PHONON AND EXCITON AMALGAMATION — A CRITERION FOR TRUE SOLID SOLUTIONS: VIBRATIONS OF CHEMICALLY AND ISOTOPICALLY MIXED PARA-DIHALOBENZENE CRYSTALS*

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The phonon and vibrational exciton spectra are suggested as criteria for true solid solutions of molecular crystals. The short range character of the interactions that determine both the phonon and exciton properties makes these bands ideal for distinguishing between truly random mixed lattices and segregated microscopic domains. Raman studies of the chemically mixed p-dichlorobenzene—p-dibromobenzene crystal and the isotopically mixed p-dichlorobenzene-h_4 —p-dichlorobenzene-d_4 crystals illustrate the principles involved. All phonon bands (external molecular vibrations) of both the chemically and the isotopically mixed crystals are in the *amalgamation limit*. While mass defects appear to determine the phonon frequency shifts in these mixed crystals, deviations from a virtual crystal model are observed and discussed. The low energy internal modes (vibrational excitons) are examined and found to be in the *separated band limit*. Treating the pure p-dichlorobenzene crystal as an isotopically mixed crystal due to the natural abundance of the chlorine isotopes reveals that the chlorine stretch at 310 cm^{-1} is also in the separated band limit. All these mixed crystal systems are concluded to be substitutionally random on the molecular scale.

1. Introduction

The effect of substitutional disorder on molecular motions of organic solids is of considerable interest in understanding the energy transport and excitation relaxations in these systems [1,2]. Recent studies conducted in our laboratories have focussed on such investigations [3—5]. The effect of isotopic perturbation [3] and successive chemical perturbations on phonon bands [4,5] in organic solids has been examined in detail. The present paper is an extension of our previous studies [3,4] with the objective to examine both internal and external (phonon) vibrations in a substitutionally disordered solid and to compare the roles of isotopic defects with those of chemical defects.

Our total experience with isotopically mixed crystals [2,3] tells us that random substitutional disorder is the rule, and these alloys can be treated as "ideal" solid solutions. For chemically mixed crystals, on the other hand, such a result is not as evident, but its possibility is of prime interest. Few methods are able to distinguish random substitution on the molecular scale from randomly distributed small aggregates of one or the other component. We note that when the size of such segregated domains is much smaller than the wavelength of light (say ≪4000 Å), neither ordinary optical nor diffraction methods (X-ray, neutron) will distinguish between random and semi-ordered forms of aggregation. On the other hand, in most molecular solids, and particularly those consisting of non-polar molecules, the phonon and vibrational exciton interactions are *short-range* and thus particularly sensitive to the organization of the aggregate on the molecular level. This sen-

sitivity has been utilized in studies of excitons and phonons in crystals [2] as well as in the study of the structure and dynamics of liquids [6]. Thus it is through the study of the phonons and vibrational excitons in the mixed crystal that we hope to shed light upon the nature of the substitutional disorder in these systems.

For this investigation, both internal and external vibrations are examined in p-dichlorobenzene-h_4—p-dichlorobenzene-d_4 isotopically mixed crystals as well as in p-dichlorobenzene-h_4—p-dibromobenzene-h_4 chemically mixed crystals. We find that irrespective of the nature of the phonon motions, they exhibit the amalgamation limit behavior both in isotopically and chemically mixed crystals. The internal vibrations are usually found to be in the separated band limit [2]. Both results are consistent with complete substitutional disorder, i.e., ideal mixing on the molecular scale.

2. Experimental

The p-$C_6H_4Cl_2$(DCB-h_4) and p-$C_6H_4Br_2$(DBB-h_4) were obtained from Aldrich Chemical Co. and were zone refined before use. The p-$C_6D_4Cl_2$ (DCB-d_4) was obtained from Merck, Sharpe and Dohme. Mixed crystals were prepared by weight and grown from the melt by the Bridgman technique. Isotopically mixed crystals (DCB-h_4—DCB-d_4) were assumed to grow at the nominal concentration. The chemically mixed crystals DCB-h_4—DBB-h_4 were analyzed by gas chromatography to determine the actual concentration.

Raman spectra were obtained using a Spex model 14018 double monochromator with 1800 grooves/mm holographic gratings. The spectral bandpass was 1 cm^{-1}. Band positions were measured relative to the laser line and were reproducible to 0.3 cm^{-1}. The absolute accuracy should be ±0.5 cm^{-1} or better. Direct current detection was used. Excitation was provided by the 5145 Å line of a Coherent Radiation argon ion laser (model CR-5) at 0.2 W. Samples were cooled to 125 K in a stream of nitrogen vapor. Temperatures were measured with a chromel—constantan thermocouple and were controlled to ±2 K. Due to the differences in location and the glass envelope around the sample, the estimated accuracy of the temperature is +5 K, -0 K.

3. Results and discussion

The Raman spectra in the phonon region of DCB-d_4, DCB-h_4, DBB and two mixed crystals are shown in figs. 1 and 2. Of the six expected phonons, five are resolved in all cases and the sixth is resolved in pure DBB (fig. 2). The sixth phonon has been observed [7] before in DBB and bromochlorobenzene, but it is not resolved in our mixed crystal studies. The mixed crystal spectra show that all phonons are amalgamated. The amalgamation of phonons is expected for isotopically mixed crystals, but amalgamation is not necessarily expected for chemically mixed crystals. A previous study [4] has shown that the entire set of p-dihalobenzene mixed crystals with DCB exhibits amalgamation. Chemi-
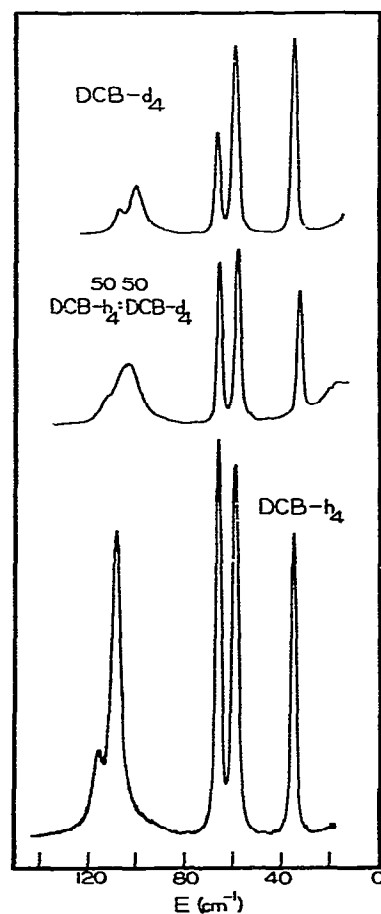

Fig. 1. Raman phonon spectra of pure and isotopically mixed crystals: DCB-d_4, 50 mole % DCB-h_4 in DCB-d_4, and DCB-h_4 at 125 K.
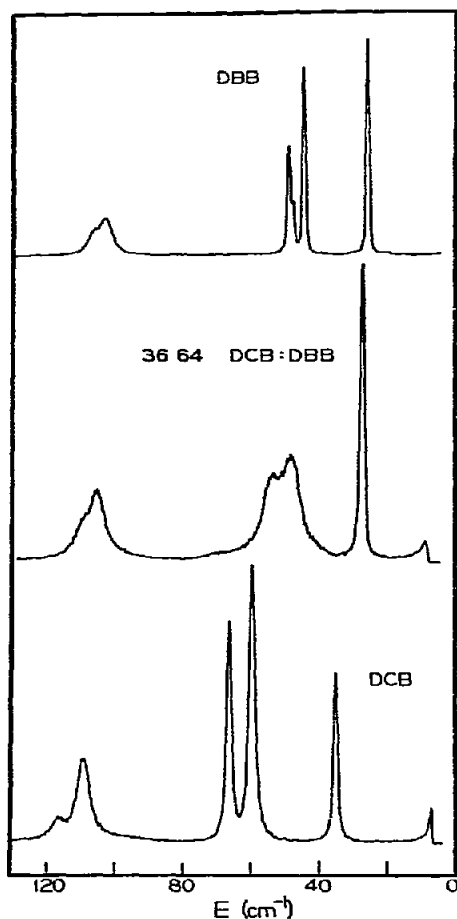
Fig. 2. Raman phonon spectra of pure and chemically mixed crystals: DBB, 36% mole DCB in DBB, and DCB at 125 K.

Fig. 3. Frequency dependence on composition in isotopically and chemically mixed crystals at 125 K: the phonon region.

cally mixed crystals of 1,4-dihalonaphthalenes also exhibit amalgamation [5]. There has been speculation [4] about the cause of amalgamation in these systems, but general conclusions require studies of many more systems.

The dependence of phonon frequency on composition is shown in fig. 3. The band at 32 cm^{-1} has been previously [4] analyzed in terms of an average T-matrix approximation (ATA) for the chemical mixed crystal. The small linear shift in the isotopic mixed crystals can be understood in terms of the virtual crystal model [2,4]. The small change in frequency in the isotopic system is expected, since this phonon mode has been assigned to motions with large amplitude on the halogens. The halogens dominate the mo-
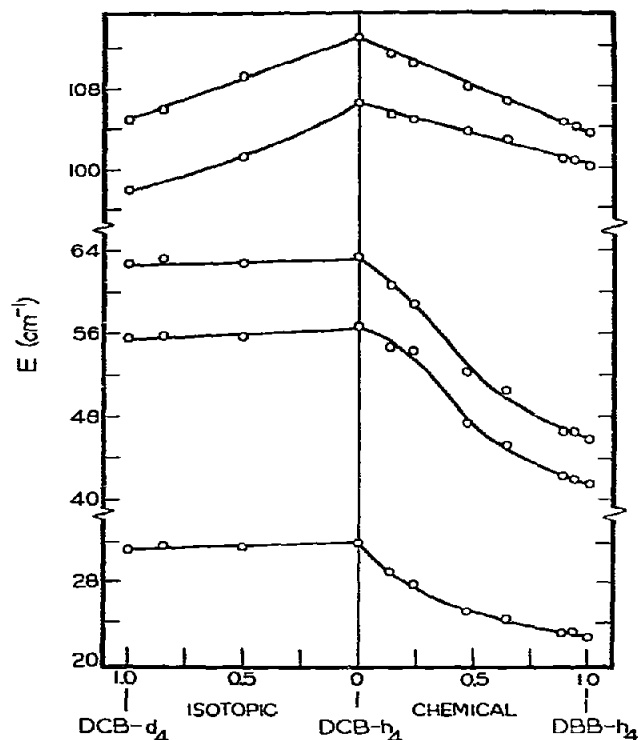
ment of inertia and the addition of small mass increments at the hydrogen positions has little effect. The dominance by the halogen is again present in the case of the doublet at 57 and 63 cm^{-1}. These phonons also show small isotope shift and large halogen shifts. The frequency dependence in the chemical mixed crystals can again be understood via an ATA model with a predominant mass defect [4]. The phonon doublet at 106 and 113 cm^{-1} (DCB-h_4) shows both large isotopic shift and large chemical shift. However, the frequency is essentially a linear function of composition. This fact indicates that the virtual crystal model may be applicable, although in order to explain both the frequency shift and the line broadening one needs the ATA model [4] (see below) or the coherent potential model (CPA) [2]. The virtual crystal model indicates a relatively small perturbation and suggests again a, predominantly, mass defect. This phonon mode has been shown [8] to correspond chiefly to libration about the molecular axis passing through the two halogens (axis corresponding to I_{min}). It is therefore expected

441

that deuteration should have a large effect on this mode. However, calculations of the moments of inertia suggest that the observed difference in frequency between DCB-h_4 and DCB-d_4 is smaller by several percent than would be expected on the basis of libration about I_{min} exclusively. Mode mixing is required to reduce the difference in frequency. In addition, if the motion were exclusively about I_{min}, there should be no shift in the chemically mixed crystals, provided there is no change in force constant. The presence of the large halogen shift is consistent with the mode mixing. Another important feature to be noted is the line broadening in the mixed crystals. A comparative study of fig. 1 and 2 shows that the doublet near 110 cm^{-1} (DCB-h_4) exhibits rather pronounced broadenings in the isotopic mixed crystal. On the other hand, the doublet near 60 cm^{-1} (DCB-h_4) shows relatively large broadenings in the chemically mixed crystal. This result is also consistent with the predictions of ATA [4] (or CPA [2,9]), which relate line broadening to the strength of the perturbation (mass defect in the present case).

Several internal vibrations show interesting crystalline effects. These are low lying modes in the region 250 to 350 cm^{-1}. Fig. 4 shows a graphical representation of these internal vibrations in pure and mixed crystals. The doublets near 310 cm^{-1} and 350 cm^{-1}, for p-dichlorobenezene, are due to a factor group (Davydov) splittings. The factor group splitting on the 350 cm^{-1} band of DCB-h_4 is 3 cm^{-1} in the pure crystal and decreases in both the chemical and isotopic mixed crystals until the components merge. This behavior is typical of the separated band limit [2,10]. The 310 cm^{-1} band of DCB-h_4 also shows separated band behavior in the isotopic mixed crystals where the magnitude of the splitting decreases as we increase the concentration of the p-C$_6$D$_4$Cl$_2$. Furthermore, the reduction in the factor group splitting is also accompanied by a lowering of the frequencies. This usually indicates that the mean frequency of the factor group components is different from the frequency of the center of such vibrational exciton band [11,2]. In other words, the center of the exciton band shows an asymmetry. This can result if there is a contribution from excitation exchange interactions between translationally equivalent molecules. An alternative interpretation is that the static D-shift term is larger for p-C$_6$H$_4$Cl$_2$ than for p-C$_6$D$_4$Cl$_2$. The corresponding band for p-C$_6$D$_4$Cl$_2$
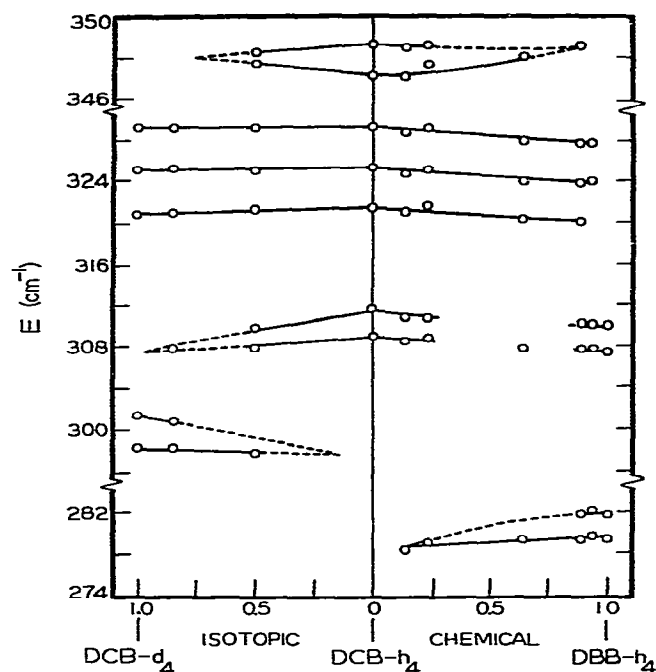

Fig. 4 Frequency dependence on composition in isotopically and chemically mixed crystals at 125 K; internal vibrations in the 274 to 350 cm^{-1} region.

is the doublet around 300 cm^{-1} which also shows the separated band behavior. Here, again, in the isotopic mixed crystal the frequency shifts to lower values, i.e. the exciton band asymmetry is towards lower frequency. The vibrational exciton bands of both p-C$_6$H$_4$Cl$_2$ and p-C$_6$D$_4$Cl$_2$ thus show asymmetries in the same direction. This establishes that the asymmetry of the exciton band is due to the former explanation rather than due to a difference in D-shifts. In other words, translationally equivalent excitation exchange interactions are about as important as the interchange equivalent ones. This band also shows interesting behavior in the chemically mixed crystal. There are close lying bands in DBB (doublet near 308) but due to different kinds of vibrational modes. The possibility of amalgamation due to an intermolecular Fermi resonance [12] was carefully investigated. The results did not indicate amalgamation.

The triplet at 321, 325, 329 cm^{-1} shows separated band limit behavior in the chemically mixed crystals. Since the change in frequency on deuteration is only 0.5 cm^{-1} for the largest shift (321), we cannot say

whether the *hydrogen* isotope species are in an amalgamation limit or a separated band limit (or in-between). However, it is obvious that the chlorine isotope species (even in "pure" DCB-h_4) are in the separated band limit. The splitting (observed triplet) is a chlorine isotope effect. Three observations lead to this conclusion: First, the splitting is maintained in both the isotopic mixed crystals and the chemically mixed crystals, indicating that the splitting is not due to the factor group. Second, the frequencies are in the appropriate ratios for masses of 74, 72 and 70 with identical force constants, and third, the intensities are always approximately 1 : 6 : 9 as expected for an isotopic ratio of 1 : 3. This clear separation of the isotope splitting in the case of DCB is remarkable. It proves that there is little intermolecular coupling for this band. Indeed, the bandwidths must be less than 4 cm^{-1} or amalgamation would occur among the three species differing by Cl isotopes. This finding suggests that chlorine atoms on adjacent molecules do not interact much as far as this mode is concerned. Since chlorine—chlorine interactions have been shown to dominate important aspects of the crystal structure [13] this result may be somewhat surprising. However, the explanation may be the fact that this mode has been shown [14] to be the symmetric chlorine stretch and only one of the Cl—Cl interactions has a large component in the direction of the motion

Finally, all the above data are consistent with a random site substitution model for DCB in DBB or vice versa. Any aggregation, even on a scale of 40 Å or less, would result in very different spectroscopic behavior, i.e. a superposition of pure crystal (DCB and DBB) spectra*. Non-random disorder on an even finer scale

would be expected to result in significant deviations from both the amalgamated band limit and the separated band limit. There is also no evidence whatsoever of any phase transition driven by a change in concentration, unlike some other systems [5].

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* Indeed, in the *p*-bromoiodobenzene—DCB system, segregation of phases does occur and gives rise to the superposition of two spectra. Such a spectrum is shown in fig. 1C of Bellows and Prasad [4]. However, in this case the two component spectra are those of solid solutions which presumably have random disorder.