-disorder transition, are shown in Figs. 1(a) and 1(b). The solid circles are the corrected data, the solid line is the Lorentzian component (plus background) of the fit described above, and the bars represent the FWHM resolution. The observed broadening shows directly that the orientational disorder in the room-temperature phase is dynamic. The elastic portion of the data lying above the solid line is due to the residual hydrogen in the sample. The intensity of this

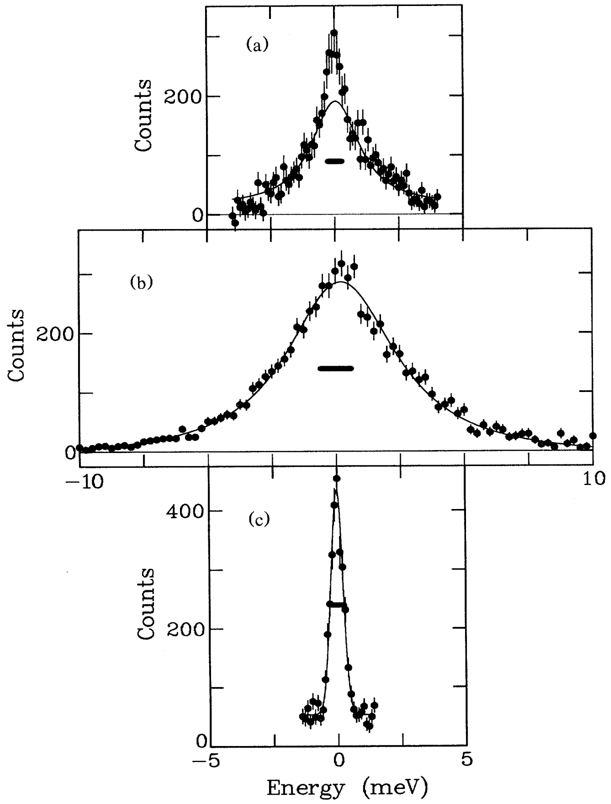

FIG. 1. Typical constant-Q scans for C_{60}. The solid line is the Lorentzian plus background components of the fit described in the text, and the bar represents the instrumental resolution. The existence of energy broadening above the transition clearly demonstrates the dynamic nature of the orientational disorder. The elastic component is due to residual hydrogen in the sample. (a) Scan at $Q=3.25$ Å^{-1} and $T=260$ K. (b) Scan at $Q=5.5$ Å^{-1} and $T=260$ K; this clearly shows that the Lorentzian component has broadened as a function of Q compared with the scan at 3.25 Å^{-1}. (c) Scan at $Q=3.55$ Å^{-1} and $T=250$ K. The disappearance of the broadening below the transition demonstrates that the dynamics has slowed by at least a factor of 20.

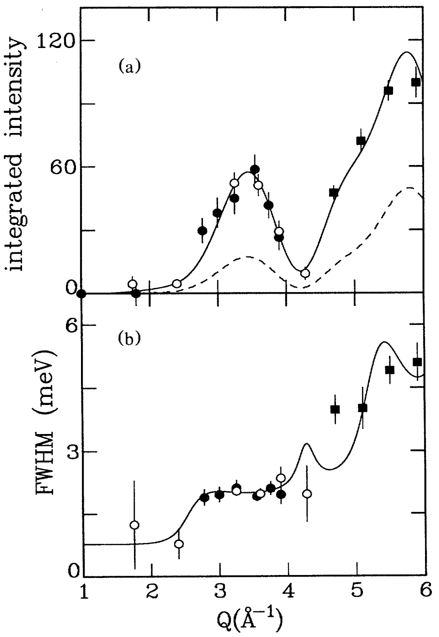

FIG. 2. Q dependence of (a) the integrated intensity and (b) the full width at half maximum of the quasielastic scattering. Here the solid (open) circles are data obtained at 260 K (520 K) using an energy resolution of 0.5 meV. The solid squares are data taken at 260 K using a resolution of 1.2 meV. The solid line is a calculation [10] where each molecule undergoes rotational diffusion with no correlation between the motions of adjacent molecules. The dashed line shown in (a) is the intensity for a model involving fourfold jumps about a twofold molecular axis, on the same scale relative to the intensities of the low-Q Bragg peaks. A rotational diffusion constant $D_R=(1.4\pm0.4)\times10^{10}$ s^{-1} well describes the Q dependence of the quasielastic scattering width at 260 K. Note that the width of the quasielastic scattering at 520 K has been scaled to this value of D_R for the sake of comparison with the model. In all cases care was taken to avoid Bragg reflections which could contaminate the data.

component is consistent with a simple Debye-Waller factor, i.e., it decreases linearly with Q^2 for the smaller Q's, so that it is much less apparent in the spectrum obtained at higher Q. Combining this information with the quasielastic scattering model described below, we estimate that the hydrogen content is 0.005 atom per C atom, in agreement with the prompt gamma results. Figure 1(c) shows a similar spectrum taken at 250 K, which is below the transition in this sample. Here the peak centered at $E=0$ is resolution limited indicating that the molecular motions have slowed by at least a factor of 20.

The integrated intensity of the Lorentzian component and its width, extracted from these fits, are displayed as a function of Q in Fig. 2. The solid (open) symbols are data taken at 260 K (520 K) while the solid lines are calculations of the intensity and width using a model developed by Sears [10]. In this model, the rotations of adjacent molecules are uncorrelated whereas individual molecules undergo rotational diffusion about a fixed center; i.e., the motion of each molecule satisfies the differential equation

$$D_R\nabla_\Omega^2 p(\Omega,\Omega_0,t)=\frac{\partial}{\partial t}p(\Omega,\Omega_0,t)\,, \tag{1}$$

where D_R is the rotational diffusion constant, ∇_Ω^2 is the Laplace operator in the space of Euler angles, and p is the probability of finding the molecule in orientation Ω at time t if it was in orientation Ω_0 at $t=0$. In particular, this model implies that the molecule reorients through a continuum of orientational Euler angles Ω and does not, for example, undergo rotational jumps between some set of preferred orientations. The quasielastic part $S_Q(Q,\omega)$

of the coherent neutron scattering function can then be expressed as

$$S_Q(Q,\omega)=\sum_{l=1}^{\infty}a_l\frac{1}{\pi}\frac{\tau_l}{1+\omega^2\tau_l^2}\,, \tag{2}$$

where

$$a_l=(2l+1)j_l^2(QR)\sum_{m,m'=1}^{60}P_l(\cos\theta_{mm'}) \tag{3}$$

and

$$\tau_l^{-1}=l(l+1)D_R\,. \tag{4}$$

Here j_l is a spherical Bessel function, P_l is a Legendre polynomial, $\theta_{mm'}$ is the angle between the position vectors joining the molecular center to the atoms m and m' within a single molecule, and R is the molecular radius of C_{60}, chosen to be 3.52 Å in these calculations. Using a standard sum formula for the j_l's, it can be shown from Eqs. (2) and (3) that

$$\langle F^2(Q)\rangle-\langle F(Q)\rangle^2=\int_{-\infty}^{\infty}S_Q(Q,\omega)d\omega\,, \tag{5}$$

where the brackets denote an orientational average and F is the structure factor for a single molecule. The left-hand side of Eq. (5) has been found to completely describe the diffuse neutron scattering observed in the high-temperature phase [1] and is shown as the solid line in Fig. 2(a). Thus there is no truly elastic contribution to the diffuse scattering.

The expression for a_l [Eq. (3)] differs from that obtained for incoherent quasielastic scattering [6] in that the sum over the Legendre polynomials for such a case only contains terms with $m=m'$, and therefore reduces to the constant value of 60 since $P_l(1)=1$ for all l. The sum in Eq. (3) completely accounts for the fact that motions between atoms within a single molecule *are* correlated, and it therefore reflects the molecular geometry. Because of the high degree of symmetry of C_{60}, one then finds that all odd-l and many even-l terms are identically zero. In fact, the only terms that significantly contribute to the scattering in the Q range of these experiments are $l=6$, 10, 12, 16, 18, and 20 for which the sum over the P_l takes the values 6.3, 224, 31, 123, 496, and 90, respectively. Thus most of the scattering is contained in the $l=10$ term, which is responsible for the peak in the integrated intensity at $Q\simeq3.5$ Å^{-1} and the flat portion of the width between $Q\simeq2.8$ and 4.0 Å^{-1}, and in the $l=18$ term which dominates contributions to the peak at $Q\simeq5.75$ Å^{-1}. The small number of terms necessary to specify $S_Q(Q,\omega)$ implies that the scattering can be well described by a single Lorentzian in spite of the fact that it is a sum of Lorentzians. This has been verified by calculating the scattering function at several values of Q and comparing the result to a single Lorentzian. In all cases the discrepancy was considerably less than the statistical uncertainty of the measurements.

The good agreement between our data and the rotational diffusion model suggests that the assumptions that go into the model, namely, that the reorientational motions of the individual molecules are random [i.e., satisfy Eq. (1)] and that there are no intermolecular correlations, are largely satisfied in the orientationally disordered phase of C_{60}. Of course, deviations from both random orientation and correlations between the motions of adjacent molecules must be present to some degree, but are so limited that the orientationally averaged scattering from a powder sample is not appreciably affected. The hydrogen in the residual solvent clearly does not have a significant influence on the fitted parameters of the Lorentzian component, since the Q dependence of the fitted intensity is just that expected from orientationally disordered C_{60} molecules [1]. The value of D_R obtained from the 260-K data is $(1.4\pm0.4)\times10^{10}$ s^{-1}. This implies that it takes a molecule about 400 ps to reorient through an angle of 180°. NMR measurements of T_1 have also been used to determine the "correlation time" τ_{NMR} of the rotational dynamics. The values of $\tau_{\mathrm{NMR}}=12$ ps [11] obtained at 300 K and 9 ps [12] found at 283 K are consistent with the results reported here since for rotational diffusion, $D_R=1/6\tau_{\mathrm{NMR}}$ [12]. However, the NMR measurements reported to date do not distinguish among reorientational jumps, rotational diffusion, or other mechanisms of diffusion. Molecular-dynamics simulations of this system predict that the molecules undergo rotational diffusion in this phase and have yielded a value of $\tau_{\mathrm{NMR}}=7$ ps at 260 K [13].

A limited number of neutron scattering measurements have also been made as a function of temperature at $Q=3.6$ Å^{-1}. In addition, measurements at several values of Q have been made at 520 K, yielding a value of $D_R=(2.8\pm0.8)\times10^{10}$ s^{-1}. All of the data are consistent with the Sears model of isotropic rotational diffusion. The observed temperature dependence of D_R is consistent with a thermally activated process having an activation energy of 35 ± 15 meV, which is in reasonable agreement with the values of 42 ± 9 meV [11] and 60 ± 5 meV [12] obtained by NMR.

The possibility that other models of the orientational dynamics give comparable agreement with the experimental results has also been considered. Instantaneous jumps between symmetry-equivalent orientations can be rejected immediately because this model implies no coherent quasielastic scattering. In addition, any model which involves only one type of jump between inequivalent positions, and therefore only one time scale, would lead to a quasielastic width independent of Q, a result which is clearly inconsistent with the data. Although the point symmetry of the space group $Fm3m$ is incompatible with the icosahedral symmetry of the molecule, models involving jumps between nonequivalent molecular orientations cannot be ruled out on the basis of symmetry alone, since the apparent $Fm3m$ symmetry could be due to microtwinning between two structures belonging to space group $Fm3$ [14]. We have therefore calculated the relative intensities of the quasielastic scattering and of the first few (low-Q) Bragg peaks for several models of orientational disorder. Figure 2(a) displays, on the same scale relative to the Bragg intensities, results for both rotational diffusion (solid line) and fourfold jumps about a twofold molecular axis (dashed line). We find that our data favor the rotational diffusion model over others we have considered. We cannot, however, distinguish between rotational diffusion and n-fold jump rotations for values of n greater than about 10.

To summarize, using coherent quasielastic neutron scattering we have established a remarkably simple picture of the rotational dynamics of C_{60} in the orientationally disordered high-temperature phase, namely, that each individual molecule undergoes rotational diffusion that is uncorrelated with the motions of its neighbors. At the phase transition the time scale slows abruptly by at least a factor of 20. These results demonstrate that the orientationally disordered phase of the C_{60} fullerite system is a prototypical example of a rotator phase in which the reorienting molecules are more nearly spherical than in any other molecular solid exhibiting similar behavior.

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