COMMENT: PHONON SPECTRUM OF MOLECULAR CRYSTALS FROM EXCITON SIDEBANDS

R. KOPELMAN, F.W. OCHS and P.N. PRASAD

Department of Chemistry, The University of Michigan,
Ann Arbor, Michigan 48104, USA

Received 18 March 1974
Revised manuscript received 28 June 1974

Phonon sidebands of excitons in molecular crystals with negligibly small excitation exchange interactions, including isotopic guest systems, are not, in general, expected to be predominantly weighted by translational modes that are predictable from Brillouin zone centre \((q = 0)\) ones. Some phonon sideband data on naphthalene, hexamethylbenzene, etc. are discussed and argued to map the extent of the phonon density-of-states as well as some of the \(q \neq 0\) singularities.

In a previous paper [1] we have suggested that the phonon sidebands of exciton transitions with negligibly small excitation exchange interactions, specifically for the case of guest emission in isotopic mixed molecular crystals, are described by:

\[
I'_f(\omega) = I'_0 G'_{op}(\omega),
\]

(1)

where \(I'_f(\omega)\) is the one-phonon contributed intensity, \(I'_0\) the zero-phonon intensity (which is assumed to be much larger than the integrated one-phonon intensity in order to justify the neglect of multiphonon contributions) and

\[
G'_{op} = (12N)^{-1} \sum_{S,q} C^f_{S,q} \delta(\omega - \omega_{S,q}),
\]

(2)

where \(C^f_{S,q}\) is an exciton-phonon coupling amplitude, dependent on the excitation \(f\) (which causes a change in force field) as well as on the phonon reduced wave vector \(q\) and the branch polarization index \(S\). It was further argued that the coupling amplitude \(C^f_{S,q}\) is not expected to have singularities as a function of energy and that the singularities of the amplitude weighted density-of-states \(G'_{op}\) should represent the singularities of the density-of-states, \(g(\omega)\),

\[
g(\omega) = (12N)^{-1} \sum_{S,q} \delta(\omega - \omega_{S,q}).
\]

(3)

It was further argued experimentally that for a number of vibronic sidebands of isotopic mixed naphthalene crystals the ten or more observed peaks map some of the singularities in the phonon density-of-states function, without necessarily being limited to \(q = 0\) points, in reasonable agreement with theoretical calculations [2], considering their approximate nature, and with neutron inelastic incoherent scattering data [3], considering their limitations due to multiphonon scattering effects, in addition to hydrogen motion weighting as well as temperature and resolution effects.

Recently, our above work was criticized by Reynolds [4]. He concludes that (I) the phonon sidebands on excitons in molecular crystals do not measure at all closely the true density-of-states but (II) a function related to some of the Brillouin zone center translational mode frequencies. We do essentially agree with the first part (I), as we only claimed to map some singularities in the density-of-states, and pointed out that the true density-of-states can only be derived from there by a "bootstrapping" technique,

\[\]
involving improved model calculations (which in
turn also rely on other measurements like Raman,
infrared, neutron scattering, etc.). However, we dis-
agree strongly with the second part (II) of Reynolds' claim [4]. i.e., that the above sidebands measure a
function related to some translational frequencies
which may "often" be predicted from data on the
Brillouin zone center (q = 0) translational modes.

Theoretically, in order to justify his claim (II),
Reynolds argues that the change in the pairwise van
der Waals force upon excitation of one molecule is
proportional to the change in the square of the inter-
molecular electronic overlap between the members
of the pair (he admits that to be crude). Furthermore,
he assumes the transition electron density to be essen-
tially spherically symmetric (for π−π* and apparent-
ly also n−π* transitions). In addition, he assumes the
transition electron density to be essentially spherically symmetric (for π−π* and apparently also n−π* transitions). In addition, he assumes the molecular electron density itself to be spherical (this
for the molecules: naphthalene, paradichlorobenzene
and pyrazine). We find the above arguments difficult
to accept. In addition, they lead to inconsistencies:
(a) A spherically symmetric molecular electron den-
sity, in addition to a spherically symmetric transition
electron density, seems to imply not only a zero
electron—rotational phonon coupling, but also a
zero rotational phonon frequency! This is in strong
contradiction to the observed q = 0 rotational pho-
nons in the Raman spectra of naphthalene [5], para-
dichlorobenzene [6], etc. which spread up to and
above 100 cm−1. (b) A spherically symmetric mole-
cule (and even the real naphthalene, pyrazine or
paradichlorobenzene molecule, even in its crystal-
line site) preserves a center of symmetry (with respect
to inversion) and, therefore, could not have a non-
vanishing coupling between a g−u electron transition
(as in Reynolds' quoted examples) and an ungerade
one-phonon translational mode (q = 0). Furthermore,
by implicitly assuming [4] a separation of rotation
from translation for all q, and by explicitly claiming
a strong branch dependence of intensities, this un-
gerade symmetry should apply for all q. This would
result in a zero intensity for all the one-phonon trans-
slational sidebands, and especially for q ≈ 0. This
contradicts again the claim that the latter would ac-
count for the most intense sideband peaks.

On the experimental side, our quoted naphthalene
data [1] have to be pushed very hard, so as to unique-
ly agree with the published far-infrared frequencies
[7] as claimed by Reynolds [4]. These data [1]
do agree as well, if not much better, with the Raman
frequencies, implying the importance of coupling
with rotational modes (which still we never claimed),
and also agree about as well with the neutron scatter-
ing data and the theoretical density-of-states peaks
[1]. Faced with 10 cm−1 uncertainties in a crowded
region we did not attempt [1] an assignment. We
doubt as well Reynolds' assignment [4]. Most im-
portantly, we refuse to accept an interpretation which
implies that the naphthalene structure with more than
ten distinct peaks derives the bulk of its intensity
from the only three possible nonzero q = 0 transla-
tional frequencies (we still believe that some of these
peaks may be related to essentially translational
modes). Furthermore, we do have additional data
[9] to show that our reported isotopic (dilute) mixed
crystal naphthalene phonon sidebands are very mild-
ly polarized. This makes less certain Reynolds expecta-
tion of "an extremely strong dependence of C_2S_g
on branch S'" (see eqs. (8) and (14) of ref. [1]). How-
ever, we do not exclude, in general, the possibility of
the existence of such sidebands in molecular crystals
(but they would not necessarily be our favorite choices
for a phonon singularity mapping investigation).

For pyrazine, both "phonon sidebands" quoted by Reynolds [4] (57 and 82 cm−1 have been demon-
strated to be artifacts, related to triplet defect origins
(with different life times and very different tempera-
ture characteristics), by Azumi and Nakano [10].
The remaining broad, single humped distribution cer-
tainly fits much better the density-of-states and the
incoherent neutron scattering, as actually quoted by
Reynolds [4] rather than the sharp peaks he expects to
match the IR peaks. Moreover, the Raman (by Ito
[11]) frequencies quoted there [10] are (at 4 K) 56
and 86 cm−1, that is, too close for comfort to the
quoted [4] infrared frequencies (77 K) of 55 and 80
cm−1. For paradichlorobenzene, it is not obvious
whether the weak and diffuse phonon sidebands and
the far-infrared data which Reynolds compares [4]
are taken for the same crystal phase [3, 12]. In addi-
tion, the 90 K Raman data [13] (monoclinic, most
likely α phase: 32, 57, 64 cm−1) seem to fit about
as well as the far-infrared data...

Moreover, they imply that the 54 cm−1 peak is an artifact.
It was indeed shown as such by Bree and Kydd [8].

November 1974
Finally, we have investigated with some care the phonon sidebands of hexamethylbenzene [14]. This molecule is certainly not less spherical than naphthalene, paradichlorobenzene or pyrazine. As the investigated crystal phase has only one molecule per primitive unit cell one would expect, following literally Reynolds’ approach [4], to have exciton–phonon sidebands exhibiting only acoustical phonons (the only translational \( q \approx 0 \) modes). In other words, the absence of a far-infrared (external phonon) spectrum [15] should correlate with the absence of an external-phonon exciton sideband. In reality [14], this sideband extends over more than 100 cm\(^{-1}\), as do the rotational Raman bands [15] (there still are translational \( q \not= 0 \) features). We therefore conclude that these data contradict Reynolds’ approach. Also, results just obtained for benzene again do not fulfill his expectations. The authors of five recent papers on the benzene phonon sidebands [16–20] all compare it to the phonon density-of-states [21] and not to the well known infrared modes [22]. This, again, does not mean that for some other systems his claim \( \Pi \) may not hold true. We only submit that it is not justified, in general, and has not been borne out so far by the few systems which have been studied thoroughly.

References

    S.D. Colson and G.L. Wheeler, private communication.