

THE LATTICE DYNAMICS OF CRYSTALLINE FURANE IN THE
LOW-TEMPERATURE PHASE

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The study of lattice dynamics plays an important role in solid state physics. The knowledge of the phonon spectra of a given crystal is an essential step towards a better understanding of the physical properties of the system considered.

The classical theory of lattice dynamics in harmonic approximation was originally developed for "atomic" solids such as ionic crystals /1/. Molecular crystals, however, exhibit some specific features and, therefore, the lattice dynamics of these systems is somewhat different from that of "atomic" crystals. The number of atoms per unit cell is relatively large and, therefore, further approximations are needed for calculation of the lattice dynamics of such systems.

Molecular crystals are usually considered in the "rigid-body" approximation. In this approximation, each molecule is treated as a rigid body with 6 degrees of freedom (3 translational and 3 rotational ones). The dynamical matrix is reduced to reasonable dimensions (6 x number of molecules per unit cell), suitable for further treatment. The potential energy of the crystal is assumed to be the sum of all pairwise interactions between atoms in different molecules. The interaction of each atom pair is of the form: $V = -A/R^6 + B|\exp -CR|$, where A, B and C depend on the atoms involved in the interaction. These quantities can be taken from other calculations /2/.

The dynamical matrix is obtained from the double differential of the intermolecular potential function with respect to displacements /3/ (rotational and translational). Before performing calculations we must be sure that the structure corresponds to an equilibrium. For this purpose it

is necessary to express the energy of the crystal, U , as a function of the lattice parameters, the orientational angles of the molecule and the position of the molecular centre of gravity in the unit cell. By minimizing the energy function $U(a,b,c\dots)$ relative to these parameters it is possible to find the equilibrium configuration necessary for the calculation of the lattice dynamics.

Furane (C_4H_4O) crystallizes in the tetragonal system, space group $D_4^2/4/$ with four molecules per unit cell $/4/$. After minimizing the lattice energy of furane as a function of four parameters (a,c,θ,X) , we calculated the lattice dynamics by a procedure similar to that given by Pawley $/3/$. Although this procedure makes it possible to calculate the static minima, the values for some of the calculated phonon frequencies are imaginary ($\omega^2 < 0$). This indicates the unstable nature of the crystal within our model. An explanation of these results would be that the potential function used is not suitable for the description of the type of interactions occurring in the furane crystal. A suitable set of A, B and C constants in the atom-atom potential function is therefore needed, and further calculations along this line are in progress. An investigation of the influence of static multipolar interactions (dipole-dipole and quadrupole-quadrupole) on the lattice dynamics of furane would also be desirable.

References

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