

phys. stat. sol. (b) 54, K37 (1972)

Subject classification: 6 and 20.1; 13.5.1; 22.9

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Optical Mapping of the Phonon Density of States in Molecular Solids¹⁾

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We present here a new method, based on optical spectra of phonon side-bands accompanying excitons that are localized on guest sites differing from the host by isotropic substitution. This method gives a mapping of van-Hove singularities and, coupled with presently available theoretical models, can give a phonon-density-of-states, with 1 cm^{-1} or better resolution, for small polycrystalline samples at a temperature of 2°K or lower.

While phonon side-bands accompanying localized (impurity) electronic transitions have been long known to contain information on the host phonon structure (1), it has also been recognised that complications due to localized or pseudolocalized phonons (2) severely curtail the practical usefulness of such studies. However, it has been recently demonstrated, both theoretically (3) and experimentally (4), that (a) isotopic substitution of complete molecules in organic crystals (i. e. per-deuteration) is not likely to create localized or pseudolocalized phonons and hence, at low concentrations, to have little effect on the host phonon bands while (b) the same isotopic substitution can easily create localized exciton states (5). It has also been shown (5) that a very weak phonon side-band (relative to the intensity of the pure exciton transition) will be dominated by phonon fundamentals (no multi-phonons). It can also be shown (5) that under such circumstances the phonon side-band gives a mapping of the singularities in the density-of-states:

$$I_1^f(\omega)/I_0^f = (6 \sigma N)^{-1} \sum_{s,q} c_{s,q}^f \delta(\omega - \omega_{s,q}) \quad (1)$$

where $I_1^f(\omega)$ is the intensity at frequency ω of the one-phonon side-band accompanying the f -th pure exciton transition of integrated intensity I_0^f , N is the number of primitive unit cells, σ the number of molecules per primitive unit cell, q the

1) Supported by: NSF Grant GP-18718 and NIH Grant NS08116.

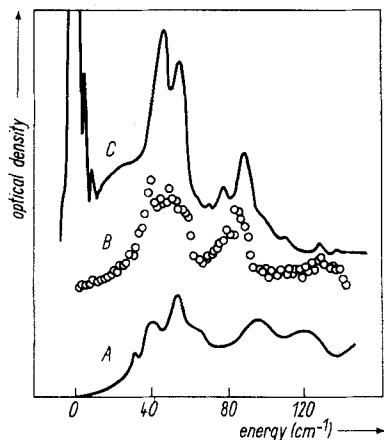


Fig. 1

reduced wave vector and s the phonon branch. Equation (1) would reduce to the phonon density-of-states if $c_{s,q}^f = 1$. In reality, this coefficient is a function of ω , but probably a rather smooth one (5):

$$c_{s,q}^f \sim \omega^{-x}, \quad 1 < x < 3. \quad (2)$$

The spectra were taken with the mixed crystals (0.25% $C_{10}H_8$ in $C_{10}D_8$) at $\approx 2^\circ K$. The details of the experiments are given elsewhere (5). The effective resolution was 1 cm^{-1} . One of our densitometer tracings is shown in Fig. 1.

We note that we have also observed a practically identical spectrum from a sample of 0.14% 2-DC $_{10}H_7$ in $C_{10}D_8$ (except for the 5 cm^{-1} defect emission), as well as similar side-bands accompanying vibronic phosphorescence origins (also fluorescence spectra that support our phonon peak assignments but are complicated by exciton delocalization (5)).

We claim that the phosphorescence side-band (curve C) in Fig. 1 represents a mapping of the $C_{10}D_8$ (host) phonon spectrum.²⁾ For comparison we show a recent theoretical calculation (curve B) by Pawley (6) of the phonon density-of-states of naphthalene ($C_{10}H_8$), based on a rigid molecule, atom-atom repulsion model (as Pawley's $C_{10}D_8$ calculation was shown only in miniature, we did not reproduce it, but it is very similar (7)). We also show, for comparison, a very recent incoherent, inelastic neutron scattering result (8) (curve A) on naphthalene ($C_{10}H_8$), at $120^\circ K$.

We think that the "incoherent" neutron data are heavily biased towards H-atom motions, and an oversimplified attempt to account for this bias (7) does not seem to bridge the gap. It seems to us that the neutron data are plagued by multi-phonon scattering, in addition. We note again that in our optical method the multi-phonon effect can be ruled out. The agreement between our data and Pawley's independent calculation seems to be beyond coincidence and lend added credibility to Pawley's

2) The weak feature at about -5 cm^{-1} (right hand side of the zero-phonon line) is due to defect phosphorescence.

choice of crystal potential.

In conclusion, the above method is very versatile as it can easily be applied to most organic crystals and it leaves room for refinement by using many available exciton bands (vibrational, electronic, vibronic), and a number of isotopic guest-host combinations.

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(Received September 8, 1972)