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P. N. Prasad [a]

[a] Department of Chemistry, State University of New York at Buffalo, Buffalo, New York, 14214, U.S.A.

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Raman Study of Molecular Motions in Organic Solids†

P. N. PRASAD‡

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, U.S.A.

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The paper presents Raman investigation of the nature of phonon motions in various organic solids and discusses chemical, physical as well as some practical applications of phonon studies. In order to characterize the nature of these motions, delocalization and relaxation of phonons are studied using the mixed crystal technique and temperature dependence of phonon spectra. The application of phonon spectra to investigate chemical perturbation of crystal structure in a group of closely related compounds is discussed. Some preliminary studies are presented on application of phonon spectra in solid state reactions. In regard to practical applications, it is shown that phonon spectra can be used to identify truly random solid solutions as well as various polymorphic forms of a given compound.

INTRODUCTION

In the framework of the rigid body model molecular motions of an organic solid can be classified in three categories:[1] (i) Internal motions which correspond to vibrations within the molecule. These motions are subject to solid state interactions only within the limits of perturbation. (ii) Semi-internal motions (semi-external motions) which correspond to very low frequency motions (internal rotations) of a group of atoms within the molecule. These motions have a large contribution to the force constant from the solid state interaction. (iii) External motions consisting of intermolecular lattice vibrations which are called phonons. These motions are derived from external rotational and translational motions of the molecule which are hindered in the solid state. Here the force constant is entirely due to the solid state interation.

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Of these motions, phonons have received little attention from chemists Phonon motions play an important role in determining physical and chemical properties of molecular aggregates. The main objective of the paper is to illustrate that study of phonons can find valuable physical chemical and in some cases practical applications in solid state chemistry.

This paper presents Raman studies of phonon motions in several molecular solids: organic crystals, charge-transfer complexes and clathrates. The presentation consists of three parts: (A) The nature of phonon motions (B) The applications of phonon spectra in studying physical and chemical transformations in solids; and (C) Some selected practical applications.

A NATURE OF PHONON MOTIONS

Results of Raman Studies are presented to elucidate the nature of phonon motions in two types of organic solids: (i) an organic crystal, which is composed of only one chemical constituent, and (ii) an ordered multi-component organic crystal which is composed of several chemical constituents. Examples of the latter are charge-transfer complexes and clathrates.

In order to characterize the nature of phonon motions in organic crystals two aspects are investigated: (i) delocalization and (ii) relaxation of phonons. Due to intermolecular transfer interaction, the phonon motions give rise to phonon bands each of which consists of closely spaced phonon levels of different wave vector K. This spread of phonon levels provides a measure of delocalization of phonons as waves over the crystal. Doped crystals can be used to derive an estimate of phonon band-width.[2] If the difference between the phonon frequency of the host pure crystal and that of the pure crystal of the impurities is smaller than the phonon band width amalgamation of phonon results. In this limit phonon bands show a monotonic shift as the concentration of the impurity increases. Figure 1 shows the amalgamation behavior for phonons in *p*-bromoiodobenzene (BIB): *p*-dichlorobenzene (DCB) system.

In order to derive an estimate of phonon bandwidth successive perturbation of phonon bands was used.[2] In this method, the host was *p*-$C_6H_4Cl_2$ (*p*-dichlorobenzene). Other isomorphic *p*-dihalobenzenes were used as guests with increasing perturbation in the order *p*-C_6H_4ClBr, *p*-$C_6H_4Br_2$, *p*-C_6H_4ClI and *p*-C_6H_4BrI. In mixed crystals all phonons remain amalgamated throughout the entire concentration range for all perturbation strengths. Figure 2 shows the monotonic variation (decrease) in frequency of lowest phonon at 125°K as a function of mole fraction of the guest (component 2). This result reveals that phonons in molecular crystals are highly delocalized and give rise to quasi-continuous density of states. The mixed

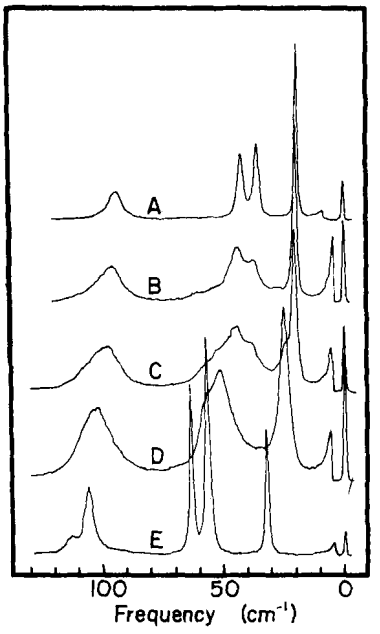

FIGURE 1 Raman spectra at 125°K of phonons in *p*-dichlorobenzene (DCB); *p*-bromo-iodobenzene (BIB) solid solutions. (A) pure BIB, (B) 68.1 mole % BIB, (C) crystal exhibiting segregated phases, (D) 2.18 mole % BIB, and (E) pure DCB.

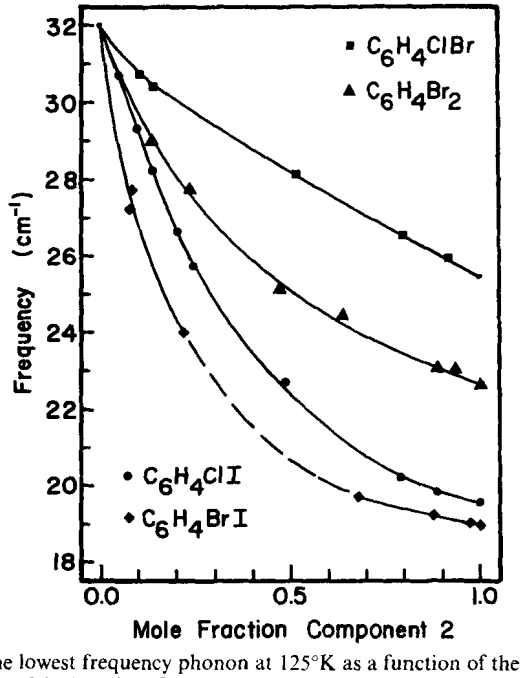

FIGURE 2 The lowest frequency phonon at 125°K as a function of the mole fraction of the second component. The host is DCB.

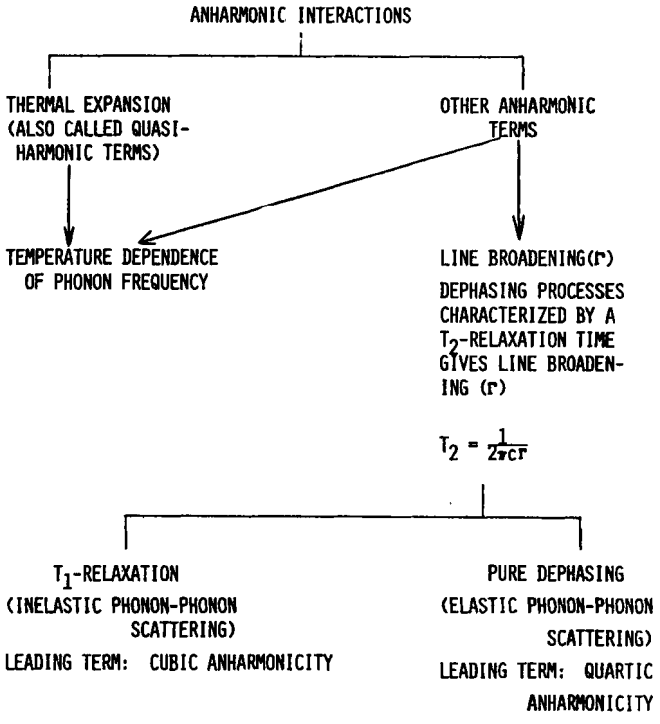

FIGURE 3 Schematic representation of the manifestation of anharmonic interactions.

crystal phonon frequency curves of Figure 2 have been theoretically fit using configurationally averaged Green's function and average T-matrix approximation (ATA).[2] The ATA approximation allows multiple scattering from some defect site but ignores intersite scattering.

Next, the investigation on phonon relaxation is discussed. These phonon relaxations destroy selective and coherent phonon population and are caused by anharmonic interactions. Figure 3 schematically shows the manifestation of anharmonic interactions. We see that anharmonic interactions cause both a temperature dependence in phonon frequencies and a thermal line broadening. These manifestations are experimentally studied. We find that for naphthalene crystals the temperature dependence of phonon frequencies is almost entirely due to thermal expansion. This point is illustrated in Figure 4 which shows the temperature dependence of a high frequency (120 cm^{-1}) phonon and a low frequency phonon (57 cm^{-1}) of naphthalene. It also shows the curve calculated on the basis of the contribution from the thermal expansion. On the other hand the line widths of these transitions are derived from T_1-relaxations due to cubic anharmonicity

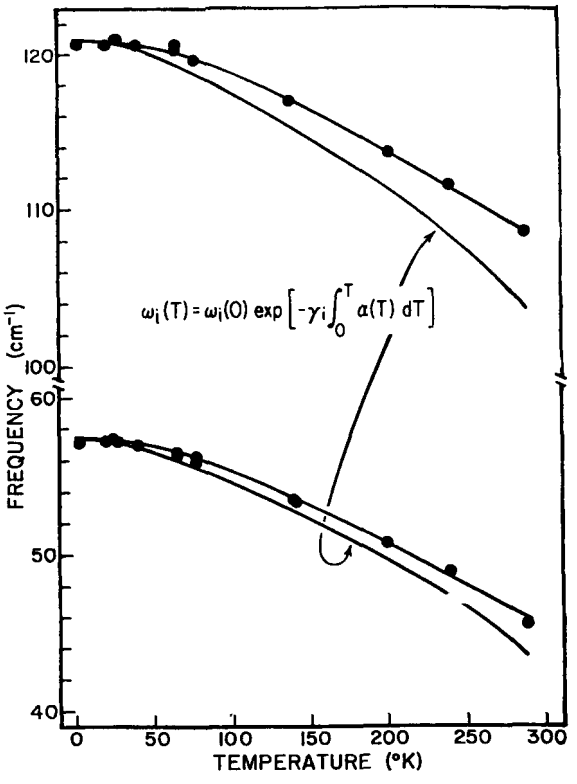

FIGURE 4 Experimentally observed temperature dependence of the frequencies of 120 cm^{-1} and 57 cm^{-1} phonons compared with the curve computed from thermal expansion.

terms in which the phonon decays into two other phonons. The experimental points as well as the theoretical curve for the line widths of the 120 cm^{-1} phonon as a function of temperature are shown in Figure 5.

Multicomponent organic crystals exhibit a wide variation in interaction between components and the geometry of their formations. Our study of phonons in these systems reveal that even though phonon motions are delocalized, they show a continuous range of behavior from highly coupled to decoupled motions.[3] In a highly coupled motion, a phonon represents a co-operative motion of all components. This is the case when the coupling between the components is strong and/or the difference between their mass coefficients small. In the event that the intercomponent coupling is weak and/or the difference between their mass coefficients large, the motions are decoupled and can be classified as motions of individual sublattices formed by each component. Figure 6 shows phonon motions in the complex naphthalene: $2SbCl_3$. Isotopic substitution of the donor (naphthalene)

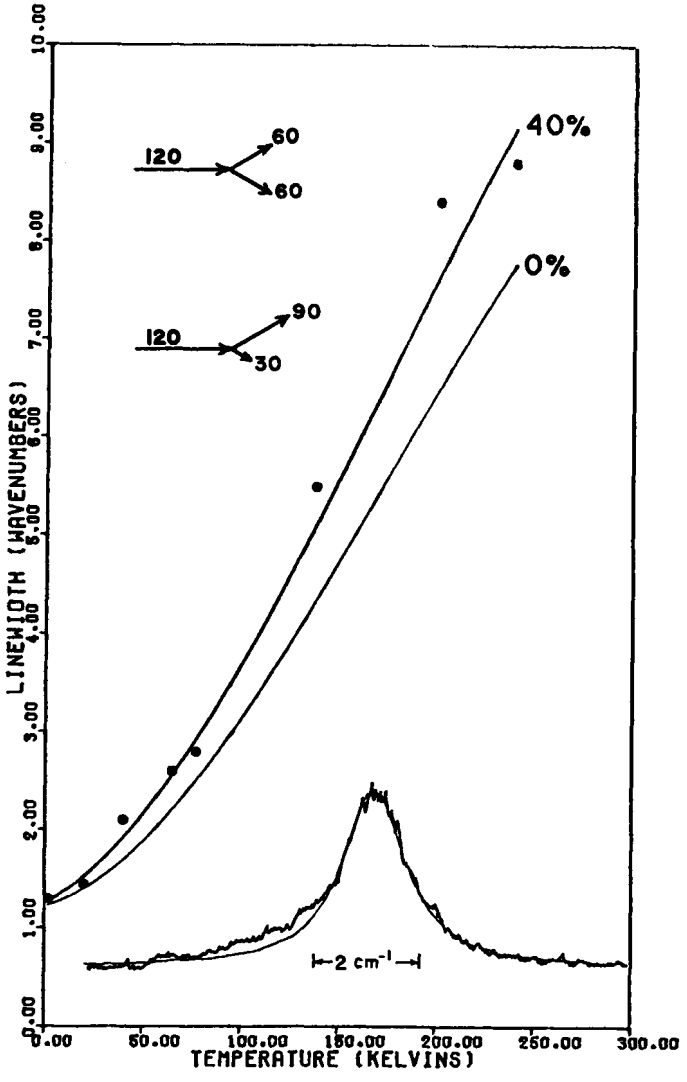

FIGURE 5 Line width and line shape of 120 cm^{-1} phonon of naphthalene. In line shape the computed asymmetric Lorentzian curve is represented by a lighter line. The theoretical line widths computed from T_1 processes are represented by the solid lines. The percentage represents the contribution due to the process in which the 120 cm^{-1} phonon decays into one 30 cm^{-1} and one 90 cm^{-1} phonons.

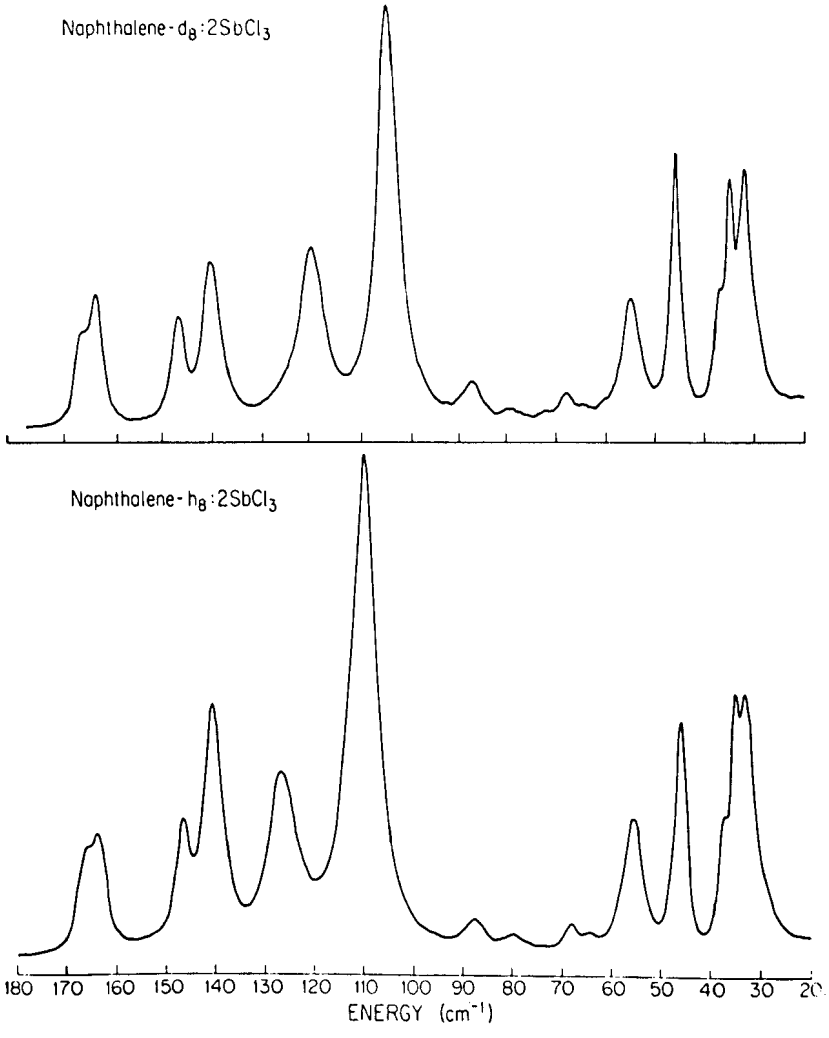

FIGURE 6 Phonon spectra of the naphthalene: $2SbCl_3$ complex at 125°K.

and chemical substitution ($SbBr_3$) of the acceptor reveal that phonon motions are decoupled.[4] A set of high frequency phonons belong to the donor sublattice. On the other hand, a set of low frequency phonons represents motions predominantly of the acceptor sublattice. Study of phonons in another type of multicomponent crystals—the clathrates show a similar behavior. However, due to compositional disorders with respect to the included guest, the phonon spectra are considerably broader. The clathrate of $Zn((4\text{-picoline})_2\text{-}(SCN)_2$ with *p*-dihalobenzene appears to be different from

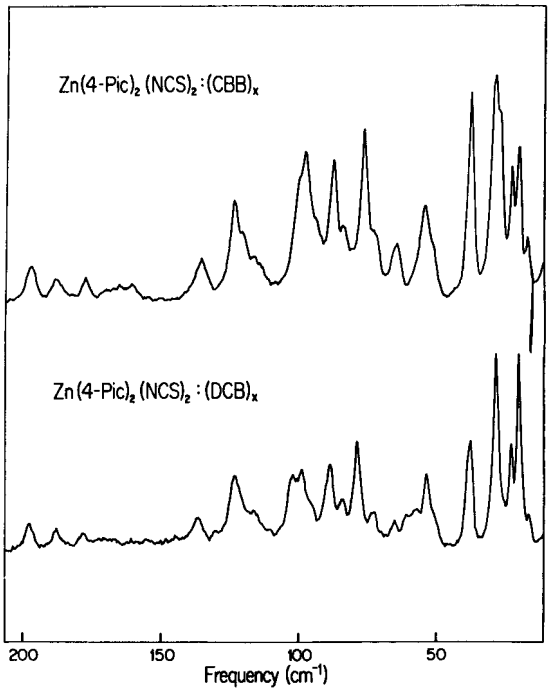

FIGURE 7 Phonon spectra at 125°K of the clathrates with Zn(4-picoline)$_2$-(SCN)$_2$ as the host and *p*-chlorobromobenzene (CBB) and *p*-dichlorobenzene (DCB) as the included guests.

this point of view. Figure 7 shows the phonon spectra which consists of sharp bands and reveals decoupled motions.

B THE APPLICATION OF PHONON SPECTRA

Physical transformation

Phonon spectra can be used to study the nature of solid state phase transformations at molecular levels by providing details of molecular and crystal symmetries and interactions. However, it is more important to a chemist who is interested in solid state reactions to understand how changing substituent groups in a group of closely related compounds affects the crystal structures. For this reason we have started the study of chemical perturbation of crystal structure and the lattice instability created by the chemical perturbation.[5–7] In organic solids the chemical perturbation can be created by successively changing a substituent group of the molecular unit or by adding a chemical impurity. The lattice instability encountered is of two types:

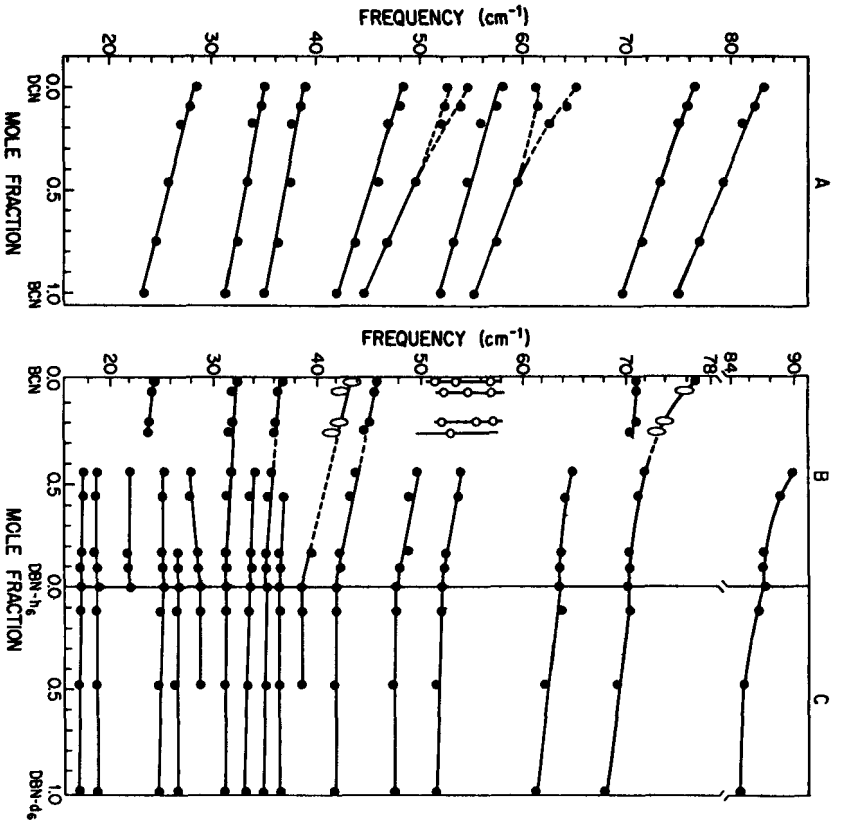

FIGURE 8 Phonon frequencies at 125°K of binary solid solutions of 1,4-dihalonaphthalenes plotted as a function of the composition.

(i) static instability when chemical perturbation creates another equilibrium geometry of lower free energy; (ii) dynamic instability when the chemical perturbation softens a non-trivial phonon motion leading it to zero frequency.

We have studied the chemical perturbation of crystal structures in dihalobenzenes and dihalonaphthalene. Only the case of 1,4-dihalonaphthalene will be discussed.[7] In Figure 8 phonon frequencies are plotted as a function of the composition in binary solid solutions of 1,4-dihalonaphthalene. We fined that 1,4-dichloronaphthalene (DCN) and 1-bromo-4-chloronaphthalene (BCN) are isomorphic (similar phonon spectra). However, substitution of another bromine gives rise to a lattice instability and, thus, a different crystal structure for 1,4-dibromonaphthalene (DBN). In BCN–DBN solid solutions there is a critical concentration region between 24 and 44 mole percent in which the lattice instability is encountered and

subsequently crystal structure changes. However, during the critical concentration region, no phonon softening occurs. Thus the lattice instability is static. Another important feature is that certain phonon branches are continuous across the critical concentration region. This behavior suggests that in going from BCN crystal structure to DBN structures, certain interaction topology is preserved. Our x-ray study of DCN and DBN show that both structures show linear stacking. Furthermore, the crystallographic screw axis of DCN structure is retained as a non-crystallographic (local) screw axis in DBN structure.[8]

Chemical transformation

Phonon study can provide valuable insight into the mechanism of solid state reactions. The analysis of phonon spectra can give information regarding the mechanism by which the product lattice forms as to whether the reaction is a single crystal–single crystal topotactic reaction. In this case an amalgamation of phonons can be expected till the cluster of the product lattice grows in size to nucleate its own structure. The phonon behavior may be similar to the one shown by BCN-DBN solid solution shown in Figure 8. Our study of trans-cinnamic acids shows that this is not the case.

However, the most important role played by phonons may be in determining the dynamical requirement. This is because large amplitude phonon motions are the analog of molecular collisions in the gas phase. Our study on this aspect is in a very preliminary stage and the discussion on this topic is more of a conjecture. We are studying the cases where the reactivity of the same compound depends on its crystalline modification. An example is trans-cinnamic acid which has two crystalline modifications: α and β forms. The β-form is more reactive. The phonon spectra of these crystalline forms as well as their respective dimers are shown in Figure 9. We find that the β-form has a very low lying phonon transition than the α-form. In this motion, the molecules will have large amplitude oscillations which may account for enhanced reactivity. However, more studies are needed to formulate an understanding of the dynamical requirement.

C SELECTED PRACTICAL APPLICATIONS

Although several applications of phonon spectra can be thought of, only two cases will be discussed. We find that phonon spectra can be used to identify a true-random solution at the molecular level.[9] This is the case when phonon amalgamation results. Even a small cluster gives the spectra of segregated

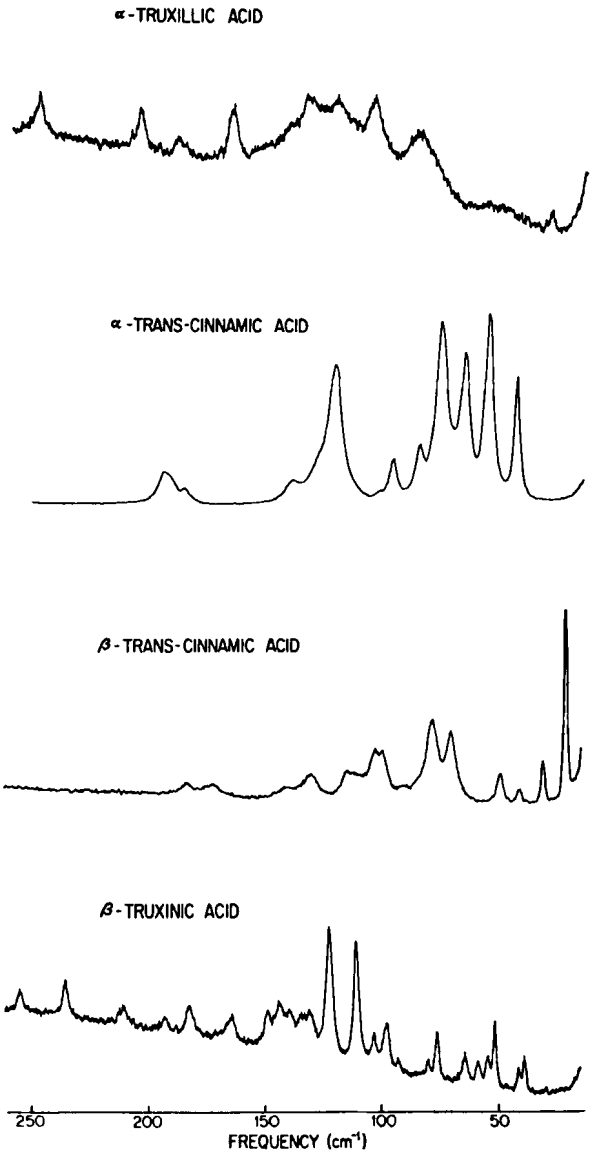

FIGURE 9 Phonon spectra at 125°K of α and β forms of trans-cinnamic acids and their respective dimers.

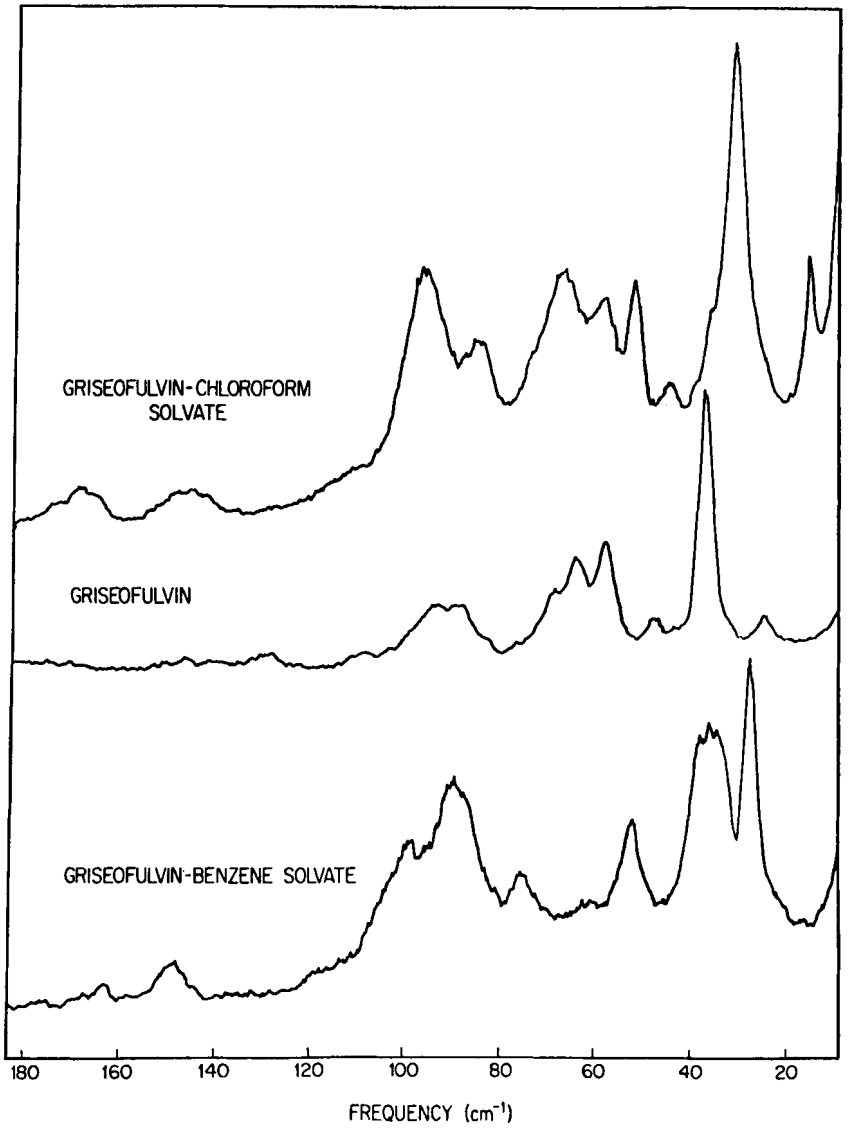

FIGURE 10 Phonon spectra at 125°K of Griseofulvin and its two solvates.

phases. The reason for this is that phonon motions are subject to short range intermolecular interaction and, thus, sample the local order.

Phonon spectra can readily be used to identify and characterize various polymorphic forms of compounds, and study their stability and transformation. One area where such a characterization is important is with Pharmaceutical compounds. The pharmaceutical solids are notorious for exhibiting polymorphism and forming solvates. One of the ways to prepare a micronized form of a drug is to prepare the solvate and drive off the solvent. Figure 10 shows phonon spectra of Griseofulvin and its two solvates.[10] The three forms are clearly distinguishable on the basis of their phonon spectra. The benzene solvate is the least stable. From experimentation point of view, no special sample preparation is required and very small samples can be used.

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