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1992 J. Phys.: Condens. Matter 4 6087

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A pair correlation function study of the structure of C₆₀

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Received 24 April 1992

Abstract. The inter- and intra-molecular structures of C₆₀ have been studied at 20 K and 295 K by means of the pair correlation function using low-angle pulsed neutron diffraction. Two methods of inversion of the structure factor data are presented. Direct inversion of the data using a Monte Carlo algorithm yields a model-independent combined intra- and inter-molecular pair correlation function. This clearly indicates, even at 295 K, the presence of two distinct C-C bond lengths of 1.377(15) Å and 1.458(6) Å. Further analysis was performed using a truncated icosahedral model for the intra-molecular behaviour in combination with a free-form Monte Carlo solution for the inter-molecular pair correlation function. This analysis confirms two distinct nearest-neighbour C-C bond lengths but indicates that the difference has a precision of order 0.005 Å. The optimal values at both 20 K and 295 K obtained from this analysis are 1.400 Å and 1.440 Å implying that the molecular structure is essentially unchanged between these two temperatures. There are, however, distinct differences between inter-molecular bonding at 20 K and 295 K that are consistent with an orientational ordering transition at 260 K. In particular, the room temperature data can be accurately modelled in terms of a face-centred-cubic structure in which the C₆₀ molecules adopt a completely random orientation with respect to one another.

1. Introduction

Fullerenes and fullerides have been extensively studied over the past two years since the discovery of bulk preparative techniques (Krätschmer *et al* 1990). The molecular structure of the prototypic fullerene, C₆₀, was postulated to be of truncated icosahedral symmetry (Kroto *et al* 1985, Kroto 1987). This has been verified by a number of different experimental and theoretical approaches (Lüthi and Almlöf 1987, Taylor *et al* 1990, Hawkins *et al* 1991, Fagan *et al* 1991, Sachinandam and Harris 1991, David *et al* 1991). Although this truncated icosahedral molecular structure is well known, the detailed crystal structure of C₆₀ is still not fully understood. Solid C₆₀ is known to exist in three phases. At the lowest temperatures ($T < 85$ K), the C₆₀ molecules are orientationally ordered, although there is strong evidence of a small amount of orientational glass behaviour. Above the ~85 K glass transition, complex reorientational hopping occurs between two energetically distinct orientational configurations (David *et al* 1992, Burgi *et al* 1992). Direct evidence of the precise reorientational behaviour has not yet been obtained. Above 260 K, quasi-elastic neutron scattering (Neumann *et al* 1991) and NMR (Tycho *et al* 1992, Yannoni *et al* 1991, Johnson *et al*

1992) measurements suggest essentially isotropic reorientational diffusion. Conventional crystallographic analysis of Bragg intensity data at room temperature indicates that the elastic scattering may be well modelled by a spherical shell of scattering density. In this paper, the room temperature crystal structure of C_{60} is analysed using a radial distribution function approach. In contradistinction to conventional Bragg peak analysis which yields the time-averaged scattering density, this method gives information about the spherically averaged instantaneous density distribution. This approach has been pursued by Li *et al* (1991). The difference in the present work is the method of structure factor data inversion. In particular, the combined use of Monte Carlo algorithms and molecular modelling outlined below enables the intra- and inter-molecular C_{60} bonding to be discussed independently. This paper describes the results of this study and consequences for future work.

2. Experimental measurements

Pure C_{60} was obtained by standard procedures. Traces of solvent were removed by heating at 170° under vacuum for several hours. This resulted in ~ 0.5 g being available for mounting in the neutron beam. The sample was contained in a thin-walled vanadium sample can of diameter 5 mm.

Neutron diffraction data were measured by the time-of-flight technique using the small angle neutron diffractometer for amorphous and liquid samples, SANDALS, at the pulsed spallation neutron source ISIS. The scattering angle ranged from $11^\circ < 2\theta < 21^\circ$. The data were normalized to the scattering from a calibration rod of vanadium using standard procedures (Soper *et al* 1989). By performing the diffraction experiment at low scattering angles the effects of nuclear recoil in corrupting the diffraction pattern were minimized. As a consequence of the small volume and can size, the absorption and multiple-scattering corrections were found to be insignificant. The resulting diffraction patterns for the two temperatures, 20 K and 295 K are shown in figure 1. Despite the low scattering angles the data are recorded out to Q -values as high as 50 \AA^{-1} and structural oscillations can be seen in the data beyond $Q = 30 \text{ \AA}^{-1}$. This large Q -range obtained at low scattering angles results from the combined advantages in time-of-flight pulsed neutron diffraction of a high flux of epithermal neutrons (with wavelengths as low as 0.05 \AA ($E = 35 \text{ eV}$)) coupled with an absence of form-factor fall-off. The large- Q oscillations shown in figure 1 correspond primarily to the intra-molecular structure of C_{60} . Sharp Bragg peaks can be discerned at small Q -values and these are more extensive at the lower temperature.

3. Data analysis

The structure factor data, $H(Q) = S(Q) - 1$, shown in figure 1 are related by Fourier transform to the pair correlation function, $g(r)$, by the equation

$$S(Q) - 1 = 4\pi\rho \int_0^\infty r^2(g(r) - 1) \frac{\sin Qr}{Qr} dr \quad (1)$$

where ρ is the atomic number density. The standard procedure for obtaining $g(r)$ is to perform a direct Fourier inversion of the diffraction data modified by a filter

function to reduce the effects of truncation resulting from incomplete 'noisy' data. This paper, however, follows a different, more reliable approach that involves the simulation of an ensemble of solutions that are simultaneously consistent with the data and also optimally smooth. In this way the effects of counting statistics, truncation, instrumental resolution and other systematic errors can be included in a consistent manner: the range of $g(r)$ values found in the ensemble for a given radius r , is an indication of the uncertainty in the solution.

Two approaches have been adopted for the analysis of the C_{60} radial distribution function. The first is essentially model independent and involves the direct Monte Carlo simulation of the complete radial distribution function for the system which is allowed to take on an arbitrary shape, subject to the $H(Q)$ data and to the restriction that the 'noise', defined in terms of the second derivative of $g(r)$, $(\partial^2 g(r)/\partial r^2)^2$ (Soper 1990), be kept below a predefined limit. This introduces the reasonable prior assumption that the radial distribution function be locally smooth. The choice of the noise level is governed by the likelihood criterion that the model $g(r)$ adequately represent the data. Too smooth a radial distribution function leads to poor data fitting whereas too noisy a $g(r)$ is unphysical. Presently the optimum noise level criterion is determined by trial and error at the beginning of the simulation. Structure factor data inversion using this technique gives a combined inter- and intra-molecular radial distribution function. This limits the information content that may be obtained about the C_{60} radial distribution function as both inter- and intra-molecular distances occur above 3 Å. However, the first peak in $g(r)$, around 1.42 Å, corresponds to the nearest-neighbour C-C bonds. This peak is clearly split into two with a peak ratio of 0.42(6):1. However, the high correlation between peak widths, resulting from instrumental resolution and thermal motion, and peak splittings leads to some uncertainty in the precise degree of bond length differences. A least-squares analysis gave bond lengths of 1.377(15) Å and 1.458(6) Å.

In the second method of solution, the intra-molecular structure is very restrictively constrained to adopt a truncated icosahedral form. The principal advantage of this approach is that the inter- and intra-molecular radial distribution functions are decoupled and may be analysed separately. The number of parameters required to describe the intra-molecular model was kept to a minimum by enforcing the full icosahedral point symmetry, I_h . The inter-molecular structure, however, is simulated in the same model-independent manner as for the total radial distribution function structure outlined for the first method, namely by adopting an arbitrary form consistent with the structure factor data. The $g(r)$ solutions are thus generated by simultaneous refinement of the intra-molecular and Monte Carlo optimization of the inter-molecular structure. It is worth stressing the importance of this simultaneous optimization since a conventional approach uses only the large- Q data to refine the intra-molecular structure. In general this is unsatisfactory since the intra-molecular structure factor extends over all Q -values and in fact the most important part of it, the area of a given molecular peak in $g(r)$, is determined at small Q .

4. A model for the truncated icosahedron

In discussing the configuration of C_{60} , the following terminology is used (David *et al* 1991): the truncated icosahedron consists of 12 pentagons and 20 hexagons; the bonds fusing two hexagons and a hexagon and pentagon are defined as 6:6 and 6:5

bonds respectively. In 'ideal' truncated icosahedral symmetry all three C-C nearest-neighbour distances are equivalent; atoms are located at

$$\alpha(0, \pm\frac{1}{2}, \pm 3\tau/2) \cup \alpha(\pm\frac{1}{2}\tau, \pm 1, \pm\frac{1}{2}(2\tau + 1)) \cup \alpha(\pm\tau, \pm\frac{1}{2}, \pm\frac{1}{2}(2 + \tau)) \cup$$

where the symbol \cup implies cyclic permutation of coordinates, τ is the golden ratio $1.61803 = \frac{1}{2}(1 + \sqrt{5})$ and α is the C-C nearest-neighbour bond length. In the absence of any molecular symmetry there are 1770 distinct interatomic distances. The very high icosahedral point group symmetry, however, introduces considerable degeneracy. In the 'ideal' truncated icosahedron in which all three nearest-neighbour distances are identical the number of unique interatomic distances within the molecule is only 21. It is well known, however, that the three degenerate nearest-neighbour distances may be divided into two equivalent intra-pentagon 6:5 bonds and a single 6:6 inter-pentagon bond while still preserving the icosahedral point group symmetry. In other words, denoting a carbon atom C0 with three neighbours, C1, C2 and C3, then $d(\text{C0-C1}) = d(\text{C0-C2}) \neq d(\text{C0-C3})$. The simplest displacement that transforms the 'ideal' to the 'real' structure involves moving a carbon atom, designated C0, towards or away from the atom, designated C3, along the inter-pentagon 6:6 bond. This is the basis of the algorithm used in this paper to model the intra-molecular pair correlation function. This movement produces an overall swelling or contraction of the molecule, so a correction must be applied to maintain a constant molecular volume. Perhaps surprisingly, this displacement only raises the number of unique intra-molecular distances to 23.

The precise displacement algorithm is as follows. Consider the 'ideal' structure with the i th atom at R_i relative to the centre of the truncated icosahedron; $R_{i,n}$ represents the position of the neighbour towards which it is going to move. The coordinates, R'_i , of the displaced atoms are generated from the relation

$$R'_i = f[(1 - \delta)R_i + \delta R_{i,n}] \quad (2)$$

where δ is the distortion imposed ($\delta < 0.5$) and f is the renormalization needed to keep the volume constant. It is straightforward to show that

$$f = [1 - \delta(1 - \delta)\beta^2]^{-1/2} \quad (3)$$

where β is the ratio of C-C bond length to C_{60} 'sphere' radius; β is given by

$$\beta = [8/(29 + 9\sqrt{5})]^{1/2} = 0.4035. \quad (4)$$

In practice the value of δ is of order 0.01; the factor f is close to unity and thus the iterative simulation procedure works well.

If d_0 is the average C-C distance in the ideal structure, then applying the displacement (magnitude δ) outlined above splits the near-neighbour distance into two:

$$d_+ \simeq d_0(1 + 2\delta \cos(60^\circ)) = d_0(1 + \delta) \quad (5)$$

$$d_- \simeq d_0(1 - 2\delta). \quad (6)$$

The longer distance occurs twice as often as the shorter one. The coordinates of the general truncated icosahedron may thus be calculated from the ideal structure

by specifying only two parameters, d_0 and δ . In practice, however, these coordinates represent the centre of mass of the atomic positions, which in the real crystal structure are delocalized by static and thermal disorder. This disorder is complicated. Individual normal modes within the C_{60} molecule result in correlated motion. However, the effect of summing all the possible modes results in an effective decorrelation of their motions when averaged over a large number of 'snapshots'. To a good approximation it may be assumed that each intratomic distance is broadened by convolution of a Gaussian profile of root mean square deviation σ . Thus when calculating the broadening which is to be applied to the inter-molecular distances the individual root mean square deviations are assumed to add in quadrature and in proportion to the separation from the atom at the origin. The relevant broadening increases as the square root of the atomic separation, d :

$$\sigma(d) = \sigma_1 + \sigma_2\sqrt{d}. \quad (7)$$

Four parameters, d_0 , δ , σ_1 and σ_2 , are thus sufficient to construct both the structure factor and pair correlation function for the intra-molecular behaviour of the truncated icosahedral C_{60} molecule.

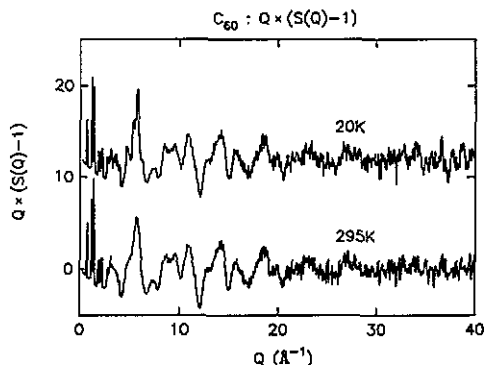


Figure 1. SANDALS diffraction data, $QH(Q)$, for C_{60} at 20 K (top) and 295 K (bottom). The data are the summed results from 360 detectors situated at angles in the range 11° to 21° using neutron energies up to 35 eV.

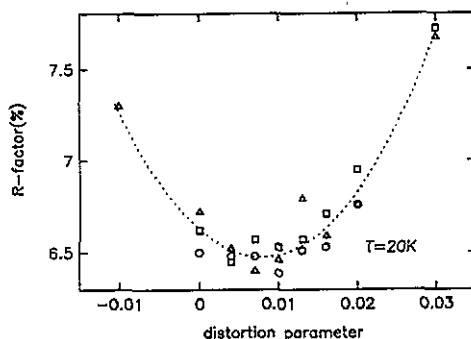


Figure 2. Variation of the R -factor of a model fit to the 20 K data of figure 1 as a function of distortion, δ , from the ideal truncated icosahedral structure. The circles represent simulations in which all parameters, d_0 , σ_1 and σ_2 (plus the inter-molecular correlation function) were refined, while the squares and triangles show simulations in which only the inter-molecular structure was refined. In terms of δ , the short bond is $d_+ \simeq d_0(1 + \delta)$ and $d_0(1 - 2\delta)$.

5. Results and discussion

In the initial simulations all four parameters, d_0 , δ , σ_1 and σ_2 were adjusted. Table 1 shows the results for the 20 K data as a function of different values of δ . The R -factor, R_f , is defined as

$$R_f^2 = \frac{\sum_Q w(Q)(D(Q) - M(Q))^2}{\sum_Q w(Q)D(Q)^2} \quad (8)$$

where $D(Q)$ represents the data as a function of Q , $M(Q)$ is the sum of intra-molecular and inter-molecular structure factors, and $w(Q)$ is a weight function normally related to the statistical errors. It can be seen that the R -factor is in fact rather insensitive to variations in the degree of distortion. It does, however, have a broad minimum centred around 0.0090. Although the parameters σ_1 and σ_2 can vary considerably, their high negative correlation means that the width of the first peak in $g_{\text{intra}}(r)$ is essentially constant for all values of the distortion and in good agreement with an earlier electron diffraction study (Hedberg *et al* 1991). The average atomic separation d_0 is also insensitive to variations in the other parameters. Consequently, in the final analyses, the values of d_0 , σ_1 and σ_2 were fixed at their average values (see table 2). Thus the only variable component of the radial distribution function for different δ was the *inter*-molecular structure. The results for the R -factor are plotted in figures 2 and 3 for 20 K and 295 K respectively. The solid lines in these figures represent least-squares fits and give R -factor minima at $\delta = 0.0079$ (20 K) and 0.0090 (295 K). The corresponding average values of d_+ and d_- are shown in table 2. These values are consistent with what has been reported previously (Hedberg *et al* 1991, Li *et al* 1991) but may be more reliable since they have been obtained from a simultaneous refinement of the entire diffraction pattern. The intra-molecular pair correlation functions for both the 20 K and 295 K data are shown in figure 4. The agreement with *ab initio* calculations is very good (Parinello 1992). There is no detectable difference between these two temperatures indicating that the molecule itself is relatively rigid.

Table 1. The R -factor for a model fit to diffraction data at 20 K as a function of the imposed distortion to the ideal truncated icosahedral structure, for the case when all parameters, d_0 , σ_1 and σ_2 and the inter-molecular structure are refined. Standard deviations are shown in parentheses.

Distortion (δ)	R -factor (%)	d_0 (\AA)	σ_1 (\AA)	σ_2 (\AA)	σ (\AA)
0.000	6.50	1.428(1)	0.045(3)	0.015(3)	0.063(5)
0.004	6.48	1.428(1)	0.046(15)	0.015(3)	0.064(9)
0.007	6.48	1.428(1)	0.046(5)	0.016(3)	0.065(9)
0.010	6.39	1.428(2)	0.038(3)	0.021(2)	0.063(5)
0.013	6.51	1.429(1)	0.041(5)	0.019(3)	0.064(9)
0.016	6.53	1.429(1)	0.032(8)	0.025(5)	0.062(14)
0.020	6.76	1.428(1)	0.031(9)	0.027(6)	0.063(16)

Perhaps the principal benefit of modelling the intra-molecular pair correlation function is that a clear picture of the inter-molecular function may be obtained at distances substantially shorter than the molecular diameter. The only constraint that was applied to the inter-molecular function was that it was forced to be zero for $r < 3 \text{ \AA}$. The results are shown in figure 5 for the two temperatures. The form of the inter-molecular radial distribution functions depended only very weakly on the precise intra-molecular coordinates. However, the change with temperature can be seen very clearly. This is associated with the transformation from ordered to disordered molecular orientations. The ordering at low temperatures is obvious from consideration of $g(r)$ between 3 \AA and 7 \AA (figure 6). There is clear indication of bond lengths at $\sim 3.15 \text{ \AA}$. This is substantially less than the C-C interplanar spacing in graphite (3.35 \AA) and agrees well with low-temperature neutron powder diffraction

Table 2. Best-fit parameters and near-neighbour peak positions for C_{60} .

	Temperature	
	20 K	295 K
d_0 (Å)	1.428	1.426
σ_1 (Å)	0.034	0.042
σ_2 (Å)	0.024	0.020
Distortion δ	0.0079	0.0090
Average near-neighbour separation (Å)	1.429	1.427
d_- (Å)	1.406	1.401
d_+ (Å)	1.440	1.440

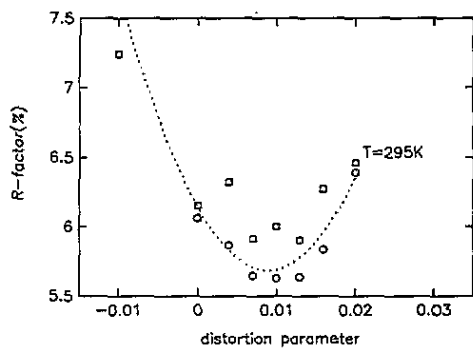


Figure 3. Variation of the R -factor of a model fit to the 295 K data of figure 1 as a function of distortion, δ , from the ideal truncated icosahedral structure.

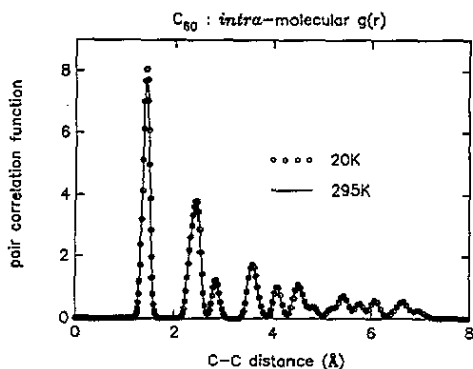


Figure 4. Calculated pair correlation function for the intra-molecular structure. The intrinsic width of the peaks is too large to resolve the splitting in the first peak.

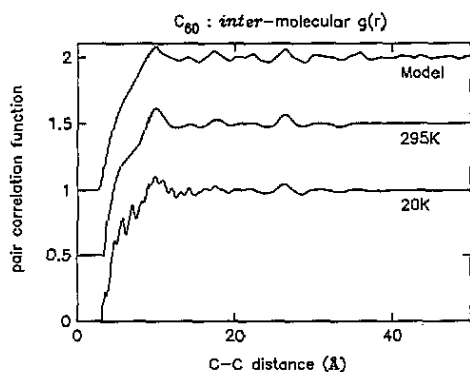


Figure 5. Calculated inter-molecular pair correlation function at two temperatures, 20 K (bottom) and 295 K (middle). The top curve shows the correlation function for an FCC lattice of d -spacing 14.16 Å convoluted with the form factor for randomly oriented truncated icosahedra of diameter 7.08 Å.

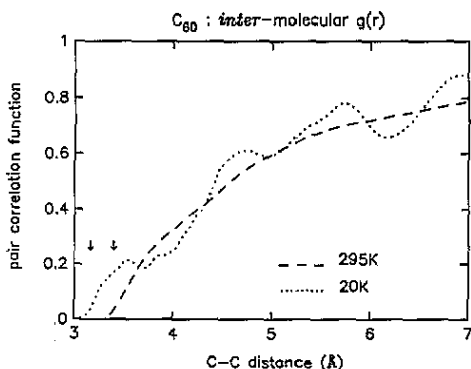


Figure 6. Calculated inter-molecular pair correlation function between 3 Å and 7 Å at 20 K (dotted line) and 295 K (dashed line). The orientational ordering can clearly be seen at 20 K; the underlying lattice is unchanged.

studies (David *et al* 1991). The absence of inter-molecular correlations at 295 K may be demonstrated by modelling the intermolecular pair correlation function for a face-centred-cubic lattice of the same unit-cell size (14.16 Å) and broadening each of the lattice peaks with the shape expected for a spherically averaged truncated icosahedra of diameter 7.08 Å. The result reproduces both the amplitude and position of the simulated peaks from the data at 295 K to high accuracy, although the latter tend to be smoother in appearance and damp out sooner with increasing r -values. This is, however, a consequence of the finite resolution in Q -space for the diffraction data.

6. Conclusions

The structure factor for C₆₀ has been measured at two temperatures using low-angle neutron diffraction. The results confirmed that the near-neighbour distance in the C₆₀ molecule can be split into two distances, 1.400 Å and 1.440 Å. This splitting is essentially unchanged at 20 K. A novel modelling technique was used to refine both the intra- and inter-molecular structure simultaneously. It was shown that because of the intrinsic widths of the molecular peaks the goodness of fit was a rather insensitive measure of the size of the splitting. This may help to explain why the literature, which covers several techniques, has not provided a consistent solution to the precise molecular geometry. Along with the molecular structure we have shown that the room temperature data can be adequately modelled in terms of randomly oriented C₆₀ molecules, while pronounced orientational order is apparent at 20 K (figures 5 and 6).

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