

RIGID-MOLECULE APPROXIMATION IN THE LATTICE DYNAMICS OF
MOLECULAR CRYSTALS

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Vibrational spectra of molecular crystals very often show a close similarity between vibrational frequencies of the free molecule and frequencies of the molecule in the crystal. These spectra also exhibit a considerable difference between intramolecular vibrational frequencies and frequencies of the other kinds of molecular motions in the lattice.

A very successful simplification of the problem of lattice dynamics can be achieved if molecules are considered to be rigid bodies performing translations and rotations about their equilibrium positions.

In our rigid-molecule model, the crystal potential energy ϕ results only from intermolecular interactions. The Taylor expansion of the potential function ϕ about the equilibrium positions is performed only to the second order $\phi = \phi_0 + \phi_1 + \phi_2$. ϕ_0 is the equilibrium potential energy where all molecular shifts are equal to zero. In the case of real crystals, such a state corresponds to stable equilibrium, so that ϕ_0 is the potential-energy minimum. The first derivatives correspond to the forces and torques on the molecules at equilibrium positions and, obviously, must vanish:

$$\left(\frac{\partial \phi}{\partial u_i(l)} \right)_0 = 0.$$

Reversely, those $6Z$ relations (in some other set of coordinates this number is even larger) and the requirement for ϕ_0 to be minimum compose a set of conditions which should be satisfied by any approximate potential function that can be used in vibrational calculations.

The final expression for the equation of motion is

$$\omega^2(\vec{q}) M U(\vec{q}) = B(\vec{q}) U(\vec{q}).$$

(M contains masses and inertial tensors of the Z molecules

in the unit cell). From general stability conditions it follows that the dynamical matrix $B(q)$ has to be hermitian for any real crystal (1). Because of that and due to the positiveness of the matrix M , the eigenvalues $\omega_1^2(q)$ ($i=1,2,\dots,6Z$) are all real quantities and also positive for real crystals (2). The occurrence of the negative eigenvalues in vibrational calculations shows that the above-mentioned conditions are not satisfied.

The constants $(\partial^2\Phi/\partial u_1(l)\partial u_1(l'))_0$ can be found from a suitably chosen potential function $V_{kk'}(r)$ which describes the interaction between the atoms k and k' belonging to the different molecules.

It is shown³⁾ that the effect of the deformable molecules on the lattice modes is more pronounced than the typical measurement errors, even in crystals with a large gap between the high- and low-frequency region. Generally, due to the interactions between inter- and intramolecular motions the frequencies of lattice modes become lowered and the dispersion of the internal modes appears.

References

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