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Librational modes in solid C_{70}

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We present a theoretical study of librational modes in solid C_{70}. Our results are applicable to Raman-scattering experiments on solid C_{70}.

The rotational dynamics and orientational order of molecules in solid fullerenes have received much attention since it became possible to produce bulk samples of solid fullerenes.[1–3] Most of the studies have been on solid C_{60}, which is the most readily obtainable among the family of solid fullerenes. The next stable solid fullerene, solid C_{70}, has not been subject to as much detailed study, mainly due to difficulties in producing high-quality samples. Recently, experimental progress has been made in producing pure C_{70}.[4–6] In particular, Verheijen *et al.*[5] have succeeded in growing large single crystals of pure C_{70}, and have used x-ray diffraction and TEM to study the different phases of solid C_{70} as the temperature changes. van Loosdrecht *et al.*[6] have performed Raman scattering on single crystalline C_{70} to study the librational and vibrational lattice modes. These experimental advances have stimulated the need for theoretical investigations of librational modes in solid C_{70}.

First, we mention briefly the work on the librational modes in solid C_{60}. The C_{60} molecule is highly symmetric, its 60 atoms are symmetrically equivalent, and its moment of inertia tensor is isotropic. Librational modes in solid C_{60} have been studied theoretically by Li, Lu, and Martin,[7] Yildirim and Harris,[8] and Que and Walker.[9] Many experimental studies have been carried out, a brief summary of which can be found in Ref. 9.

The structure of the C_{70} molecule is more complex than C_{60}. With symmetry group D_{5h}, C_{70} has an elongated ovoid shape, five inequivalent C atoms, and eight different bonds. It is convenient to choose the fivefold-symmetry axis as the z axis. Then the moment of inertia tensor is diagonal, with $I_{xx} = I_{yy} > I_{zz}$. Verheijen *et al.*[5] find that, at low temperatures, C_{70} molecules in solid C_{70} form a deformed hcp lattice. From x-ray diffraction data they suggest that the space group of solid C_{70} is the monoclinic space group $P112_1/m$. The structural model they propose is shown in Fig. 1. All molecules have their fivefold-symmetry axes aligned perpendicular to the hexagonal plane. In the figure each molecule is represented by a pentagon; the tips of the pentagon correspond to hexagon centers at the equator. Molecules A and B are centered in the $z = 0$ hexagonal layer, molecules A' and B' are in the next layer. Verheijen *et al.*[5] suggest that the angle β is either close or equal to 120°. Actually, Fig. 1 corresponds to space group $P112_1/m$ only if $\beta \neq 120°$. If $\beta = 120°$, it corresponds to the orthorhombic space group $Pbcm$, which is still consistent with the x-ray data if one assumes that the x-ray data result from a superposition of three different domains.

Considering the structural model of Verheijen *et al.*, Agterberg and Walker[10] find that β should be exactly 120° to assure that the structure is a minimum energy configuration. Hence they rule out the space group $P112_1/m$ if the equilibrium C_{70} positions and orientations are as suggested by Verheijen *et al.*[5] The space group $P112_1/m$ is still possible if the equilibrium C_{70} positions and orientations are slightly different from the model of Verheijen *et al.* In addition, Agterberg and Walker[10] find that a model in which the positions of A' and B' molecules are exchanged is also a possible structure consistent with the x-ray data. (Again $\beta = 120°$.) The space group for this latter model is $Pbnm$.

We now look into the librational modes of solid C_{70} under the assumption of the above possible space groups. As shown in Ref. 9, the librational motion of molecules can be described by the rotation angles

$$\theta \begin{pmatrix} \mathbf{i} \\ s \\ \alpha \end{pmatrix},$$

where $\mathbf{i}$ labels the unit cell, s labels molecules within a unit cell, and α labels components with respect to the crystal axes. The librational motion is governed by the force constant

$$\Phi \begin{pmatrix} \mathbf{i} & \mathbf{i}' \\ s & s' \\ \alpha & \alpha' \end{pmatrix},$$

which is the second derivative of the total potential en-

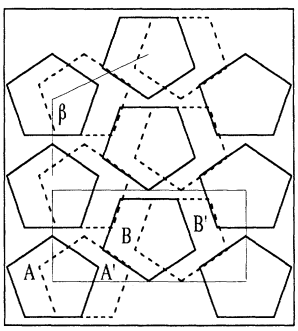

FIG. 1. Structural model of Verheijen *et al.* (Ref. 5) for solid C_{70}. All C_{70} have their fivefold-symmetry axes aligned perpendicular to the plane. Hence each C_{70} is represented by a pentagon in the figure. The solid pentagons are centered in the $z = 0$ layer, and the dashed pentagons in the next layer. For $\beta = 120°$ the unit cell is orthorhombic as shown.

ergy with respect to

$$\theta\begin{pmatrix}\mathbf{i}\\ s\\ \alpha\end{pmatrix} \text{ and } \theta\begin{pmatrix}\mathbf{i}'\\ s'\\ \alpha'\end{pmatrix}.$$

We define the dynamical matrix D as

$$D\begin{pmatrix}s\ s'\\ \alpha\ \alpha'\end{pmatrix};\mathbf{q}\Big) = \sum_{\mathbf{i}'}\Phi\begin{pmatrix}\mathbf{i} & \mathbf{i}'\\ s & s'\\ \alpha & \alpha'\end{pmatrix}e^{i\mathbf{q}\cdot(\mathbf{R}'_{\mathbf{i}}-\mathbf{R}_{\mathbf{i}})}, \quad (1)$$

and the matrix D' as

$$D'\begin{pmatrix}s\ s'\\ \alpha\ \alpha'\end{pmatrix};\mathbf{q}\Big) = D\begin{pmatrix}s\ s'\\ \alpha\ \alpha'\end{pmatrix};\mathbf{q}\Big) - \omega^2 I_{\alpha\alpha'}(s)\delta_{ss'}. \quad (2)$$

Here s,α are row indices, s',α' are column indices. $I_{\alpha\alpha'}(s)$ is the moment of inertia tensor of molecule s. The libron frequencies ω are determined by setting the determinant of the matrix D' to zero. In the following we consider the Brillouin-zone center $\mathbf{q}$=0 because of its correspondence with Raman scattering. At the Brillouin-zone center, the form of the dynamical matrix is determined by the point group. For the above proposed crystal structures of C_{70}, each unit cell has four different molecules A, A', B, and B', which we label by $s = 1,2,3,4$, respectively. For space group $Pbcm$ with point group D_{2h}, the librational vector space is represented by $A_g\oplus B_{1g}\oplus 2B_{2g}\oplus 2B_{3g}\oplus 2A_u\oplus 2B_{1u}\oplus B_{2u}\oplus B_{3u}$ at the Brillouin-zone center. The six gerade modes are Raman active. The dynamical matrix at the Brillouin-zone center has the form

$$D(\Gamma) = \begin{pmatrix}
d_{1x1x} & d_{1x1y} & 0 & d_{1x2x} & d_{1x2y} & 0 & d_{1x3x} & d_{1x3y} & 0 & d_{1x4x} & d_{1x4y} & 0\\
 & d_{1y1y} & 0 & -d_{1x2y} & d_{1y2y} & 0 & -d_{1x3y} & d_{1y3y} & 0 & d_{1x4y} & d_{1y4y} & 0\\
 & & d_{1z1z} & 0 & 0 & d_{1z2z} & 0 & 0 & d_{1z3z} & 0 & 0 & d_{1z4z}\\
 & & & d_{1x1x} & -d_{1x1y} & 0 & d_{1x4x} & -d_{1x4y} & 0 & d_{1x3x} & -d_{1x3y} & 0\\
 & & & & d_{1y1y} & 0 & -d_{1x4y} & d_{1y4y} & 0 & d_{1x3y} & d_{1y3y} & 0\\
 & & & & & d_{1z1z} & 0 & 0 & d_{1z4z} & 0 & 0 & d_{1z3z}\\
 & & & & & & d_{1x1x} & -d_{1x1y} & 0 & d_{1x2x} & -d_{1x2y} & 0\\
 & & & & & & & d_{1y1y} & 0 & d_{1x2y} & d_{1y2y} & 0\\
 & & & & & & & & d_{1z1z} & 0 & 0 & d_{1z2z}\\
 & & & & & & & & & d_{1x1x} & d_{1x1y} & 0\\
 & & & & & & & & & & d_{1y1y} & 0\\
 & & & & & & & & & & & d_{1z1z}
\end{pmatrix},$$

with 16 independent elements. The eigenvectors are

$$\begin{aligned}
&A_g : (0,0,1,0,0,-1,0,0,-1,0,0,1)/2,\\
&B_{1g} : (0,0,1,0,0,1,0,0,1,0,0,1)/2,\\
&B_{2g} : (1,0,0,-1,0,0,-1,0,0,1,0,0)/2,\\
&\quad (0,1,0,0,1,0,0,1,0,0,1,0)/2,\\
&B_{3g} : (1,0,0,1,0,0,1,0,0,1,0,0)/2,\\
&\quad (0,1,0,0,-1,0,0,-1,0,0,1,0)/2,\\
&A_u : (1,0,0,1,0,0,-1,0,0,-1,0,0)/2,\\
&\quad (0,1,0,0,-1,0,0,1,0,0,-1,0)/2,\\
&B_{1u} : (1,0,0,-1,0,0,1,0,0,-1,0,0)/2,\\
&\quad (0,1,0,0,1,0,0,-1,0,0,-1,0)/2,\\
&B_{2u} : (0,0,1,0,0,1,0,0,-1,0,0,-1)/2,\\
&B_{3u} : (0,0,1,0,0,-1,0,0,1,0,0,-1)/2.
\end{aligned}$$

The A_g, B_{1g} modes are librations about the molecular long axes, and the B_{2g}, B_{3g} modes are librations about the molecular short axes. Upon block diagonalization, entries for the Raman active modes in the matrix $D''(\Gamma) = TD'(\Gamma)\tilde{T}$ are

$$\begin{aligned}
&A_g : d_{1z1z} - d_{1z2z} - d_{1z3z} + d_{1z4z} - \omega^2 I_{zz},\\
&B_{1g} : d_{1z1z} + d_{1z2z} + d_{1z3z} + d_{1z4z} - \omega^2 I_{zz},
\end{aligned}$$

$$B_{2g} : \begin{pmatrix} d_{1x1x} - d_{1x2x} - d_{1x3x} + d_{1x4x} & d_{1x1y} + d_{1x2y} + d_{1x3y} + d_{1x4y}\\ & d_{1y1y} + d_{1y2y} + d_{1y3y} + d_{1y4y}\end{pmatrix} - \omega^2 I_{xx}E,$$

$$B_{3g} : \begin{pmatrix} d_{1x1x} + d_{1x2x} + d_{1x3x} + d_{1x4x} & d_{1x1y} - d_{1x2y} - d_{1x3y} + d_{1x4y}\\ & d_{1y1y} - d_{1y2y} - d_{1y3y} + d_{1y4y}\end{pmatrix} - \omega^2 I_{xx}E.$$

In addition, the vibrational space is reduced to $2A_g \oplus 2B_{1g} \oplus B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u} \oplus 2B_{2u} \oplus 2B_{3u}$. The six gerade external phonon modes are also Raman active. It is interesting to note that the results for the space group $Pbnm$ are identical to those for $Pbcm$.

For space group $P112_1/m$ with point group C_{2h}, the 12-dimensional librational space can be reduced to $2A_g \oplus 4B_g \oplus 4A_u \oplus 2B_u$ at the Brillouin-zone center. Since only the A_g and B_g modes are Raman active, six nondegenerate libron frequencies are expected at the Brillouin zone center. The dynamical matrix has the form

$$D(\Gamma) = \begin{pmatrix}
d_{1x1x} & d_{1x1y} & 0 & d_{1x2x} & d_{1x2y} & 0 & d_{1x3x} & d_{1x3y} & 0 & d_{1x4x} & d_{1x4y} & 0 \\
 & d_{1y1y} & 0 & d_{1y2x} & d_{1y2y} & 0 & d_{1y3x} & d_{1y3y} & 0 & d_{1x4y} & d_{1y4y} & 0 \\
 & & d_{1z1z} & 0 & 0 & d_{1z2z} & 0 & 0 & d_{1z3z} & 0 & 0 & d_{1z4z} \\
 & & & d_{2x2x} & d_{2x2y} & 0 & d_{2x3x} & d_{2x3y} & 0 & d_{1x3x} & d_{1y3x} & 0 \\
 & & & & d_{2y2y} & 0 & d_{2x3y} & d_{2y3y} & 0 & d_{1x3y} & d_{1y3y} & 0 \\
 & & & & & d_{2z2z} & 0 & 0 & d_{2z3z} & 0 & 0 & d_{1z3z} \\
 & & & & & & d_{2x2x} & d_{2x2y} & 0 & d_{1x2x} & d_{1y2x} & 0 \\
 & & & & & & & d_{2y2y} & 0 & d_{1x2y} & d_{1y2y} & 0 \\
 & & & & & & & & d_{2z2z} & 0 & 0 & d_{1z2z} \\
 & & & & & & & & & d_{1x1x} & d_{1x1y} & 0 \\
 & & & & & & & & & & d_{1y1y} & 0 \\
 & & & & & & & & & & & d_{1z1z}
\end{pmatrix},$$

with 26 independent elements. Eigenvectors of the A_g modes are

$$(0,0,1,0,0,0,0,0,0,0,0,1)/\sqrt{2},$$
$$(0,0,0,0,0,1,0,0,1,0,0,0)/\sqrt{2}.$$

Eigenvectors of the B_g modes are

$$(1,0,0,0,0,0,0,0,0,1,0,0)/\sqrt{2},$$
$$(0,1,0,0,0,0,0,0,0,0,1,0)/\sqrt{2},$$
$$(0,0,0,1,0,0,1,0,0,0,0,0)/\sqrt{2},$$
$$(0,0,0,0,1,0,0,1,0,0,0,0)/\sqrt{2}.$$

Hence the A_g modes are librations about the molecular long axes, and the B_g modes are librations about the molecular short axes. By adding a minus sign to the last nonzero entry in each of the A_g eigenvectors, we get two eigenvectors for the B_u modes. Similarly, four eigenvectors for the A_u modes can be obtained from the B_g eigenvectors. Using the above 12 vectors as row vectors of a matrix T, we can block diagonalize the matrix D' in the fashion $D''(\Gamma) = TD'(\Gamma)\tilde{T} = A_+ \oplus B_+ \oplus B_- \oplus A_-$, where $A_\pm, B_\pm$ are symmetric matrices given by

$$A_\pm = \begin{pmatrix} d_{1z1z} \pm d_{1z4z} & d_{1z2z} \pm d_{1z3z} \\ & d_{2z2z} \pm d_{2z3z} \end{pmatrix} - \omega^2 I_{zz} E,$$

$$B_\pm = \begin{pmatrix} d_{1x1x} \pm d_{1x4x} & d_{1x1y} \pm d_{1x4y} & d_{1x2x} \pm d_{1x3x} & d_{1x2y} \pm d_{1x3y} \\ & d_{1y1y} \pm d_{1y4y} & d_{1y2x} \pm d_{1y3x} & d_{1y2y} \pm d_{1y3y} \\ & & d_{2x2x} \pm d_{2x3x} & d_{2x2y} \pm d_{2x3y} \\ & & & d_{2y2y} \pm d_{2y3y} \end{pmatrix} - \omega^2 I_{xx} E,$$

where E is the identity matrix. The A_+ (B_+) matrix corresponds to A_g (B_g) modes, and B_- (A_-) corresponds to A_u (B_u) modes. In addition, the vibrational space is represented by $4A_g \oplus 2B_g \oplus 2A_u \oplus 4B_u$. The six gerade external phonon modes are also Raman active.

The above symmetry analysis of librons in solid C_{70} is independent of model potentials for intermolecular interactions. To obtain numerical results for libron frequencies, an explicit model potential for intermolecular interactions is necessary. However, neither the Lennard-Jones potential[11] nor the potential proposed by Sprik, Cheng, and Klein[12] produce crystal structures consistent with Ref. 5. Hence a microscopic model potential for interactions between C_{70} is urgently needed. Agterberg and Walker[10] have proposed a phenomenological model potential which is capable of producing structures consistent with Ref. 5. But for the study of librons, the usefulness of this model potential is hindered by the presence of 12 parameters currently unknown.

In conclusion, we have carried out a group theoretical analysis of librons in solid C_{70}, applicable to Raman experiments. For any of the possible space groups mentioned in this paper, six libron modes and six external phonon modes (all nondegenerate) are Raman active at

the Brillouin-zone center. Raman experiments on solid C_{70} have been carried out,[6] but so far it has not been possible to distinguish which modes are phonons and which are librons in the data. Further progress in this field will be initiated by the development of a microscopic model potential which produces a crystal structure consistent with experiments.

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