

EXTERNAL, INTERNAL AND SEMI-INTERNAL VIBRATIONS IN MOLECULAR SOLIDS: SPECTROSCOPIC CRITERIA FOR IDENTIFICATION*

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A new method to identify the nature of vibrations in molecular crystals as external or internal is proposed. The criterion is that in isotopic mixed crystals of protonated and corresponding perdeuterated compounds, the external motions (phonons) are in the amalgamation limit, while the internal modes, and the "semi-internal" methyl torsions, are usually in the separated band limit. This criterion is supported by experimental isotopic mixed crystal studies of many molecular crystals. Previous criteria, like temperature and isotope shifts, are shown to be less reliable. Anthracene and biphenyl Raman spectra, as well as literature data, are used as illustrations.

1. Introduction

In molecular crystals, the vibrations are usually classified [1] as: (i) *internal vibrations* which are essentially intramolecular motions and subject to solid state interactions only within the limits of perturbation, (ii) *external vibrations* which correspond to the motion of the molecule as a whole and are entirely solid state effects because in free molecular states these motions have zero vibrational frequency. Also in some molecular crystals, motions like torsions exist which cannot strictly be classified as internal or external vibrations [2]. Though they are intramolecular motions and have barriers which are intramolecular in origin, they very often have a large contribution to the barrier from the solid state interaction. We thus classify them in category (iii) *semi-internal vibrations*.

To identify internal vibrations, the criterion often used is that these vibrations are little affected by solid state interactions and have roughly the same frequency as they have in the gas or even in solution. This correlation is very often used to identify the intramolecular mode. This, however, is not always useful. There are systems like biphenyl which do not have the same geometry in the gas phase [3] (where the two benzene

rings are not planar) and in the room temperature solid phase (where the two benzene rings seem to be planar [4]). The correlation may not be of much help in such cases. Another criterion [5] used is that intramolecular modes in the solid phase are temperature independent. This has been often used to distinguish a low lying intramolecular mode from lattice modes. Recently we have found that in many systems (durene, anthracene, biphenyl) the low lying intramolecular modes are temperature dependent. The temperature dependence criterion can thus be misleading.

Another distinction between internal and semi-internal modes, and the external mode is based on isotope shifts. These are mostly predictable and generally much smaller for external vibrations (phonons). This distinction is obviously part of the general use of isotope shifts in the identification of normal modes. Specifically, the semi-internal methyl group torsions are usually identified on the basis of isotope shift. The ratio of the perproton methyl torsion frequency and the corresponding perdeutero methyl torsion frequency in a simple model is 1.41 which corresponds to the ratio of the square roots of the moments of inertia of the CH_3 and CD_3 groups. We have encountered significant deviations [6] (1.3 compared to 1.4) in this value and in our opinion, this criterion has to be used with care.

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Another possible criterion, though rarely used, is the magnitude of the crystal bandwidth relative to the basic excitation energy. Intramolecular modes (internal and semi-internal) will usually have much smaller relative bandwidths than phonons, due to the relatively smaller intermolecular interaction. This is the reason why intramolecular modes are usually classified as vibrational excitons, while phonons rarely are [2, 7]. In practice bandwidths are usually studied only indirectly, via the Davydov components [8], and, in addition to problems of assignment, some crystals, like those with one molecule per unit cell, have only one Davydov component, thus not enabling any estimate of the bandwidth.

In this paper we propose a new method of distinction between internal and semi-internal modes, and the external mode. It is based on an "experimental amplification" of some of the above criteria, specifically combining the following two: the relative bandwidth and the isotope shift. It is well known that for an isotopic mixed crystal one gets two limiting cases. I. The *separated band* limit [8], for cases where the bandwidth is small compared to the isotope shift ("trap depth"). II. The *amalgamation* limit [9], for cases where the isotope shift is small compared to the bandwidth. We also note that in isotopic mixed crystals the bandwidth is easily revealed, thus avoiding some of the problems associated with Davydov components in neat crystals.

Our method is also supported by experimental isotopic mixed crystal studies of many molecular crystals: dimethylacetylene [10], benzene [7], durene [2], hexamethylbenzene [6], biphenyl (ref. [11] and reported in this paper), naphthalene [8, 9], anthracene (reported in this paper) and phenanthrene [12]. From these investigations we developed the criterion that in isotopic mixed molecular crystals of protonated and corresponding perdeuterated compounds, the lattice motions (phonons) are in the amalgamation limit [9], while the internal motions and the semi-internal methyl torsions are usually in the separated band limit [2, 8].

We have also tested the above criterion on low lying Raman active intramolecular modes of durene, anthracene and biphenyl, where a significant temperature dependence has been observed. It again seems to work well in these cases.

2. Experimental

Single crystals (neat and isotopic mixed) grown from the melt in a capillary under vacuum were used for the experiments. Regulated flow of cold nitrogen vapor provided a variable temperature bath from room temperature down to 100°K. To get lower temperatures (25°K) helium vapor was used. The spectra were recorded on a Ramalog Spex double spectrometer model 1401 using 4880 Å laser emission from a Coherent Radiation Laboratory argon ion laser for excitation. The spectral resolution was 1 cm⁻¹.

3. Results and discussion

The temperature dependence study shows that the phonon frequencies shift about 10–20% in going from room temperature to 100°K. The sharpening is the most remarkable feature. In most of the cases the factor group splittings (5 to 20 cm⁻¹) on the Raman phonons are not even resolved at room temperature but they are usually resolved at 100°K. Such temperature dependence studies on phonon states already exist in the literature. The paper by Ito et al. [13] describes the temperature dependence of Raman active phonons in many molecular crystals. Usually, the change from 100°K to lower temperature is small. The durene crystal, however, seems to be an exception. Here, though the phonon frequencies do not shift that much in going from 100°K to 25°K, the line-width decreases very significantly. Some features which are not resolved at 100°K get very well resolved at 25°K. Details of the temperature dependence study on durene are reported elsewhere [2, 14]. Here we would simply like to emphasize that this difference in temperature dependence of the vibrational frequency and that of its line-width arises because they are usually not caused by the same anharmonic interaction. The line broadening is caused by two mechanisms [15, 16]: (i) The lifetime broadening due to relaxation effects. This involves anharmonic processes in which the vibration decays into two or more other vibrations conserving both the momentum (wave vector) and energy. (ii) Fluctuation broadening which does not involve any vibrational relaxation but a scattering mechanism: the broadening is not caused by decay of the vibration but only due

to scattering of this vibration with other vibrations and involves quartic anharmonicity terms. On the other hand, the temperature dependent frequency shift, is caused by anharmonic interactions which do not require energy conservation. Also, the thermal expansion of the lattice contributes only to the frequency shift but not to the line broadening.

The internal modes have been assumed in the past to be temperature independent. We have seen temperature dependent frequency shifts on one internal mode in durene, on two internal modes in anthracene and on three internal modes in biphenyl. The temperature shifts of the two anthracene fundamentals and of the three biphenyl fundamentals are shown in figs. 1 and 2. The temperature dependence of the durene vibration is reported in detail elsewhere [14]. In the case of durene the 272 cm^{-1} fundamental of durene- h_{14} shows an increase of 9 cm^{-1} in going from room temperature to 100°K . In the case of anthracene- h_{14} the mode at 285 cm^{-1} increases by 6 cm^{-1} while the fundamental at 242 cm^{-1} increases by 3 cm^{-1} in going from room temperature to 100°K †. Biphenyl shows an interesting temperature dependence. The mode at 250 cm^{-1} (biphenyl- h_{10} value) decreases in frequency

† Bree and Kydd [17] have observed temperature dependence on the corresponding anthracene- d_{10} modes near the melting point.

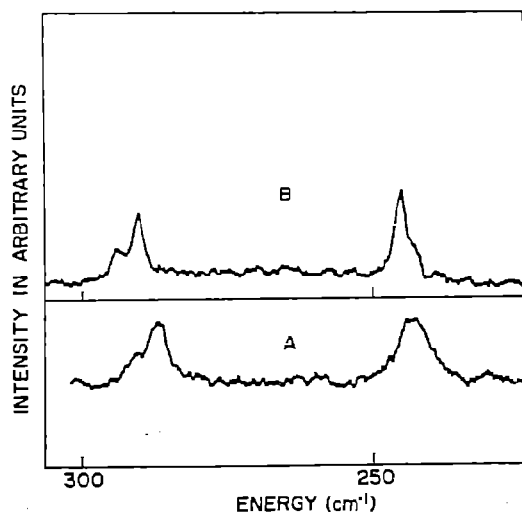


Fig. 1. Raman spectra of neat anthracene- h_{10} crystal: A is the spectrum at room temperature, B that at 100°K . The resolution is 1 cm^{-1} .

by 5 cm^{-1} while the one at 330 cm^{-1} increases by 5 cm^{-1} going from room temperature to 100°K . Also the mode at 1149 cm^{-1} of biphenyl- h_{10} shows a decrease of 4 cm^{-1} for the same temperature change‡. The corresponding perdeutero compounds show similar features. In a recent paper [14] we have discussed the origin of this temperature dependent shift in durene and from our various considerations we have suggested that the major contribution to the temperature shift does not come from the thermal expansion of the lattice. Anharmonic interactions which exist even in a lattice without thermal expansion may often dominate over the contribution due to thermal expansion. We thus see that the temperature dependence criterion for distinguishing between external and internal modes seems to be unreliable, if not misleading.

For semi-internal motions, like methyl torsion, very often the following criterion is used: the ratio of the per proto frequency to the corresponding perdeutero frequency is 1.41, which corresponds to the square root of the ratio of the moments of inertia of the CH_3

‡ Pasquier [18] has also observed temperature dependence on biphenyl modes. While he reports that almost every intramolecular band in the biphenyl Raman spectrum is temperature dependent, we see significant temperature shifts on only three intramolecular fundamentals.

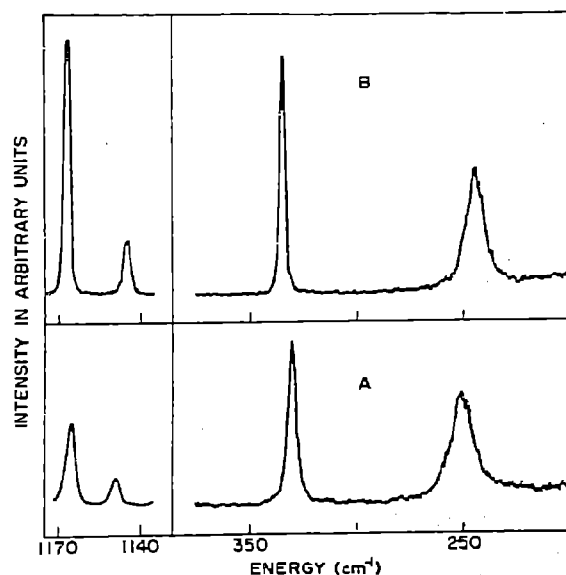


Fig. 2. Raman spectra of neat biphenyl- h_{10} crystal: A is the spectrum at room temperature, B that at 100°K . The resolution is 1 cm^{-1} .

and CD_3 groups. This is true in a simple minded picture where the methyl groups are assumed to be rotating against a molecular unit of infinite moment of inertia. Calculations have been made considering the moment of inertia of the molecular unit rotating against the methyl group and a value of 1.40 has been obtained in the case of hexamethylbenzene [19]. Furthermore, the intermolecular interaction can alter this value substantially. As a matter of fact, we find this ratio to be only 1.32 in the case of hexamethylbenzene [6]. Also in durene [2] this ratio is 1.37. In hexamethylbenzene we think that this deviation is caused by interaction of methyl torsions with phonons [6].

In isotopic mixed crystals the phonons obey the *amalgamation limit* in which the frequency shifts continuously from one component (perproto) to another (perdeutero) as one changes the concentration of the perdeutero compounds [9]. A typical spectrum obtained is shown in fig. 3 which is obtained for anthracene isotopic mixed crystals at 100°K . The reason that phonons are usually in the amalgamation limit is that the isotopic perturbation on the lattice motion is small compared to the lattice-dynamical interactions. For most intramolecular modes, both internal and semi-internal (but not, perhaps, for biphenyl ring torsion, *vide infra*), the isotopic perturbation is large. In the exciton theory formalism this means that the isotopic frequency shift (trap-depth) is large compared to the vibrational exciton bandwidth. For this reason these modes are in the separated band limit. In other words, if one makes a 50% crystal solution of perproto and perdeutero compounds, one will see transitions due to both perproto and the corresponding perdeutero compound. Fig. 4 shows such a study on the temperature dependent intramolecular modes of biphenyl. We clearly see that the middle spectrum is a superposition of the top and bottom spectra which correspond, respectively, to biphenyl- h_{10} and biphenyl- d_{10} . We have tested this criterion also in dimethylacetylene [10], benzene [7], naphthalene [8, 9], hexamethylbenzene [6] and phenanthrene [12] and it seems to work well.

The distinction between internal modes and semi-internal modes is made by their dissimilarity. The semi-internal modes (methyl torsions) are very anharmonic and show large temperature broadening and shift while the internal modes are sharp. The methyl torsions, which we have classified as semi-internal motions, show

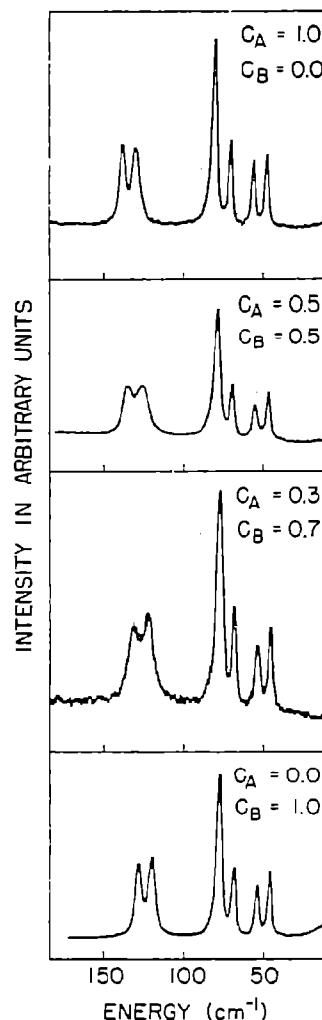


Fig. 3. Raman spectra of neat and isotopic mixed anthracene crystals at 100°K and at a resolution of 1 cm^{-1} : C_A is the concentration of anthracene- h_{10} , C_B that of anthracene- d_{10} .

great resemblance to phonons so far as line broadening and temperature dependence of the frequency shift are concerned. In durene, for example [2], the transitions due to methyl torsions are so broad at room temperature that they can hardly be seen. Even at 100°K they are so broad that the Davydov splitting of 10 cm^{-1} on the 195 cm^{-1} torsion of durene- h_{14} (and the 142 cm^{-1} torsion of durene- d_{14}) cannot be seen. With significant decrease in line-width following the lowering of the temperature, this Davydov splitting is clearly resolved at 25°K [2]. A similar line sharpening is seen

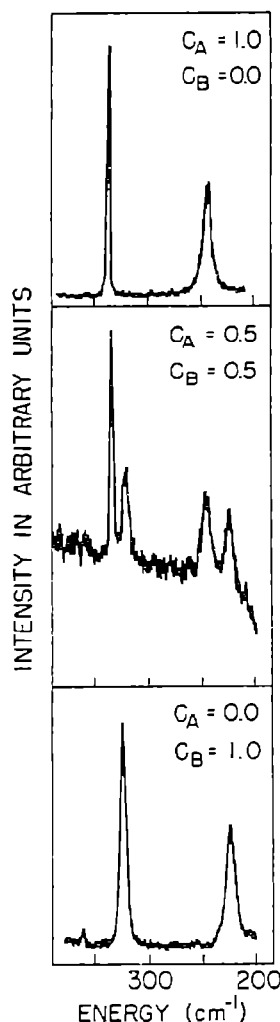


Fig. 4. Raman spectra of neat and isotopic mixed biphenyl crystals at 100°K and at a resolution of 1 cm^{-1} : C_A is the concentration of biphenyl- h_{10} , C_B that of biphenyl- d_{10} .

in the case of the hexamethylbenzene torsion [6].

Because of the broadening the methyl torsions might be confused with phonon overtones or combinations as the lowest methyl torsions usually lie in that range. Our criterion proves to be helpful in this concern as methyl torsions are in the separated band limit while the phonons are in the amalgamation limit. This criterion has been of great assistance in the investigations of durene [2] and hexamethylbenzene [6].

At the end, we would like to point out that our criterion depends only on the condition that for internal and semi-internal modes the isotopic shift (trap-

depth) is large compared to the exciton bandwidth. This is almost invariably the case with the hydrocarbons because the deuteration shifts of vibrational frequencies are large. In systems like hexachlorobenzene, however, there is no hydrogen and isotopic substitution of ^{35}Cl by ^{37}Cl will involve a small frequency shift. Also, semi-internal motions like biphenyl ring torsions, which have small isotopic shifts, may be in the amalgamation limit (we are currently working on it). For these cases our criterion may not work (neither for any C-13 shifts). In view of these limitations we suggest that our method should not always be taken as the sole criterion but be used judiciously or as complementary to other criteria of identifying the nature of the vibration.

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