Molecular geometry in fullerene C_{60}:
A direct determination of the bond-length difference $d_{C-C} - d_{C=C}$

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The molecular structure factor of fullerene C_{60} has recently been determined with a high accuracy using neutron scattering over a large momentum-transfer range. The two bond lengths d_{C-C} and $d_{C=C}$ have been measured with a precision of 10^{-3} Å. As the temperature is lowered from 295 K down to 4 K, the single bond is elongated and the double bond shortened, but the radius of the sphere remains almost unchanged. Unfortunately, the covariance matrix obtained from the fit shows that the two lengths are strongly correlated; this means that any error made on the determination of one bond length is compensated by an opposite error on the other bond length without significantly increasing the χ^2 and, thus, the exactness of the reported temperature effect could be argued against. We present in this paper an alternative way of processing the data which allows us to remove almost completely the coupling, using an appropriate change of variables. The temperature effect is confirmed and resolved with a better accuracy.

INTRODUCTION

We have recently reported a study on the molecular geometry of the fullerene C_{60} from the analysis of the structure factor; the data were obtained from neutron-scattering momentum transfer (up to 20 Å^{-1}) (Ref. 1). In this limit ($Q > 6.5$ Å^{-1}), only the molecular structure factor contributes to the scattering.

The equation of the scattering cross section used in the fitting procedure was

$$\frac{d\sigma}{d\Omega} = A_0(1 + A_1Q^2 + A_2Q^4 + A_3Q^6)$$

$$+ B \sum_{i \neq j(m)} \left[\bar{b}_i\bar{b}_j \frac{\sin(Qr_{ij})}{Qr_{ij}} \right. $$

$$\left. \times \exp\left[\frac{-\langle \delta r_{ij}^2 \rangle Q^2}{2} \right] \right], \quad (1)$$

where the first polynomial accounts for the self-scattering and inelasticity corrections on the self-scattering; no recoil correction was necessary, owing to the high mass of the molecule. The second term accounts for interatomic correlations, the sum being extended on the m atoms of the molecule; b_i, b_j are the coherent scattering lengths, r_{ij} is the distance between atoms i and j, and $\langle \delta r_{ij}^2 \rangle$ the mean-square deviation in the harmonic approximation.

In the fullerene C_{60}, within the truncated icosahedron scheme, there are 1770 pairs of atoms which reduce to 23 distinct interatomic distances; these distances actually depend on two bond lengths only (C—C bonds called p as pentagon and C=C bonds called h as hexagon), all the angles being fixed by this particular geometry.

It was found that the temperature effect was much larger on the two bond lengths h and p than on the radius of the sphere; the shortening of p as temperature is raised from 4 to 150 K is roughly counterbalanced by an elongation of h. Indeed $p - h$ varies from 0.079 (3) Å at 4 K to

0.062 (3) Å at room temperature; in the same range, the radius of the sphere varies at most by a few thousandths of an angstrom. As discussed in Ref. 1, using a simple model, this effect may be interpreted as a variation of the bond number with temperature.[2,3]

However, the reality of the variation of the two bond lengths with temperature could be contested if one examines the covariance matrix returned by the fitting procedure. As indicated in Ref. 1, and seen in Table I which reports a part of the covariance matrix, the values of the two bond lengths h and p are remarkably uncoupled from the other parameters of Eq. (1) but there exists a strong negative coupling between the two lengths (the experimental conditions were $\lambda = 0.585$ Å, $T = 295$ K, and a Q range extending from 6.5 to 20 Å^{-1}). Indeed, with such a strong and negative coupling, any error made on one bond length would be almost compensated by an opposite error on the other length without increasing significantly the residue and also keeping the radius of the sphere almost constant.

A way to solve the problem is to seek an appropriate

TABLE I. Correlation matrix obtained for the two bond lengths p and h (Ref. 1). One notes that the coupling betwen the two lengths and the other parameters is weak, but the bond lengths are strongly coupled to each other. The matrix is obtained for a run made at 295 K, $\lambda = 0.585$ Å and a Q range extended from 6.5 to 20 Å^{-1}.

	p	h
p	1.000	
h	−0.763	1.000
$\langle \delta p \rangle$	−0.015	−0.062
$\langle \delta h \rangle$	0.094	0.023
B	−0.054	0.047
A_0	0.033	−0.005
A_1	−0.049	−0.039
A_2	−0.066	0.077
A_3	0.082	−0.108

TABLE II. The same correlation matrix as in Table I, but with a new set of variables $p + h$ and $p - h$. The coupling between the two parametesr is almost as strong as in fit 1.

	$p + h$	$p - h$
$p + h$	1.000	
$p - h$	**−0.712**	1.000
$\langle \delta p \rangle$	−0.148	0.023
$\langle \delta h \rangle$	0.087	0.048
B	−0.101	−0.101
A_0	0.181	0.181
A_1	0.132	−0.196
A_2	−0.135	0.201
A_3	0.133	−0.198

change of parameters in order to reduce the coupling with the idea that one of the new parameters be $p - h$; it would thus be possible to obtain directly the difference of bond lengths and its uncertainty from the fit. The other variable was chosen as $p + h$. All interatomic distances entering in the definition of the molecular structure factor were thus written as a function of the new parameters $p + h$ and $p - h$. Unfortunately, the coupling situation remains almost unchanged, that is to say a weak coupling between the lengths and the seven others parameters and a normalized coupling of -0.71 between $p + h$ and $p - h$ (Table II).

The results dramatically improve if the intramolecular distances are expressed as a function of $2p + h$ and $p - h$, $2p + h$ being a sort of natural variable for a truncated icosahedron;[4] indeed, since there are twice as many single bonds as double bonds, the factor $2p + h$ enters in the definition of all intramolecular distances. The full correlation matrix for the spectrum discussed in Table I is reported in Table III. The coupling between $2p + h$ and $p - h$ drops to $+0.09$; for others experiments it can be as low as $+0.030$. The bond lengths and mean square deviations obtained at three temperatures and two wavelengths are reported in Table IV fits a to c'.

Within the uncertainty, the value of $2p + h$ is almost temperature independent; one finds a difference of 0.1% between the measurements made at two wavelengths, certainly due to the wavelength calibration. On the other hand, the decrease of $p - h$ as temperature increases is confirmed and determined with a better accuracy in ab-

sence of coupling; the difference of bond lengths ranges from 0.078 (3) Å at 4 K to 0.059 (3) Å at 150 and 295 K.

An intriguing point is that the absolute value of $2p + h$ is much better defined than the value of $p - h$, 10^{-3} Å against 3×10^{-3} for $p - h$, that is to say, ratios of 0.02% and 3%, respectively. Since this effect is so well reproduced for the three temperatures and two wavelengths, it is tempting to search for a physical explanation of this behavior. For example, a modulation of the bond number as discussed in Ref. 1 could produce a distribution of bond lengths h and p with an almost constant $2p + h$ value; indeed $2p + h$, closely related to the radius of the sphere was shown to be almost independent on the bond number. Polarization from the neighboring molecules could produce such modulation. Since a single value is used in the fit for each bond length, and not a distribution, the visible effect would be to reduce the precision on the determination of $p - h$ and not on $2p + h$. But as it is shown in the next section, we found out that this effect was only due to experimental limitations (Q range and statistics).

SIMULATION

The same computations were performed on simulated diffraction patterns. Realistic simulated diffraction pattern may easily be obtained making use of Eq. (1) and a convolution to a given statistics (statistical errors in the range of the experimental errors were used). The obtained spectra may then be processed as that of a real experiment. The results are reported in Table IV fit d for two wavelengths, 0.58 Å as used for the experiments, and 0.30 Å; the values used in the simulation are reported in brackets.

Surprisingly, the uncertainty obtained on $p - h$ is the same as that of real experiments ($\approx 3 \times 10^{-3}$), and also three times larger than that observed on $2p + h$. It shows that the uncertainty on $p - h$ is due to experimental problems (limited Q range and a given statistics) and not to the physics of the molecule. Indeed the present experimental setup and an error of a half percent allow a precise determination of bond lengths in the range of an angstrom but does not possess the resolving power to separate two objects of similar size with a high precision. As shown from the simulation performed in a more extended Q range, using a wavelength of 0.30 Å, the rela-

TABLE III. The full covariance matrix for the run presented in Table I using another set of variables $2p + h$ and $p - h$. The coupling between the two parameters is very weak and positive.

	$2p + h$	$p - h$	$\langle \delta p \rangle$	$\langle \delta h \rangle$	B	A_0	A_1	A_2	A_3
$2p + h$	1.000								
$p - h$	**0.091**	1.000							
$\langle \delta p \rangle$	−0.178	0.038	1.000						
$\langle \delta h \rangle$	0.201	0.037	−0.793	1.000					
B	0.002	−0.122	0.343	0.028	1.000				
A_0	−0.033	0.035	0.068	0.020	0.347	1.000			
A_1	0.022	−0.063	−0.103	−0.010	−0.302	−0.888	1.000		
A_2	−0.015	0.082	0.126	−0.079	0.266	0.782	−0.971	1.000	
A_3	0.045	−0.075	−0.115	0.055	−0.275	−0.832	0.982	−0.979	1.000

TABLE IV. All runs reported in Ref. 1 have been reprocessed using the new parameters $2p + h$ and $p - h$ (fits a to c'); the wavelength, temperature, and the Q range used in the fit are reported in columns 1–3; the values of $2p + h$, $p - h$ and the mean deviation of h and p are reported with their uncertainty in columns 3–6; the residue of the fit is reported in the last column. The difference of bond length $p - h$ is decreased by 0.015 Å beween 4 and 150 K; within the uncertainty, the values found at 150 and 295 K are the same. Fit d is made on a simulated experiment using a statistical error of 0.5%. As for real experiments, the uncertainty observed on $p - h$ is three times larger than that of $2p + h$ with $\lambda = 0.5684$ Å.

$N°$	λ (Å)	T (K)	Q range (Å^{-1})	$2p + h$ (Å)	$p - h$ (Å)	$\langle \delta h \rangle$ (Å)	$\langle \delta p \rangle$ (Å)	Residue %
a	0.5684 (6)	4	6.5–20	4.2982 (14)	0.0772 (36)	0.059 (3)	0.063 (3)	0.31
a'	0.7058 (13)	4	6.5–16	4.3059 (10)	0.0736 (40)	0.053 (5)	0.062 (4)	0.33
b	0.7058 (13)	150	6.5–16	4.3060 (6)	0.0585 (24)	0.055 (5)	0.062 (4)	0.50
c	0.5684 (6)	295	6.5–20	4.2962 (10)	0.0592 (31)	0.059 (4)	0.064 (3)	0.65
c'	0.7058 (13)	295	6.5–16	4.3046 (5)	0.0608 (22)	0.057 (5)	0.067 (5)	0.49
d	0.5684		6.5–20	4.2972 (11)	0.0650 (34)	0.063 (3)	0.067 (3)	0.49
	0.29		6.5–33	4.2975 (9)	0.0624 (19)	0.064 (2)	0.067 (2)	
				[4.2979]	[0.0626]	[0.063]	[0.068]	

tive precision obtained on $p - h$ improves. Finally, from all calculations performed on simulated spectra, it was found that the difference between the parameters used as input and calculated was always in good agreement with the calculated uncertainty.

CONCLUSION

If all the interatomic distances of the C_{60} molecule entering in the equation of the molecular structure factor are written as a function $2p + h$ and $p - h$ instead of p (C—C bond length) or h (C=C bond length), the coupling observed in the correlation matrix between these parameters almost completely vanishes. Furthermore, the precision obtained on $p - h$ is not as good as that on $2p + h$; simulations showed that this effect was not due to inhomogeneities in bond lengths but arose from experimental limitations (Q range and statistics). Nevertheless the precision obtained on $p - h$ is sufficient to ascertain and state more exactly the variation of bond lengths with temperature.

Even if the temperature effect in the fullerene C_{60} remains small, the change of bond lengths between 0 and 150 K is more than ten times larger than that generally found in molecules. For example, the variation of the C—O bond between 0 K and room temperature is 3×10^{-4} Å in CO_2; also 3×10^{-4} Å for the N—O bond length in N_2O and 6×10^{-4} Å for the S—O bond in SO_2. A clear explanation of this effect has still to be found. But qualitatively, it is unlikely for us that thermal excitations of internal modes (and anharmonicity) could produce such an effect. On the other hand, polarization of the partial double bond may significantly change bond lengths; for example, the C—C bond length near the NO_2 group in nitrobenzene is 1.411 Å to be compared to 1.393 Å for the C—C bond opposite to the NO_2 group. In the refinement of the structure of powder C_{60} at 5 K, David[5] found that the C—C bond length in a pentagon facing a hexagon of another C_{60} molecule was somewhat larger than the bond in a pentagon not facing a hexagon.

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