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Structure and lattice dynamics of the ordered phase of solid C_{70}

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Harmonic lattice dynamics calculations have been performed on the low temperature structure of solid C_{70}. The theoretically obtained lattice structure agrees with the experimentally determined low temperature structure and the symmetry is found to be $P2_1/m$. The orientationally ordered equilibrium is obtained by using van der Waals interactions only, i.e. without including Coulomb interactions. The calculations yield additional information on the orientational ordering. The calculated frequencies of the 12 Raman active lattice modes agree quantitatively with the recently observed Raman spectrum. The frequencies of the nine complementary IR active lattice modes are predicted.

1. Introduction

Since the discovery of a method to produce fullerenes in large amounts [1] many studies have been performed on these exciting all-carbon molecules. First experimental results on the structure of high purity solid C_{70} were presented by Vaughan et al. [2] over a year ago. Recently, experimental data on the crystal structure and dynamics of C_{70} single crystals have become available [3,4]. The C_{70} molecule can be described as two half C_{60} molecules joined together by a belt of hexagons [5], as experimentally confirmed by Johnson et al. [6] using 2D-NMR. At high temperatures, above 350 K, the elongated-soccerball shaped C_{70} molecules can rotate quasi freely in the crystal lattice. At these temperatures there is a coexistence of two crystal structures, face centered cubic (fcc) and hexagonally close packed (hcp), of which the former one seems to be favoured at still higher temperatures [2]. Crystals grown by sublimation at 870 K have predominantly the fcc growth habit, although a minor fraction of the crystals grown has the hcp morphology. X-ray diffraction [3] shows that the hcp-grown crystals also exhibit microscopically an ideal hcp structure at high temperatures with rotations around both the long and short molecular axes. Upon cooling these crystals to room temperature the rotations around the short axes freeze out and the long axes of the molecules align along the hexagonal *c* axis, resulting in a deformed hcp structure. Somewhat below room temperature the orientational disorder around the long axis freezes out as well. For this phase an ordered superstructure with four molecules per unit cell is observed. It should be noted that no well defined low temperature crystal structures are obtained when fcc-grown crystals are cooled down.

In this Letter, harmonic lattice dynamics calculations on the low temperature monoclinic structure of solid C_{70} are presented. For the calculations we used rigid C_{70} molecules with only van der Waals interaction between them. The structure resulting from a lattice energy minimization is compared to the experimentally determined structure and insight is gained in the orientational ordering of the molecules. The frequencies of the lattice modes are calculated for a variety of interaction potentials.

2. Lattice dynamics calculations

To perform lattice dynamics calculations on the low temperature monoclinic phase of solid C_{70} we applied a standard harmonic lattice dynamics program for molecular crystals, details of which can be found elsewhere [7]. Rigid C_{70} molecules are used, with the atomic positions within each molecule deduced from the five, experimentally determined, nonequivalent atomic positions [8] by applying the symmetry operations of the D_{5h} point group. The calculations are performed for zero temperature where an orientational ordering exists, i.e. the molecules do not rotate but have only small amplitude librations around a well-defined equilibrium structure. The interaction between the molecules is modeled as the sum over atom–atom interactions. To describe the atom–atom interaction several potentials known from literature, both of the Lennard-Jones and of the exp-6 type, are used [1]. It should be explicitly noted that no Coulomb interaction terms have been included, as will be discussed later. The lattice sum is performed over all molecules within a 25 Å range. The lattice energy is minimized with respect to the lattice parameters and with respect to the positional coordinates and the Euler angles of the four molecules in the unit cell. The experimental values are used as the initial values of the 30 minimization parameters. No symmetry restrictions have been imposed on any of these parameters. For the energetically most favourable lattice structure thus obtained the frequencies and eigenvectors of the librational and translational inter-molecular modes are computed. The results calculated for wavevector $\boldsymbol{k}=\boldsymbol{0}$ can be directly compared with experimental Raman data. The transformation properties of the eigenvectors under the symmetry operations of the $P2_1/m$ space group enable us to make an unambiguous symmetry assignment of the modes.

The experimentally observed structure that is used as starting input for the structure optimization is a monoclinic structure with the unique b_m axis along the former hexagonal c axis and an angle β close to, but not necessarily identical to, 120°. The a_m axis is identical to the hexagonal a axis. It is observed experimentally that the monoclinic unit cell is doubled along the c_m direction, which corresponds to one of the former a axes. This doubling of the unit cell is ascribed to an orientational ordering in the former hexagonal plane. It is assumed that in the low temperature structure all C_{70} molecules are aligned with their long axes parallel to the b_m axis. Given this assumption, which is shown to be valid in the calculations, the orientation of the molecules can be described by the angle ϕ by which the molecules are rotated around their long axis. At $\phi=0°$ the corner points of the top (and bottom) pentagons of the C_{70} molecules are directed along the minus a_m axis. From the experimental data a model describing the orientational ordering was proposed [3] in which the molecules in a row along the a_m axis are oriented identically and molecules in two adjacent rows differ by 180° [mod.72°] in orientation. It was argued that this arrangement of molecules would yield the deepest lattice energy minimum.

3. Results and discussion

The crystal structure obtained via minimization of the lattice energy is in good agreement with the experimentally determined structure. In table 1 the results obtained for various potentials are listed, together with the experimental results. The values for the lattice parameters a, b and c agree to within two percent with the experimentally determined values. The angles α and γ are always found to be 90°. The angle β is found to be close to 120°, as can be seen in table 1. These results are in agreement with similar calculations by Guo et al. [11]. The positions of the molecules within the unit cell deviate only slightly ($\leqslant 1\%$) from the ideal lattice positions. The orientations of the long axes of the molecules are found to be parallel to the b_m axis, so the calculations justify the assumption mentioned earlier. The energetically most favourable lattice structure is a monoclinic structure, with a doubling of the unit cell along the c_m axis due to the orientational ordering, which involves a rotation of the molecules around their long axis. It is important to note that the calculated lattice structure obeys the experimentally observed monoclinic symmetry; the angles ϕ_i of molecules i ($i=1, ..., 4$) are related via ϕ_3 (ϕ_4) $=180°$ [mod.72°] $+\phi_2$ (ϕ_1). The $2_1/m$ screw axis is parallel to the b_m axis and intersects the a_m–c_m plane at position (x, z) with $x=0.1663$ and $y=0.3390$, still reflecting the apparent hexagonal symmetry of the high temperature phase. The spacegroup is therefore $P2_1/m$. The molecules are located at positions with site symmetry m. The mirror planes perpendicular to the screw axis

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[1] The exp-6 potentials are taken from ref. [9], the LJ(1) potential is taken from ref. [10], and the LJ(2) potential is taken from ref. [3].

Table 1
Results of the calculations for various potentials. The Lennard-Jones potentials (LJ) are given by $V=Ar^{-12}-Br^{-6}$, with A in kcal/mol Å^{12} and B in kcal/mol Å^{6}, the exp-6 potentials (Exp-6) are given by $V=\mathcal{A}\exp(-\mathcal{B}r)-\mathcal{C}r^{-6}$, with $\mathcal{A}$ in kcal/mol, $\mathcal{B}$ in Å^{-1} and $\mathcal{C}$ in kcal/mol Å^{6}. Shown are the results for the lattice parameters a, b, c and β (α and γ were always found to be 90°), the orientational ordering angle ϕ_0, as discussed in the text and the lattice energy E_{lat} in kcal/mol

	Exp.	LJ(1)	LJ(2)		Exp-6(1)	Exp-6(2)	Exp-6(3)
A	–	531070	581470	$\mathcal{A}$	79520	83630	74460
B	–	343.9	428.1	$\mathcal{B}$	3.60	3.60	3.60
				$\mathcal{C}$	606	568	506
a	9.98	9.90	9.83	a	9.87	9.93	9.93
b	19.96	20.04	19.88	b	19.93	20.05	20.05
c	18.51	18.34	18.26	c	18.33	18.43	18.43
β	≈ 120	119.65	119.64	β	119.67	119.68	119.68
ϕ_0	–	6.57	6.62	ϕ_0	6.25	6.24	6.24
E_{lat}	–	−41	−55	E_{lat}	−77	−68	−61

cut through the middle of the C_{70} molecules at (0, 0, 0) and (0.322, 0.178, 0.500).

As seen from table 1 the calculated lattice energies for the various potentials differ considerably. The aim of the calculations was primarily to understand the C_{70} crystal structure and the inter-molecular mode spectrum. These quantities are mainly sensitive to the shape of the interaction potential around the equilibrium position and not that much to the absolute value of the binding energy. No experimental data on the absolute value of the lattice energy for low temperature monoclinic C_{70} are available. Comparing the lattice energy with the experimentally determined high temperature heat of sublimation of 45 kcal/mol [12] shows that the LJ(1) potential gives the most realistic lattice energy value.

From the calculations some additional conclusions on the orientational ordering can be drawn. The ordering found by the calculation, shown schematically in fig. 1, differs somewhat from the simple model proposed by Verheijen et al. [3] mentioned above. Considering only the $P2_1/m$ symmetry two independent angles, ϕ_1 and ϕ_2, are needed to unambiguously describe the structure. In the model of Verheijen et al. it is assumed that these angles are $\phi_1=0°\,[\mathrm{mod.}72°]$ and $\phi_2=180°\,[\mathrm{mod.}72°]$. From the calculations it follows, however, that the difference $\phi_1-\phi_2$ is not equal to $180°\,[\mathrm{mod.}72°]$. Instead, it is found that the (in principle) independent angles ϕ_1 and ϕ_2 are related via $\phi_2=180°\,[\mathrm{mod.}72°]-\phi_1$. Therefore the structure can be described by a single angle ϕ_0, as indicated in fig. 1. This angle ϕ_0, as obtained for various potentials, is also given in table 1.

To gain more insight in the nature of the orientational ordering fig. 1 shows a view from the center of molecule 1, in the origin of the unit cell, towards molecule 2. It can be seen that the relative orientation of the molecules is such that the C atoms tend to face the hexagons of the neighbouring molecule. To correctly describe the orientational ordering in solid C_{60} it is essential that a Coulomb interaction is included in addition to the C–C van der Waals interaction [13]. In a C_{60} molecule 60 "single" and 30 "double" bonds are present, which can be modeled by extra electron charge density at the center of the double bonds compensated by electron charge deficiency at the single bond centers. Although similar, but considerably more complex, models have been proposed for C_{70} [14] the present calculations indicate that including the van der Waals interactions alone is sufficient to correctly describe the orientational ordering in solid C_{70}.

After the minimization the frequencies and eigenvectors of the lattice modes are calculated. The librational (ℓ) and translational (t) inter-molecular modes in $P2_1/m$ C_{70} are classified as $\Gamma^{\ell}=2A_g^{\ell}+4B_g^{\ell}+2B_u^{\ell}+4A_u^{\ell}$ and $\Gamma^{t}=4A_g^{t}+2B_u^{t}+2B_g^{t}+A_u^{t}$. Of these 21 modes only the 12 gerade modes are Raman active [4], whereas the IR spectrum will originate from the 9 ungerade modes. The calculated frequencies and the symmetry assignment for these modes are given in table 2 for the various potentials used.

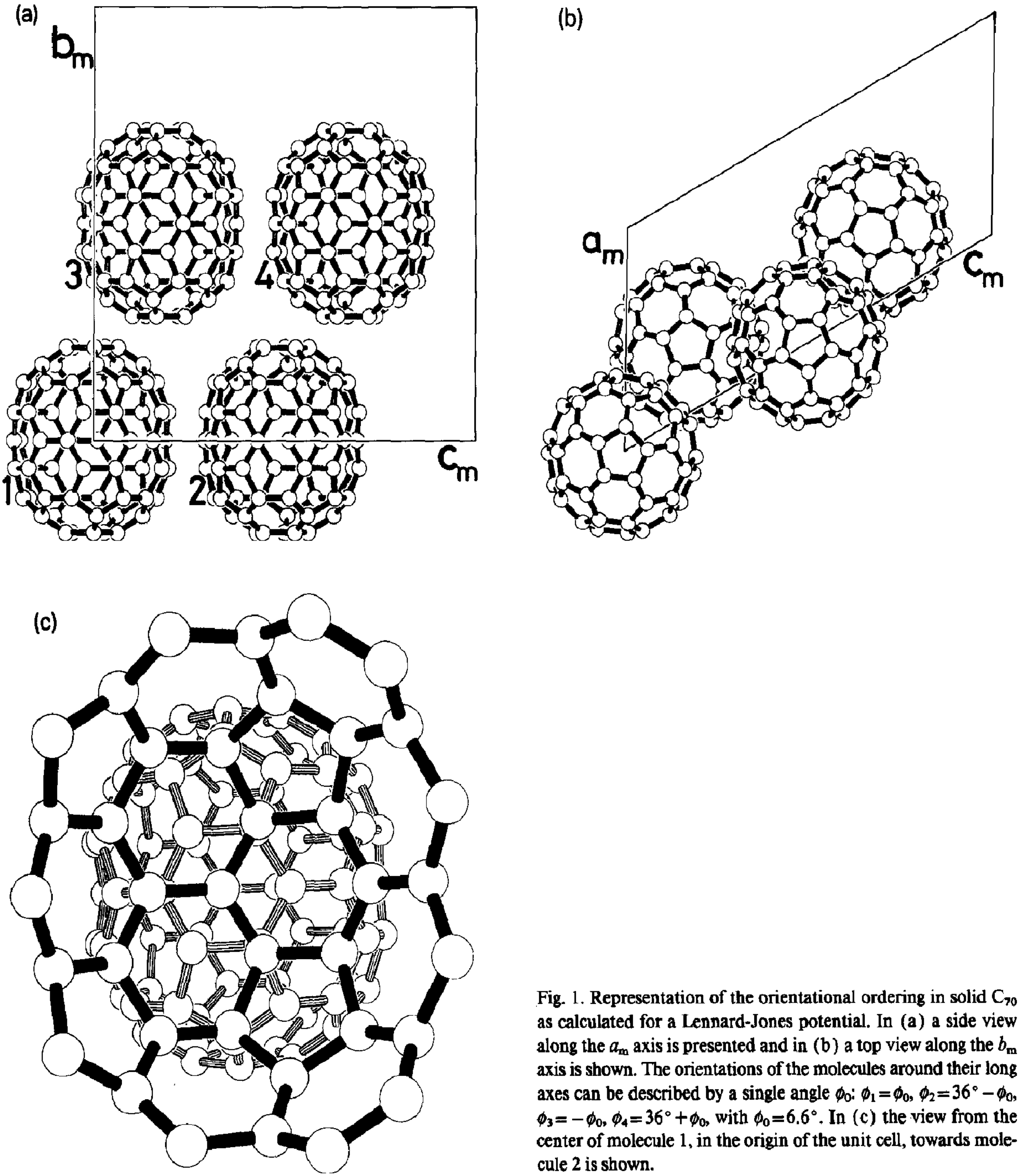

Fig. 1. Representation of the orientational ordering in solid C_{70} as calculated for a Lennard-Jones potential. In (a) a side view along the a_m axis is presented and in (b) a top view along the b_m axis is shown. The orientations of the molecules around their long axes can be described by a single angle ϕ_0: $\phi_1=\phi_0$, $\phi_2=36°-\phi_0$, $\phi_3=-\phi_0$, $\phi_4=36°+\phi_0$, with $\phi_0=6.6°$. In (c) the view from the center of molecule 1, in the origin of the unit cell, towards molecule 2 is shown.

It is observed that the librational modes span the 15–25 cm^{-1} range and that the translational modes are separated from these, spanning the 25–60 cm^{-1} range. In the first column of table 2 the experimentally determined frequencies are given. Although an assignment of these modes in the low frequency part (the "crowded" part) of the spectrum is not unambiguous, the overall agreement between the theoretical predictions and the experimental observations is good. Again the LJ (1) potential gives the best

Table 2

Calculated frequencies in cm^{-1} and symmetry assignment for the librational (ℓ) and translational (t) lattice modes of solid C_{70} for various potentials. The experimentally determined frequencies are also given

Exp.	LJ(1)	LJ(2)	Exp-6(1)	Exp-6(2)	Exp-6(3)	Sym.
12	15.14	18.01	19.78	18.35	17.32	A_g^ℓ
	15.19	17.81	20.52	19.18	18.10	A_u^ℓ
12	15.50	18.22	20.49	19.18	18.11	B_g^ℓ
	16.18	19.07	21.60	20.01	18.89	B_u^ℓ
15	16.37	19.25	22.71	21.12	19.93	A_g^ℓ
	16.74	19.97	22.13	20.56	19.41	B_u^ℓ
	16.76	19.76	22.42	20.89	19.72	A_u^ℓ
15	16.95	19.98	22.96	21.38	20.18	B_g^ℓ
	18.50	21.98	23.98	22.29	21.04	A_u^ℓ
	18.60	22.06	24.43	22.71	21.44	A_u^ℓ
19	19.79	23.55	26.01	24.12	22.77	B_g^ℓ
21	21.04	25.05	27.47	25.47	24.05	B_g^ℓ
27	24.00	28.39	31.26	29.48	27.83	A_g^t
30	25.86	30.52	34.03	31.78	30.00	A_g^t
32,33	30.81	36.67	39.69	36.93	34.86	A_g^t
	33.29	39.16	44.08	41.25	38.94	B_u^t
36	33.35	39.59	43.55	40.58	38.31	B_g^t
	39.42	46.48	51.96	48.58	45.86	A_u^t
51	50.20	59.34	65.96	61.60	58.15	B_g^t
	51.30	60.62	67.08	62.64	59.14	B_u^t
53	52.46	61.94	68.84	64.33	60.73	A_g^t

fitting results. This is explicitly demonstrated in fig. 2 where the experimental Raman spectrum and the stick spectrum deduced from these data, as reported by van Loosdrecht et al. [4], are compared to the theoretical Raman spectrum obtained with the LJ(1) potential (see table 1). The predicted IR spectrum

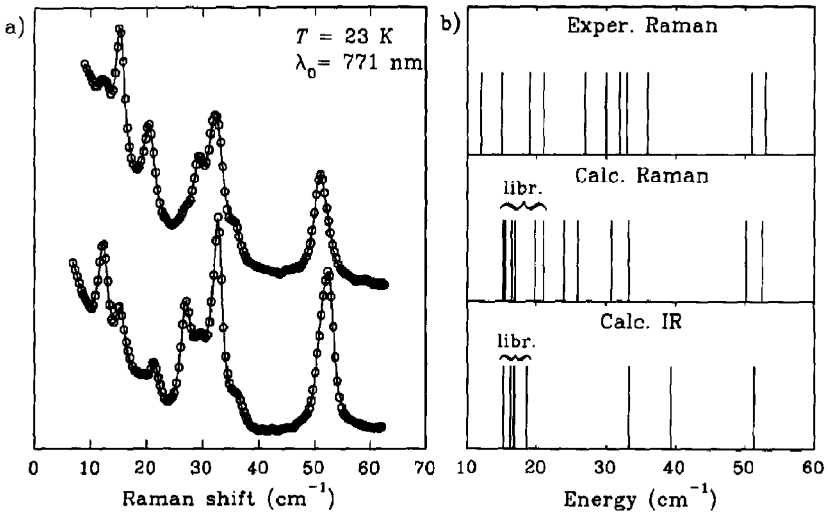

Fig. 2. Experimental Raman spectrum [4] and calculated Raman and IR spectra. The upper experimental spectrum in (a) is recorded in a back scattering geometry from a (101) plane and the lower spectrum is taken from a (100) plane. In (b) the experimental Raman frequencies deduced from the spectra in (a) are shown together with the calculated Raman and IR frequencies.

calculated from the same LJ(1) potential is also shown in fig. 2, and awaits experimental confirmation.

4. Conclusions

Lattice dynamics calculations on the low temperature structure of solid C_{70} have been performed, using simple atom–atom van der Waals potentials to describe the interactions between the rigid C_{70} molecules. The theoretically obtained crystal structure agrees with the experimentally determined low temperature structure; the symmetry is found to be $P2_1/m$. The calculations yield more insight in the orientational ordering, which involves a fixed rotation of the four molecules in the unit cell around their long axes, and which can be described by a single angle ϕ_0: $\phi_1=\phi_0$, $\phi_2=36°-\phi_0$, $\phi_3=-\phi_0$, $\phi_4=36°+\phi_0$, with $\phi_0\approx 6.5°$. The calculated frequencies of the 12 Raman active lattice modes agree quantitatively with the recently observed Raman spectrum. The frequencies of the nine complementary IR active lattice modes are predicted.

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