Molecular Dynamics in K_3C_{60}: A ^{13}C NMR Study

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Measurements of the ^{13}C NMR spectrum, spin-lattice, and spin-spin relaxation rates in K_3C_{60} reveal the existence of two distinct molecular motions of the same C_{60} molecule above 200 K, with respective activation energies of 2600 ± 300 and 6800 ± 500 K. We propose a simple model to explain these data implying fast axial jump rotation of the C_{60} molecules combined with slow jumps around perpendicular axes. The analysis of the spectra indicates an abrupt change in the molecular motion below 200 K suggestive of a phase transition also evidenced by calorimetric measurements.

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One of the first questions to clarify towards the understanding of the fullerene-based superconductors A_3C_{60} (A=K, Rb, etc.) [1,2] is the symmetry of the crystal structure and, in particular, of the crystalline field felt by the C_{60} molecule. In the fcc structure found by x-ray diffraction [3], the crystalline field of cubic symmetry does not lift the triple degeneracy of the t_{1u} molecular orbitals forming the conduction band, and this result is the starting point of substantial theoretical work [4] on the electronic properties of these systems. This crystal structure, however, is incompatible with the icosahedral symmetry of the C_{60} molecule, and either an orientational disorder [3] or a symmetry-lowering distortion of the fcc structure necessarily occurs. As demonstrated in pure C_{60} [5–10], the NMR study of the molecular dynamics can yield information on the changes of local symmetry.

In this paper we address the molecular dynamics in K_3C_{60} by studying the ^{13}C NMR spectrum, spin-lattice relaxation time T_1, and spin-spin relaxation time T_2 between 30 and 400 K. Accurate spin-lattice relaxation measurements reveal a maximum in T_1^{-1} at $T = 230$ K not detected in previous work [11,12]. We show that this peak arises from fast reorientations of the C_{60} molecule and find that the correlation time and activation energy of this motion are similar to the values observed in the orientationally ordered phase of pure C_{60} [8]. The temperature dependence of T_2^{-1} reveals the simultaneous existence of a slow motion of the same molecule with a correlation time and activation energy consistent with those found by Barrett and Tycko [13] using a 2D NMR technique, and by neutron scattering [14]. We suggest that the two different motional correlation times arise from an *anisotropic* angular jump diffusion and successfully model the shape of the NMR line above 200 K. The abrupt change of the spectrum as well as a preliminary differential thermal analysis suggest a phase transition at 200 K.

The K_3C_{60} powder sample used in this study is the same as in Ref. [12]. While in the previous measurements no special care was taken to optimize the spectral resolution, here the axis of the sample tube has been aligned along the field ($H_0 \approx 7$ T) to obtain better field homogeneity. The half width at half maximum of the Fourier transformed (FT) spectrum is $\delta\nu = 0.38$ kHz above 310 K. A typical width for the $\pi/2$ pulse is 14 μs corresponding to an rf field magnitude $H_1 \approx 14$ G. Measurements with very long repetition times allowed us to observe the signal of pure C_{60}, and we found that about 15% of our sample is unreacted C_{60}. The T_1 data have been taken with the inversion-recovery method on the free induction decay (FID) with quadrature detection. The recovery curves have been measured on the K_3C_{60} signal position of the FT spectra obtained from the FID, and, consequently, do not involve any component of the pure C_{60} residuum. This explains the basic differences compared to previously published data on the same sample [12]. The T_2 measurements have also been performed on FT spectra of half of the spin echo signal obtained with a $\pi/2 - \tau - \pi$ pulse sequence, with a repetition time about T_1 at each temperature.

Examples of recovery curves taken at the center and the tail of the K_3C_{60} line, 3 kHz apart on the side opposite to the C_{60} signal, are shown in the inset of Fig. 1. They show single exponential behavior with the same T_1

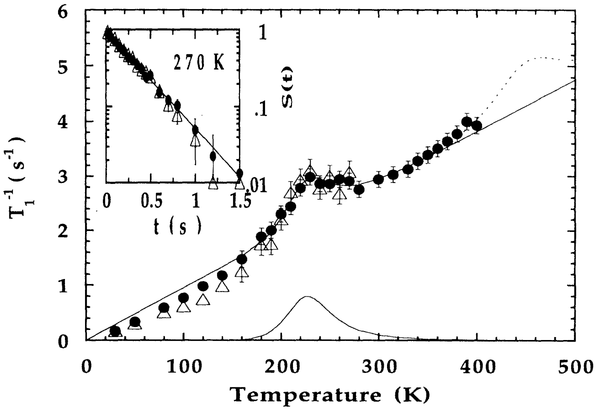

FIG. 1. Temperature dependence of T_1^{-1} obtained at the peak (solid circles) and at the tail (open triangles) of the spectra. The data with error bars are for exponential recoveries. Those without error bars are defined from the $1/e$ decay time for nonexponential recoveries. The full lines are a fit to Eq. (1) with an activated motion, and the contribution of this molecular motion. The dotted line is obtained with two activated motions (see text). Inset: recovery curves $S(t) = [M(\infty) - M(t)]/M(\infty)$ at 270 K.

down to 160 K, below which a nonexponential behavior progressively develops. The distribution in T_1 at low temperatures is an intrinsic property of the electronic states of this material as discussed in Ref. [12]. It is shown there that the structurally inequivalent carbon sites in the frozen state possess distinct spin densities, giving different T_1 at different sites.

As seen in Fig. 1, T_1^{-1} exhibits the already reported [11,12] roughly T-linear variation expected for normal metals [15], but also a broad peak centered around 230 K associated with molecular motion. One might attribute it to spin diffusion between pure C_{60} and K_3C_{60} domains, since a maximum in T_1^{-1} is also found in pure C_{60} at a similar temperature [8]. If such a thermal contact between ^{13}C spins were present, we should expect a short T_1 for the C_{60} phase in our sample, induced by the T_1 of metallic K_3C_{60}. The very fact that a repetition time as long as a few minutes is required to detect the C_{60} signal above room temperature is a direct proof that the two spin baths are decoupled (see also Fig. 4). Therefore, *the peak in T_1^{-1} is intrinsic to the K_3C_{60} phase and not related to the residual pure C_{60} phase.*

In general, T_1^{-1} is expressed in terms of the Fourier component at the resonance frequency ω_0 of the transverse local field at the nuclear sites [15]. It is assumed that the correlation function of the fluctuating field associated with the molecular motion has an exponential decay with a correlation time τ_c. If the electronic band structure is considered as independent of the molecular motions, the two relaxation processes can be added. Then T_1^{-1} can be written as

$$T_1^{-1} = \alpha T + (\gamma H_{\rm loc})^2 2\tau_c \left(1 + \omega_0^2\tau_c^2\right)^{-1} , \qquad (1)$$

where γ and $H_{\rm loc}$ are the ^{13}C nuclear gyromagnetic ratio and the amplitude of the fluctuating local field, respectively. The second term gives a maximum contribution $(T_1^{-1})_{\rm max}$ to T_1^{-1} for $\omega_0\tau_c = 1$. Then we can extract the value of $H_{\rm loc}$ from the amplitude of $(T_1^{-1})_{\rm max}$, once the T-linear contribution has been subtracted. Here, we used $\alpha = (9.5 \pm 0.2) \times 10^{-3}\ {\rm s^{-1}K^{-1}}$ from the data around 350 K. With $(T_1^{-1})_{\rm max} = 0.8 \pm 0.2\ {\rm s^{-1}}$ at 230 K, $\gamma H_{\rm loc} = 3.1 \pm 0.4$ kHz is obtained with $\tau_c = 1/\omega_0 \sim 10^{-9}$ s. As shown later, the width of the spectrum observed at 30 K, in the frozen state, was estimated to be $\delta\nu = 2.9 \pm 0.3$ kHz after correction for the inhomogeneity of the external field. This agreement allows us, at this stage, to assign the peak in T_1^{-1} to the modulation of the local field at carbon sites by molecular motion.

With the above values of α and $H_{\rm loc}$, and assuming an Arrhenius law $\tau_c^f = \tau_0^f \exp(T_a^f/T)$, we carried out a least-squares fit to the data between 160 and 330 K. The result shown in Fig. 1 gives $T_a^f = 2600 \pm 300$ K, $\tau_0^f = 2 \times 10^{-14\pm0.7}$ s. These values are similar to those ($T_a = 2900$ to 3500 K and $\tau_0 \sim 10^{-14}$ s) found in pure C_{60} in the orientationally ordered phase [8,10]. If this motion was a simple isotropic diffusive rotational motion of the C_{60} spheres, the NMR spectra should broaden when $\gamma H_{\rm loc}\tau_c^f \sim 1$, i.e., at $T \approx 120$ K with the present parameters. However, as it can be seen in Fig. 2(a), the NMR line broadening actually occurs in a wide T range starting at 300 K, with two (or three) steplike anomalies in $\delta\nu(T)$ around 270 and 200 K (and 100 K).

The motional correlation time found in Ref. [13] at $T = 200$ K is 10^7 times longer than our τ_c^f extrapolated to the same temperature. In order to test for the existence of long correlation times we have performed T_2 measurements which are sensitive to slow motion. We noticed first that a short component in the echo decay appears below 330 K, which is associated with the observation of a broad tail in the spectra, as we shall see later. Its T_2^{-1} increases very fast with decreasing T down to 300 K, as it can be seen in the right hand part of Fig. 2(b).

While T_1 processes also contribute to T_2, the dominant phase memory loss in T_2 is due to slow fluctuations of the local field along H_0. The expression for T_2^{-1} in the presence of molecular motion is given by [15]

$$T_2^{-1} = (\gamma H_{\rm loc})^2[\tau_c + \tau_c(1 + \omega_0^2\tau_c^2)^{-1}] + (T_2^{-1})_{d-d} , \qquad (2)$$

in the "fast" motion limit ($\gamma H_{\rm loc}\tau_c < 1$). The second term in the bracket is always negligible here as $T_2^{-1} \gg T_1^{-1}$. The last term is a dipole-dipole (d-d) contribution, which is only partly averaged in the solid as the rotational motion of the C_{60} does not modulate isotropically the relative positions of the nuclei which are not located on the same C_{60} ball. For a rough estimate of $(T_2^{-1})_{d\text{-}d}$, we have calculated the d-d contribution to the second moment of the spectrum in a simple model where

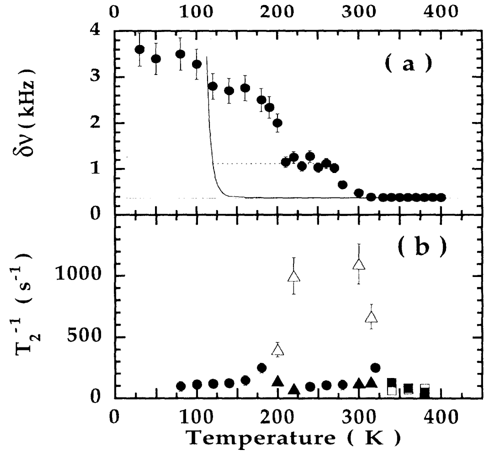

FIG. 2. (a) Temperature dependence of the linewidth $\delta\nu$ defined as the half width at half maximum on the side opposite to the pure C_{60} signal. The full and dotted lines sketch the T dependence expected for an isotropic diffusion and a uniaxial rotation, respectively. (b) Temperature dependence of T_2^{-1}. The solid and open squares above 340 K represent T_{2L} and T_{2G} in fits to $M(2t) = M_0 \exp[-2t/T_{2L} - (2t/T_{2G})^2/2]$. The solid circles are for exponential recoveries. The open and solid triangles are the short and long T_2, in fits with the sum of two exponentials.

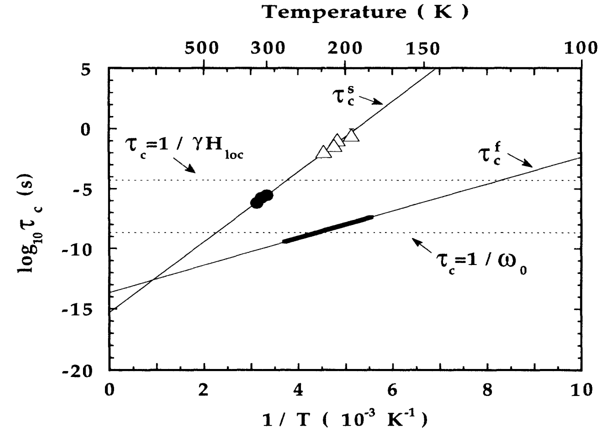

FIG. 3. Variation versus $1/T$ of τ_c estimated from T_1 (thick line) and T_2 (solid circles), together with the data of Ref. [13] (triangles). The solid lines show the best fits τ_c^f and τ_c^s to activated behavior.

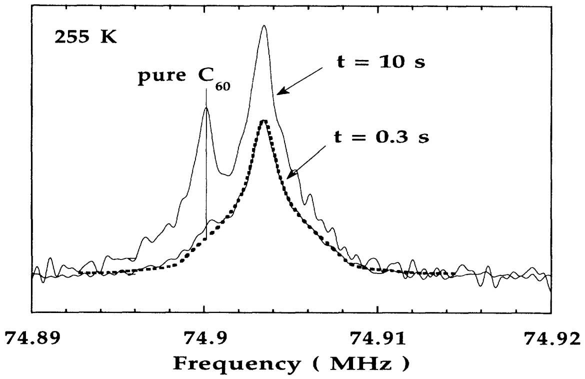

FIG. 4. FT spectra obtained from the FID signals with two different repetition times t, showing the large difference in T_1 for the K_3C_{60} and C_{60} phases in our sample. The thick dotted line is the calculated line shape for uniaxial rotation.

all the ^{13}C nuclear spins of a C_{60} molecule (0.66 in average) sit at the center of the C_{60} sphere. This model yields 120 and 75 s^{-1} for the ^{39}K-^{13}C and the ^{13}C-^{13}C nuclear *d-d* interactions, respectively. The slightly smaller values observed at high T agree with the above estimate. Without a more refined calculation of the *d-d* contributions in presence of motion, we could only deduce here τ_c for three data points at 300, 310, and 320 K, for which $(T_2^{-1})_{d\text{-}d}$ can be nearly neglected.

The relevant values of τ_c obtained from the short component of T_2 with $\gamma H_{\rm loc} = 3.1$ kHz are plotted as $\log_{10}\tau_c$ vs $1/T$ in Fig. 3, together with those given by Barrett and Tycko [13] between 195 and 220 K, and with the activated behavior estimated from T_1^{-1}. The first two sets of data can be interconnected by a line shown as τ_c^s in Fig. 3, yielding $T_a^s = 6800 \pm 500$ K, $\tau_0^s = 7\times 10^{-16\pm 0.8}$ s. This activated process is very different from the one resulting in τ_c^f inferred from the T_1 data. This fact establishes the existence of two different molecular motions in the investigated T range (200 to 400 K). Let us point out that both τ_c^f and τ_c^s should contribute to T_1^{-1}, the latter giving a maximum for $\omega_0\tau_c^s = 1$, i.e., $T \approx 420$ K (Fig. 3). An upturn in the T_1^{-1} data is indeed seen above 350 K in Fig. 1 and is well fitted by Eq. (1), when the contributions of both τ_c^f and τ_c^s are used.

We can gain some information on the nature of the molecular motions by considering in some detail the spectral shapes, particularly for $200\text{ K} < T < 300$ K. In this range the FID spectra appear inhomogeneous: they consist of a broad tail and a central narrow part (Fig. 4). Further, below 270 K, the intensity of the spectra deduced from the spin echo signal is progressively reduced with respect to the FID spectrum, the ratio being about 50% for $T = 255$ K. This reduction comes mainly from the loss of the tail of the spin echo spectra. Therefore, the tail has a very short T_2 (< 1 ms) which cannot be measured by spin echo for $T < 270$ K. Finally the experimental fact that T_1 is the same at the peak and the tail of the spectrum (Fig. 1) points out that the *^{13}C atoms which give the broad tail of the NMR signal are involved in two distinct molecular motions.*

In order to explain this composition of two motions on the same molecule, we consider hereafter an anisotropic rotational diffusion, which has been proposed for pure C_{60}, but not clearly evidenced yet [5,7]. The rotation is fast around an axis fixed in the lattice frame, and slow around the perpendicular axes. As long as $\gamma H_{\rm loc}\tau_c < 1$ for both motions ($T > 330$ K), the overall motion appears isotropic in NMR and the spectrum only shows a single narrow line. When $\gamma H_{\rm loc}\tau_c^s > 1$, the averaging becomes incomplete, and the spectrum should become characteristic of the fast axial rotation. In this case the ^{13}C nuclei are no longer equivalent in the molecular motion. From Fig. 3, this situation occurs for $T < 266 \pm 5$ K, where the inhomogeneous spectrum and the T_2 data reflect the inequivalent carbon nuclei. A narrow line at the isotropic NMR shift position arises from molecules for which the angle θ between H_0 and the axis of fast rotational jumps is close to the magic angle $\theta_m \approx 55°$. Here T_2 is long because "perpendicular" jumps do not lead to fluctuation in the longitudinal component of the local field. The tail of the signal—with short T_2—results from molecules with θ far from θ_m.

To test the proposed model qualitatively, an estimate of the principal values of the shift tensor (K_a, K_b, K_c) is required. The isotropic part of the shift, $K_{\rm iso} = (K_a + K_b + K_c)/3 = 186$ ppm, is obtained from the signal position at high T (> 300). In contrast to pure C_{60}, the spectrum is nearly symmetric, and its peak position does not change within 5 ppm from 30 to 400 K. We are thus led to consider that the shift tensor has an asymmetry parameter $\eta = (K_a - K_b)/(K_c - K_{\rm iso}) \approx 1$, with a normal to the C_{60} sphere. The FID spectrum in Fig. 4, agrees quite well with that calculated for $K_a = 186$, $K_b = 32$,

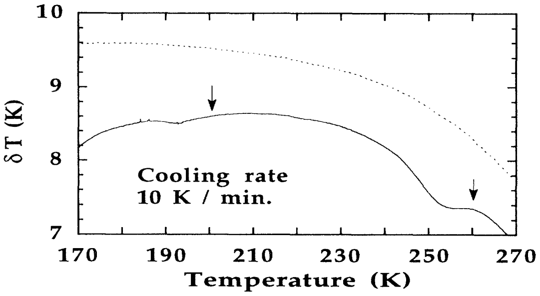

FIG. 5. DTA scans for decreasing temperature of our K_3C_{60} sample (solid line) and of an Al_2O_3 reference sample (dotted line) under the same experimental conditions. The arrows indicate the onset of the two features.

and $K_c = 340$ ppm, assuming fast axial rotation for a powder sample. The characteristic features, a broad tail and a sharp line at the central position, are well reproduced in the model. These considerations might as well apply in Rb_3C_{60} to the ^{13}C NMR spectrum of Ref. [11], with a more axial hyperfine field tensor, however.

At lower T, no further modification in the spectral shape is expected, as long as the uniaxial rotation is sufficiently fast [$\gamma H_{\mathrm{loc}} \tau_c^f < 1$, i.e., $T > 120$ K (Fig. 3)]. Although $\delta\nu(T)$ displays a plateau from 250 to 200 K [Fig. 2(a)], its sharp increase at 200 K signals a freezing of the motions or the occurrence of a phase transition. Let us also notice that T_2^{-1} for the short T_2 component of the signal decreases abruptly with decreasing T near 200 K [see Fig. 2(b)]. We also find that below 200 K the echo signal recovers an intensity comparable to that of the FID signal. These are further indications that the local fields become quasistatic. At low T the only decay process for T_2 is the d-d interaction, which explains the limiting value for T_2^{-1} at low T.

Strong evidence for the existence of a phase transition at 200 K has been obtained from a differential thermal analysis (DTA) performed on the same sample. As seen in Fig. 5, the DTA signal displays two features similar in shape. We attribute one of them to the 260 K phase transition of the residual pure C_{60} in the sample. The other one—with an onset around 200 K and a specific enthalpy about 1 order of magnitude smaller—we identify with a phase transition in K_3C_{60} also evidenced by the NMR measurements.

It should be noted here that the shift tensor we use to explain the spectrum in Fig. 4 above the phase transition would result in a linewidth twice as large as the width observed at low T in the frozen state. The phase transition may be responsible for the change of the shift tensor [16].

In conclusion, we have characterized the molecular dynamics in K_3C_{60} by ^{13}C NMR and propose an anisotropic rotational diffusion tensor for the C_{60} molecule. This result is incompatible with the high symmetry of the x-ray structure [3], and suggest a static distortion of the lattice—with perhaps a short spatial coherence—even above 200 K. We find evidence of a phase transition at 200 K, implying a further lowering of symmetry. The relation of our findings to the recent observation [17] of 3 (rather than 2) ^{87}Rb NMR lines in Rb_3C_{60}, as well as the effect of the structural distortion on the density and correlations of the electronic states remain to be further investigated.

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