Synchrotron X-Ray Study of Orientational Order in Single Crystal C_{60} at Room Temperature

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Synchrotron x-ray Bragg intensities from a C_{60} single crystal were used to evaluate the nonuniform atomic density distribution on a C_{60} sphere at 300 K. Coefficients of the symmetry-adapted spherical harmonics up to $l=18$ are required with a resulting density deficiency of $\sim 16\%$ in $\langle 111 \rangle$ directions and four lobes of $\sim 10\%$ excess about $\langle 110 \rangle$. The results are discussed in terms of an effective potential which a single C_{60} sees in the cubic field of its neighbors. Initial calculations give a maximum rotational potential barrier height of about $2kT$ or ~ 600 K.

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An outstanding issue in our understanding of the structure and dynamics of solid C_{60} is the experimental determination of the interaction potential energy between C_{60} molecules. Early x-ray powder diffraction data indicated that, to a good approximation, these molecules could be taken as spinning freely at room temperature [1] in a face-centered-cubic (fcc) structure ($Fm3m$). At lower temperature, depending upon the sample, a phase transition has been observed between 250 and 260 K into a rotationally ordered cubic phase ($Pa\bar{3}$) in which the icosahedrally symmetric molecules of the fcc phase assume discrete orientations about a set of $\langle 111 \rangle$ directions [1,2]. Our current interest centers on the degree to which these C_{60} molecules are oriented randomly at room temperature (i.e., whether their charge density is uniform over a spherical surface) especially as recent neutron scattering [3] and NMR data [4] have indicated a hindered rotation in the high-temperature phase, namely, a rotational diffusion constant incompatible with free rotation.

We present here evidence of pronounced deviations from isotropic random orientations of the C_{60} molecule based on a single-crystal room-temperature x-ray study. Such evidence is less convincingly extracted from powder data because all reflections with the same wave vector magnitude, $|\mathbf{k}|=(4\pi\sin\theta)/\lambda$, overlap, thereby concealing the required directional information. There are nonetheless a number of excellent powder diffraction studies in which the spherically averaged room-temperature structure is presented and in which its temperature dependence is explored [1,2,5,6]. We believe, however, that the present work is the first to demonstrate unambiguously the actual room-temperature atomic density distribution in the hindered rotation phase.

The Fourier transform of the atomic density $\rho(\mathbf{r})$ for this system can be approximated by

$$\rho_{\mathbf{k}}=f_c(k)\sum_{n,i}e^{i\mathbf{k}\cdot(\mathbf{r}_n+\mathbf{r}_i)}\,, \tag{1}$$

where $\mathbf{r}_n$ locates the center of the molecule, and $\mathbf{r}_i$ is the position of the ith carbon atom relative to the center of the molecule, assuming a rigid molecule. $\mathbf{r}_i$ is a dynamical variable due to the possibility of the molecule rotating as a rigid object. We have assumed that the electronic wave functions for all the atoms are identical thus permitting, as usual, the use of an atomic scattering factor f_c for each carbon atom.

The $\mathbf{r}_i$ coordinates may be described by a set of three Euler angles, $\boldsymbol{\omega}$, giving the rotation of axes fixed in the rigid molecule relative to the coordinate system fixed in the crystal. We take $\boldsymbol{\omega}=0$ for the molecule oriented with three of its twofold axes aligned along the three axes of the crystal. Then $\rho_{\mathbf{k}}$ can be expressed in terms of symmetry-adapted spherical harmonics $S_l^\tau(\hat{\mathbf{k}})$ [$\hat{\mathbf{k}}\equiv(\theta,\phi)$ in the crystal frame] and molecular rotator functions $U_l^{1\tau}(\boldsymbol{\omega}_n)$ [7,8], where l is the order of the harmonic. It can then be shown [7–9] that

$$\rho_{\mathbf{k}}=4\pi\sum_{n}\sum_{l,\tau}i^l j_l(kR)g_l^1 S_l^\tau(\hat{\mathbf{k}})U_l^{1\tau}(\boldsymbol{\omega}_n)e^{i\mathbf{k}\cdot\mathbf{r}_n}f_c(k)\,, \tag{2}$$

where $j_l(kR)$ is the lth order Bessel function and R is the radius of the molecular sphere.

Equation (2) follows from the expansion of $e^{i\mathbf{k}\cdot\mathbf{r}_i}$ in spherical harmonics and the definitions of the symmetry-adapted rotator functions given in Ref. [8]. The $S_l^\tau(\hat{\mathbf{k}})$ transform as particular representations of the cubic group. $\tau=[\Gamma,\nu,i]$ where Γ denotes the representation, ν the index of multiplicity of the representation, and i the row of a given representation. The molecular rotator functions $U_l^{1\tau}(\boldsymbol{\omega}_n)$ are linear combinations of the Wigner rotation matrix elements. The 1 denotes the identity representation of the icosahedral group, while τ is a particular representation of the cubic group. Only the identity representation appears because any rotation of the molecule that takes it into itself leaves the density invariant. The molecular form factor $g_l^1 = \sum_{i=1}^{60} S_l^1(\theta_i,\phi_i)$ (θ_i and ϕ_i are coordinates of the carbon atoms in the fixed frame of the molecule), where $S_l^1(\theta_i,\phi_i)$ is the linear combination of spherical harmonics of order l that transforms as the identity representation of the group of the icosahedron. The experimental bond lengths [2,5] are used in the calculation of g_l^1.

The average of $\rho_{\mathbf{k}}$ will then be

$$\langle\rho_{\mathbf{k}}\rangle = 4\pi f_c(k) \sum_{\tau l} \sum_{\mathbf{k}_0} i^l j_l(kR) g_l^1 S_l^\tau(\hat{\mathbf{k}}) \langle U_l^{1\tau}(\boldsymbol{\omega})\rangle \delta(\mathbf{k}-\mathbf{k}_0) , \tag{3}$$

where $\mathbf{k}_0$ is a Bragg vector of the fcc lattice, and we have dropped the subscript n from the average of $U_l^{1\tau}(\boldsymbol{\omega})$, since it is the same for every site. Γ is now restricted to the representation A_{1g}, whereby $i=1$, and the only remaining index is v which labels the particular representation within A_{1g} and may take on more than one value.

The relative intensities of the Bragg peaks are determined by the structure factor for the (rotating) molecule, which can also be expressed as a series in the symmetry-adapted spherical harmonics [8,9],

$$F_c(\mathbf{k}) = 4\pi f_c(k) \sum_{l} \sum_{v} i^l j_l(kR) C_{lv} S_l^v(\hat{\mathbf{k}}) , \tag{4}$$

where only l and the number v remain as parameters in $S_l^v(\hat{\mathbf{k}})$. From a comparison of Eqs. (3) and (4), the coefficients of the series may then be seen to be proportional to the average of the molecular rotator function, i.e.,

$$C_{lv} = g_l^1 \langle U_l^{1v}(\boldsymbol{\omega})\rangle . \tag{5}$$

If the rotation of the individual molecules were unhindered, all terms in the series except $l=0$ would be zero, and the structure factor would be independent of the direction of $\hat{\mathbf{k}}$. The $l \neq 0$ coefficients of the series give the deviation from unhindered rotation. Their values depend upon the probability distribution $P(\boldsymbol{\omega})$ for an individual molecule, and have been determined from Bragg intensity data using Eq. (4) as discussed below. $P(\boldsymbol{\omega})$ must be invariant under any cubic symmetry operation and many of the g_l^1 vanish because of molecular symmetry. This, in principle, restricts l to the values 0,6,10,12,16,18, etc., for which one can form representations of the icosahedral group, and allows us to represent the average atomic density distribution $\langle\rho_{\mathbf{k}}\rangle$ [Eq. (3)] in terms of relatively few coefficients.

The probability distribution $P(\boldsymbol{\omega})$ defines an effective potential for the rotation of a single molecule through $P(\boldsymbol{\omega}) = e^{-\beta V(\boldsymbol{\omega})} / \int d\boldsymbol{\omega}\, e^{-\beta V(\boldsymbol{\omega})}$ and $V(\boldsymbol{\omega})$ can be expanded as a series of molecular rotator functions

$$V(\boldsymbol{\omega}) = \sum_{l,v} x_l^v U_l^{1v}(\boldsymbol{\omega}) \tag{6}$$

with the x_l^v coefficients to be determined. The coefficients x_l^v can then be obtained by adjusting them to reproduce the cubic harmonic coefficients, C_{lv}, in the expansion of $F(\mathbf{k})$ as determined from single crystal Bragg data.

Our single crystals were sublimation grown from chromatographically purified C_{60} as described by Meng *et al.* [10] and several samples were examined both for mosaic spread and for growth twins. The selected crystal had a narrow mosaic spread of 0.03° and contained only two twin components (the smaller one of which was 7.2% of the total volume of $0.24\times0.075\times0.15$ mm^3). The crystal was mounted in He in a Lindemann glass capillary tube for the extended experiment at the National Synchrotron Light Source (NSLS) on beam line X7B.

Data were collected at a wavelength of 0.921 Å using a pair of (111) Si monochromators and a cylindrical focusing mirror. A small ion chamber near the sample monitored I_0, the incident intensity, and the scintillation detector was set to exclude $\lambda/3$. The lattice constant $a_0 = 14.1589(8)$ Å was determined by a least-squares fit to 2θ values for 28 reflections. Data were usually collected in a bisecting mode ($\omega = 2\theta/2$) and ω scans were used to measure integrated intensities. After every 15–20 reflections a standard (444) reflection was scanned and the slow variation in the plotted value of this integrated intensity was used to correct all measured intensities for beam variations. Data on both twins were taken for a total of 1103 integrated reflections leading to a set of 317 unique peaks. These included both independent and overlapping twin reflections which could be treated as additive in their intensities. The final data set was corrected for glass absorption. Sample absorption was essentially negligible because of the low absorption coefficient of the C_{60}. Standard Lorentz and (small) polarization factors were applied to the integrated intensities. It is important to note that the measured k range extended out to 9.65 Å^{-1} which enabled us to evaluate C_{lv} coefficients out to $l=30$. The variance σ^2 was derived from the counting statistics.

The structure refinement was carried out with a modified version of the crystallographic least-squares program of Lundgren [11]. The residual, $\sum w|F_0^2 - F_c^2|^2$ [where F_0 and F_c are respectively the observed and calculated values in Eq. (4)], was minimized with weights $w=\sigma^{-2}(F_0^2)$, summing over the 317 independent observations with $F_0^2 > -\sigma$. The C_{60} molecules were located at the fourfold (a) sites of $m3m$ symmetry in the fcc lattice [2]. Molecular rotational and translational motions were assumed to be independent; the latter was described by the single harmonic Debye-Waller parameter allowed by crystal site symmetry.

The adjustable parameters for refinement were the radius R and expansion coefficients C_{lv}. Other variable parameters were the Debye-Waller factor, one global scale factor, and an isotropic secondary extinction parameter for a type 1 crystal [12]. The refinement was initiated with parameters $R=3.54$ Å, $C_{0,1}=1.0$, for assumed spherically symmetric distribution. The expansion coef-

TABLE I. Molecular parameters for C_{60}: radius R (Å); isotropic temperature factor ($U_{\mathrm{iso}} \times 10^2$ Å^2) which yields an rms molecular displacement of $\sim 1\%$ of the lattice parameter; symmetry-adapted function coefficients ($\times 10^3$). The temperature factor has the form $\exp(-U_{\mathrm{iso}}k^2/2)$. The values of the cubic harmonic coefficients $C_{l\nu}$ which are also allowed by the icosahedral molecular symmetry are given on the second line. The additional three cubic harmonic coefficients, whose values must vanish for icosahedral symmetry, are on the third line and are zero within experimental error. (The R-factor ratio test [15] shows that including the nonicosahedral cubic harmonic parameters in the icosahedral model refinement is not statistically significant at the 0.1% significant level.)

			Radius	U_{iso}				
			3.5429(6)	2.23(3)				
$C_{0,1}$	$C_{6,1}$	$C_{10,1}$	$C_{12,1}$	$C_{12,2}$	$C_{16,1}$	$C_{16,2}$	$C_{18,1}$	$C_{18,2}$
1000	−23.0(17)	12.8(14)	9.4(17)	26.0(13)	−7.7(23)	−0.4(20)	−3.0(24)	23.7(20)
$C_{4,1}$	$C_{8,1}$	$C_{14,1}$						
−2.7(17)	−3.4(22)	1.4(16)						

ficients of harmonics allowed by $m3m$ (A_{1g}) [13] were varied from initial zero values in sets with increasing orders of l. Parameter shifts at convergence were all $< 0.001\sigma$ after three or fewer iterations. The coefficients of harmonics of orders $l \le 18$ which conform to both site and molecular symmetries, $m3m$ and $m\bar{3}\bar{5}$, provided values $> 3\sigma$ and improved fits to the data. Including cubic $C_{l\nu}$ coefficients with $18 < l \le 30$ did not further improve the fit. The 111 and 220 reflections had $> 40\%$ extinction corrections and they were omitted in the final refinement; none of the resulting molecular parameters was changed by more than 1σ.

The final $C_{l\nu}$ parameters are listed in Table I, together with a refined molecular radius R and displacement U_{iso} parameter values. Corresponding indices to fit $R(F^2)$, $wR(F^2)$, S [14] are 0.051, 0.064, 1.169 with the all cubic $C_{l\nu}$ terms, and 0.052, 0.064, 1.175 with terms conforming solely to icosahedral symmetry. By comparison, the spherically symmetric density model gave a markedly inferior fit to the data, with $wR(F^2)$ of 0.116. It is gratifying to note that, using the above procedure, the data themselves select as significant only those coefficients expected from symmetry arguments. The final parameters in Table I were taken for evaluating the effective carbon number density $\rho(\mathbf{r})$ [9],

$$\rho(\mathbf{r}) = 4\pi \sum_l \sum_\nu C_{l\nu} S_l^\nu(\theta,\phi)\delta(r-R)\,,$$

where $\hat{r} \equiv (\theta,\phi)$, to produce the contour map shown in Fig. 1 in which $\rho(\mathbf{r})$ is normalized to be equal to unity for a uniform density over the sphere and the contour levels are in steps of $\pm 3\sigma = 0.024$. This gives a density deficit of $\sim 16\%$ in the $\langle 111 \rangle$ direction and four lobes of excess density about $\langle 110 \rangle$ of $\sim 10\%$, along with other detail.

Clearly our results demonstrate that the C_{60} molecule is not freely rotating at room temperature. Using the coefficients $C_{l\nu}$ given in Table I we are also currently evaluating $P(\boldsymbol{\omega})$ and $V(\boldsymbol{\omega})$ for this crystal. While these

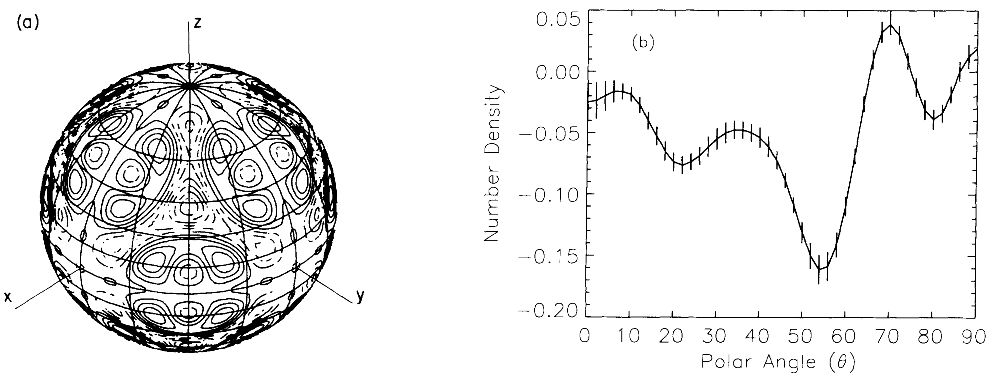

FIG. 1. (a) Atomic number density on the spherical surface evaluated from coefficients $C_{l\nu}$ obtained by refinement with contour intervals of $\pm 3\sigma = 0.024$. The $C_{0,1}$ term was omitted from the summation $4\pi\sum_l\sum_\nu C_{l\nu}S_l^\nu(\theta,\phi)$ to emphasize differences from spherical symmetry and dashed contours indicate a density deficit while solid contours indicate an excess over the uniform density. (b) A θ plot of $\rho(\mathbf{r}) - 1$, normalized as discussed in the text, along constant $\phi = 45°$ ($x = y$) through the $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions including estimated standard deviations. Number density thus refers to a fractional excess or deficit over the unit value for uniform density.

results will be presented elsewhere [16] it should be noted that the single particle orientational barrier heights are quite low for certain rotational paths but show a maximum of $\sim 2kT$ or 600 K. This value, which is in the range of activation energies measured for rotational diffusion [3,4], should provide one test for theories of intermolecular interaction in these crystals [17].

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