

## VIBRATIONAL EXCITON CLUSTER STATES, PERCOLATION AND PAIRWISE INTERACTIONS: BENZENE $A_{2u}$ BAND ‡

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Infrared spectra of isotopic mixed benzene crystals ( $C_6H_6/C_6D_6$ ) were obtained at about boiling nitrogen temperature, with emphasis on the umbrella mode (at about  $700\text{ cm}^{-1}$ ). These are interpreted in terms of guest cluster spectra (monomers, pairs, etc.) up to about 55% mole. Static percolation sets in at about 50%, resulting in an extended exciton band. The line positions, line intensities and the percolation concentration all agree quantitatively with an effective *2-dimensional square lattice exciton interaction topology*. This means that very short range, nearest neighbor interchange equivalent, excitation exchange interactions dominate over the long range transition-dipole type terms even in this most intense, dipole allowed IR band. These results fully support our recent picture of the umbrella mode exciton band, in both solid and liquid benzene. Similarities between these solid and liquid exciton bands are pointed out. The existence of pseudolocalized states, in the middle of the energy band of the extended states, is illustrated.

### 1. Introduction

Vibrational exciton states have been an important tool for the understanding of excitations in solids, especially molecular solids [1–14]. They have also played an important role in the investigation of intermolecular interactions [15–19], phase transitions, molecular relaxation and molecular structure in crystals and liquids [20,21].

We would like to emphasize here the transition from localized to extended excitations, where the pertinent order parameter is the isotopic composition. Simultaneously, we investigate the nature, range and topology of the dynamical intermolecular forces (exciton interactions), the appropriateness of the cluster-state model and the structure of the exciton band, all for the case of the “umbrella” vibrational mode of benzene. This energy band has a width comparable to the first singlet and triplet electronic exciton bands of benzene [9,12,22] making it a convenient tool for

the study of the various phenomena associated with Frenkel excitons.

The idea of using isotopic dilution and concentration studies for the elucidation of crystal interactions probably goes back to Hiebert and Hornig [23], with a somewhat analogous approach, using chemical mixed crystals, coming from Hrostowski and Pimentel [24]. Further refined use of such techniques for the study of energy states and energy transfer in molecular crystals is found in the works of Robinson, Colson and their collaborators [22,25–28], as well as those by Nixon et al. [29–31], Hochstrasser et al. [32,33] and the recent large volume of ESR work (see, for example, ref. [34]). The utilization of “resonance pair” (“mini-exciton”) systems for the study of molecular-crystal excitations has started at about the same time both for electronic excitons [35–38], and vibrational excitons [39,40]. However, while the electronic studies have been developed to a high degree of sophistication both experimentally and theoretically [41–48], the vibrational studies seem to have lagged behind.

Exciton percolation [43,46,49–52] has both dynamic and static implications. The dynamic aspects involve a critical transition from a regime of exciton

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conduction (transport) to exciton insulation. The static aspects involve the onset of an energy band consisting of extended eigenstates, i.e., truly delocalized exciton wavefunctions. The concepts of "Anderson transition" and "Anderson localization", which play a central role in current condensed state physics [53], are related to the static percolation problem. The recent utilization of the percolation concept includes studies on exciton interactions and coherence [54], electron conduction [55] and the nature of phase transitions [56]. We notice that for mixed crystals with one-dimensional topologies [23,33] percolation cannot occur.

## 2. Preliminary discussion

As mentioned, the benzene crystal has been used extensively in the study of electronic and vibrational exciton interactions. Work by Bernstein et al. [9] summarized and refined the theoretical framework for a discussion of these effects. The vibrational exciton structure has been worked out for many of the vibrational bands of benzene [9,12,39], but there have been no experimental studies on the development of clusters and/or percolation in isotopic mixed benzene crystals. Recently, Hoshen and Kopelman [57] presented a theoretical model for the cluster development in non-linear systems, and applied it to the benzene crystal for the  $A_{2u}$  vibrational mode. The present study is an experimental test of this model, as well as of the concept of static (band) percolation [43,46]. It is also related to our study of exciton interactions in liquid benzene [21].

The benzene molecular group is  $D_{6h}$ . The space group is  $D_{2h}^{15}(P_{bca})$  and there are four molecules per primitive unit cell [58]. The site group is  $C_i$ . The four sets of interchange equivalent molecules [59,60] corresponding to the four sites per unit cell are labeled [9] I, II, III and IV.

In the  $A_{2u}$  vibrational mode ( $690\text{ cm}^{-1}$  for  $C_6H_6$ ,  $500$  for  $C_6D_6$ ) the  $bc$  in-plane interaction  $M_{I\ III}$  is the most important interaction [39]. Thus one can consider the benzene molecules as having a two-dimensional (square lattice) interaction topology in a three-dimensional crystal.

Using the assumption of a square lattice topology, it is evident that the four in-plane ( $bc$  plane) nearest

neighbor interactions ( $M_{I\ III}$ ) are the most important ones. Therefore, only clusters formed within this plane and connected by  $M_{I\ III}$  interactions will be considered. The cluster topologies and probabilities are given in table 1. In the present work the monomer state is most important (as it could be easily resolved). The concentration of the monomer in the guest/host system\* is given by  $C_m = C_A(1 - C_A)^4$ , where  $C_m$  is the monomer concentration,  $C_A$  is the concentration of the guest in the host and the exponent reflects the fact that there are four nearest neighbors (square lattice topology).

One can determine the magnitude of the  $M_{I\ III}$  interaction (molecular exciton pairwise interaction) by examination of low concentration samples of the guest in the host, i.e., where only monomers and dimers are expected in appreciable amounts. From our 5.2%  $C_6H_6$  in  $C_6D_6$  spectra (see below), the energy difference between monomer and dimer is  $2.8\text{ cm}^{-1}$ . Since the  $M_{I\ III}$  interaction is the most important one, one can assign the molecular exciton interaction energy as  $2.8\text{ cm}^{-1}$  (note that superexchange interactions [42,61] are negligible). The other nearest neighbor interactions ( $M_{I\ II}$  and  $M_{I\ IV}$ ) can be found by an analysis of the pure crystal data [13,39,62]. The model presented by Hoshen and Kopelman [57] used this value for  $M_{I\ III}$ .

Using the probabilities of the various clusters and the value for the exciton pairwise interaction it is possible to generate, as a function of concentration, the expected transitions (both energy and relative intensity) for the various cluster states. These predicted spectra will be discussed below in relation to the experimental results. For a complete discussion of this method, see ref. [57].

It should be noted that in our present experimental setup only the monomer would be resolved clearly. This is due not only to instrumental limitations but also to the natural width of the lines. Also, we could only resolve cluster states for the  $C_6H_6$   $A_{2u}$  mode. For all other vibrational modes, both in benzene and perdeuterobenzene (including the perdeuterobenzene  $A_{2u}$  vibrational mode) the molecular exciton pairwise interaction is appreciably smaller than in the  $C_6H_6$   $A_{2u}$  mode and thus the transitions from the various clusters are much closer together in energy.

\* In the present study, the  $C_6H_6$  is the guest molecule in a  $C_6D_6$  host.

Table 1  
Mole percent concentrations of guest molecules, for clusters of interest <sup>a)</sup>

Total guest (C <sub>6</sub> H <sub>6</sub> )	Monomer	Dimer	Trimer	Tetramer	(N > 4)-mer
1	0.9606	0.0376	0.00167	0.00007	0.00006
5	4.073	0.735	0.155	0.0305	0.0074
10	6.561	2.126	0.832	0.307	0.174
20	8.192	4.194	2.819	1.791	3.004
30	7.203	4.235	3.602	2.910	12.049
50	3.125	1.563	1.465	1.318	42.529
75	0.293	0.055	0.035	0.021	74.596

<sup>a)</sup> Defined by nearest neighbor only interactions. Based on Hoshen and Kopelman [57].

### 3. Experimental methods

Isotopic mixtures of benzene (C<sub>6</sub>H<sub>6</sub>) and perdeuterobenzene (C<sub>6</sub>D<sub>6</sub>) were prepared using a weighing method, and the concentrations of some of the samples were determined by mass spectroscopic methods. The benzene was "thiophene free analytical Reagent grade", obtained from Mallinckrodt Chemical Works. The perdeuterobenzene was 99.5 atom percent pure and was obtained from Merck, Sharp and Dohme of Canada, Ltd. Neither was further purified for these studies.

The benzene crystals were formed in a vacuum by spraying the vapor from the mixture onto a KBr window cooled to approximately boiling nitrogen temperatures. There was, unfortunately, no way to precisely control sample thickness.

The spectra of both the benzene and perdeuterobenzene A<sub>2u</sub> vibrational modes (about 690 cm<sup>-1</sup> and 500 cm<sup>-1</sup>, respectively) were taken on a Beckman IR-12 with a resolution of 1 cm<sup>-1</sup>. The energies were calibrated with CO<sub>2</sub> and H<sub>2</sub>O bands.

### 4. Experimental results and discussion

In the following, several spectra (figs. 1 and 2) will be discussed. Each of the sub-figures consists of an experimental spectrum and a theoretical group of lines which represent transitions due to guest clusters within the crystal. The positions and relative intensities (represented by the length of the lines) of the expected transitions were calculated by Hoshen and Kopelman [57]. The line at about 697 cm<sup>-1</sup> repre-

sents the transition due to a monomer. The lines to lower energy represent, respectively, the dimer, trimer and various tetramers. Transitions for clusters larger than tetramers were not calculated.

It can be seen by an examination of the probabilities of the various clusters in table 1, that at dilute concentrations of benzene in perdeuterobenzene only monomers should be present. In fig. 1a, the theoretical prediction for a 1% sample reflects this by showing only the monomer line. The 0.6% experimental sample spectrum shows only one line at about 697 cm<sup>-1</sup>, representing the monomer.

As the concentration is raised to about 5% (fig. 1b), the theoretical model indicates that some dimer and trimer features should be present at this concentration. The data from the 5.2% benzene samples shows the development of a peak due to the dimer. In this case, since one expects so little trimer concentration, the satellite peak represents the transition of the dimer.

As the concentration is increased to about 10% (fig. 1c), the theoretical model indicates that the amount of monomer relative to larger clusters is decreasing, as shown by the relative height of the monomer line with respect to the dashed line. Here the dashed line represents the total *non-monomer* intensity on the low energy side of the monomer and is placed at the "center-of-gravity" of the *non-monomer* lines. Since only the monomer could be resolved, the dashed line can be compared to the *non-monomer* peak. The experimental spectrum from the 8.5% sample shows good agreement between the experimental peaks and the model, both in relative intensities (monomer to the larger clusters) and in energy position (here one can compare the position of the dashed

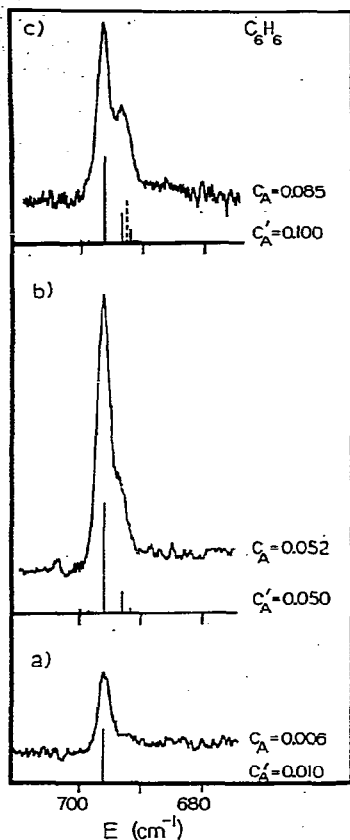


Fig. 1. (a) An infrared spectrum of 0.006 mole fraction of  $C_6H_6$  (in  $C_6D_6$ ). The theoretical calculation for an 0.01 mole fraction gives essentially only one line, due to the isolated guest species ("monomer"), while the intensity of the cluster lines (dimer, trimer, etc.) is too low to be visible. The energy position of the "calculated" monomer line has been fitted to that of the experimental peak. Dimer, trimer etc. features are too weak to be discerned. (b) The infrared spectrum of 0.052 mole fraction  $C_6H_6$  (in  $C_6D_6$ ), with comparison to a theoretical calculation for an 0.05 mole fraction sample. The latter now includes discernible "dimer" and "trimer" lines. Only the relative intensities and energies of the cluster states are meaningful. The spectrum appears to show a "dimer" hump at the correct energy and with the "expected" relative intensity. (c) Same as above, but for an experimental concentration of 0.085. The calculated cluster states (at an 0.10 mole fraction) are shown in full lines while the dashed line is a weighted composite line ("non-monomer") located at the center of gravity of the cluster (non-monomer) spectra and with a composite intensity (relative to the "monomer"). There is good agreement between the relative energy and intensity of the "non-monomer" and "monomer" lines (theoretically derived) and those of the experimental peaks.

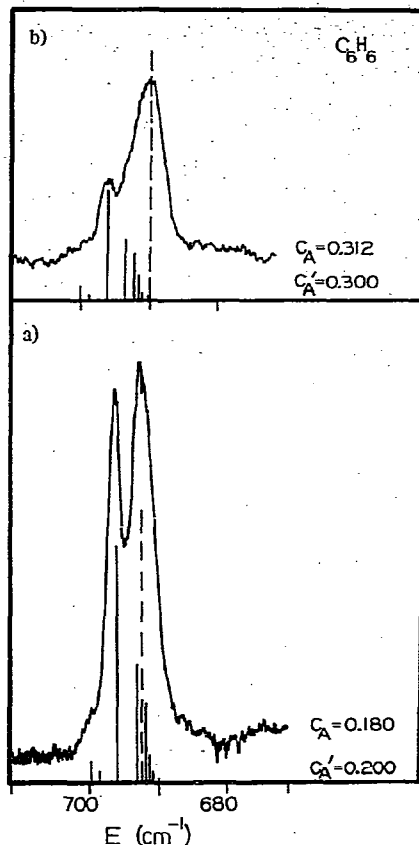


Fig. 2. (a) Same as fig. 1c, but with an experimental mole fraction of 0.180 and a calculated one [57] of 0.200. Again the agreement appears to be good for both the energy position and the relative intensity of the weighted "non-monomer" line. (b) Same as (a), except that here the position of the theoretical "non-monomer" weighted line (dashed) is fitted to the experimental peak. However, the relative intensity of the calculated 0.30 (mole fraction) sample appears to be in very good agreement with the relative intensity of the experimental peaks (derived from a sample with 0.312 mole fraction  $C_6H_6$ ). Note shift in scale.

line to the experimental *non-monomer* line).

The model predicts for a concentration of 20% (fig. 2a) that the intensity due to clusters larger than the monomer is now greater than that due to the monomer. Included here in this dashed line are the intensities due to cluster states not calculated in the theoretical model\* (i.e., pentamers and higher order

\* However at this concentration these clusters are in low concentration (3%) - see table I.

clusters). The agreement between experiment and theory is again good, both for positions and relative intensities. (Note that the pentamers etc. positions were assumed to be those of the tetramers.)

In the 30% theoretical prediction (fig. 2b), more than 50% of the intensity of the non-monomer band is due to clusters of size larger than four. Here this intensity (pentamers and larger clusters) was included in the height of the dashed (theoretical) line but its position was fitted to the experimental data (as it was not possible to calculate the positions of the larger clusters). There is again good agreement in the relative intensity of the monomer with respect to the larger clusters. The asymmetry on the high energy side of the peak due to the larger clusters is due to the dimers and trimers.

As predicted by our model, the concentration of the monomer is given by  $C_m = C_A(1 - C_A)^4$ . In this study, the area under the monomer peak was measured with a planimeter, assuming symmetrical band shapes. This area is given here by  $S_m$ , and was normalized for constant thickness of crystal. This area is then proportional to the concentration of the monomer ( $C_m$ ). Therefore  $S_m = KC_A(1 - C_A)^4$  where  $K$  is some constant.

Fig. 3 shows a plot of  $S_m$  versus  $C_A$ , both for the experimental and theoretical results. The agreement is good and indicates that the model is correct. An important aspect of this functional relationship is

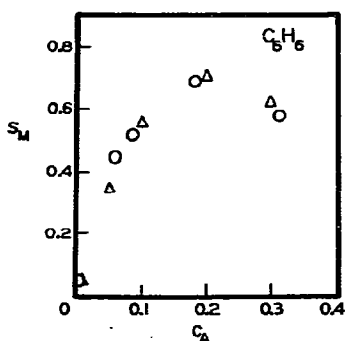


Fig. 3. Monomer spectral intensity ( $S_m$ ) versus  $C_6H_6$  mole fraction ( $C_A$ ). For the experimental points  $S_m$  was derived by integrating the area of the peak (see text). Note that the maximum is at  $C_A = 0.2$  (compare table 1). The theoretical points (triangles) are from ref. [57].

that the monomer concentration has a maximum at 20%. A plot of dimer concentration, for example, versus  $C_A$ , would show a similarly-shaped curve but shifted to higher concentration (maximum at 25%).

A better indication that the assumption of a square lattice topology is correct can be found in fig. 4. Since  $S_m = KC_A(1 - C_A)^4$ , assuming a square lattice topology,  $\ln(S_m/C_A) = 4 \ln(1 - C_A) + \ln K$ . In fig. 4,  $\ln(S_m/C_A)$  is plotted versus  $-\ln(1 - C_A)$  and yields a slope of approximately  $-4.2$ , indicating that our assumption is correct. The discrepancy from the value of four is within the experimental uncertainties. However, such a discrepancy is also expected due to contributions from larger clusters and from interactions with next nearest neighbors (which were not used in the calculations of this model).

From the isotopic mixed crystal data it is possible to calculate the pure crystal density-of-states [62,63]. This can be done with a knowledge of the interaction topology and the magnitude of the molecular pairwise exciton interactions. The pure crystal density of states for benzene, using  $M_{1111}$  of  $2.8 \text{ cm}^{-1}$ , was calculated by Hoshen and Kopelman [57] and was found to be in good agreement with earlier work done by Laufer and Kopelman [61,62].

For the simple square lattice topology the critical percolation concentration (mole fraction) is [64] 0.593. This means that a truly extended exciton band must exist, beginning at this concentration (assuming

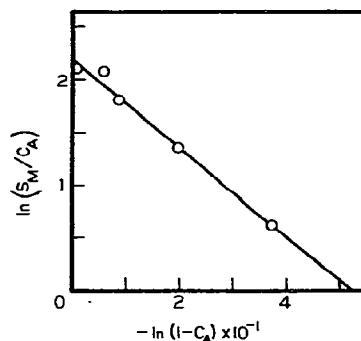


Fig. 4. Log-log plot of the monomer "reduced" spectral intensity ( $S_m/C_A$ ) versus the host mole fraction (note that  $1 - C_A = C_B$ ). This is based on a general formula  $S_m \propto C_A C_B^Z$ , where  $Z$  is the effective coordination number. The latter is directly given by the slope of the log-log line. The result is  $Z = 4.2$  (note that the negative sign of the slope was chosen arbitrarily, based on convenience).

negligible site shifts due to isotopic substitution). This band is actually expected to be formed at a lower concentration, due to the next nearest neighbor interactions. A more complete discussion on the formation of such a band is under preparation, but some general criteria have been given by Hong and Kopelman [43], and recently by Colson et al. [65] and by Kopelman et al [52,66]. As the next nearest neighbor interactions appear to be about an order of magnitude lower than the nearest ones, some pseudo-extended states may be formed well below  $C = 0.593$ . However, in the present experimental situation, where only the monomer state transition is well resolved\* from the cluster state transitions, the most pertinent question is: At what concentration will "pseudo-monomer" state transitions disappear? The reason for such a disappearance may be a reduction in intensity, a loss of the discrete nature of the eigenstate, or a combination thereof. The reduction in intensity may be caused by: (1) statistical considerations (probability of cluster formation); (2) intrinsic loss of intensity to the surrounding band, similar to that of an impurity state located, to first order, inside a host energy band [46]; (3) an apparent effect due to spectral broadening.

We notice that, assuming a true square lattice topology, small clusters, and especially monomers, survive at concentrations well above the percolation concentration [64], i.e. for  $C > 0.593$ . In first approximation, these monomers should be responsible for discrete states and transitions in the middle of the exciton band. On the other hand, the exciton band due to the "infinite" (extended) cluster is expected to behave roughly according to a model like the coherent potential approximation (CPA) [46], i.e., exhibit pseudo-Davydov components closer to the band edge (see below). However, to higher approximation, due to the next-nearest and longer range interactions, such a monomer peak might be reduced in intensity due to all three reasons mentioned above for the region below percolation ( $C < 0.593$ ). On the other hand, such pseudolocalized states might actually show up at roughly the band-center (which is roughly the same as the location of the peak in the density-of states) [62], in a manner similar to that predicted

\* It is, however, overlapped by certain trimer, tetramer, etc. transitions [57].

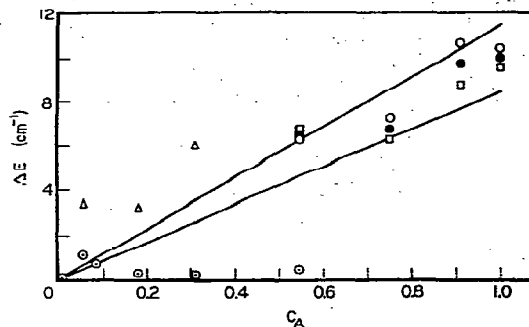


Fig. 5. Extended and localized exciton spectra.  $C_A$  is the benzene  $C_6H_6$  mole fraction.  $\Delta E$  is the distance of the peak from the center of band (monomer energy at low concentration, i.e.  $696.0 \text{ cm}^{-1}$ ), except for the full circles ( $\bullet$ ), where  $\Delta E$  represent half the energy between the highest and lowest energy peaks ( $1/2$  the "Davydov splitting"). Open circles ( $\circ$ ) represent the lower Davydov components. Squares ( $\square$ ) represent the upper Davydov components. Dotted circles ( $\odot$ ) represent "other" cluster states (dimers, trimers, ...). The solid lines represent outer limits (based on experimental errors) for the points that are due to extended exciton spectra, as predicted from the *separated band limit*, i.e. a line simply proportional to the concentration and passing through the origin (see ref. [46, eq. 146]):  $\Delta E(C_A) = C_A \Delta E^0$ , where  $\Delta E^0$  is the value for the pure crystal ( $C_A = 1$ ).

for the C-13 impurity species [61] and possibly observed [67] in the neat crystal spectrum. We feel that our spectra, as well as the earlier ones by Hall [68], do show a persistence of localized (or pseudolocalized) cluster states, up to a concentration of 0.55 (see fig. 5) and possibly 0.66 (fig. 21 of Hall [68]). Simultaneously, we see the appearance of a typical exciton band (delocalized) spectrum, starting at about 0.5 (fig. 21 of Hall [68]) and definitely at 0.55 mole fraction (fig. 5). The manifestation of the extended exciton states, covering the extended guest cluster [49], is given by the Davydov components. One can see in fig. 5 that the Davydov components of the neat crystal spectrum (100%  $C_6H_6$ ) simply "move together" monotonically with reduced  $C_6H_6$  concentration. This is exactly the expected result for the *separated band limit* (see ref. [46, eq. 146]), a limit easily justified here due to the large separation between the  $C_6H_6$  and  $C_6D_6$  molecular ("parent") energies, i.e., about  $175 \text{ cm}^{-1}$ , compared to an exciton interaction of about  $3 \text{ cm}^{-1}$ . So how is the 0.55

mole fraction exciton absorption both "extended" and "localized"? The answer is, as mentioned above, and earlier [43]: There are some small "minicluster" states [49] (monomers, etc.), giving localized (or pseudolocalized) absorptions right in the middle of the exciton energy band. We can see the beginning of this coexistence of localized and extended features at about  $C = 0.50$  (Hall [68]) and its end at about  $C = 0.67$  (Hall [68]). Certainly, at  $C = 0.75$  (fig. 5), there is very little cluster (monomer) absorption left at  $697 \text{ cm}^{-1}$ . This is probably due to the highly reduced concentration of miniclusters (monomers, etc.) at 0.75. We note that the monomer concentration (table 1) is reduced by an order of magnitude between 0.50 and 0.75 mole fraction and that of trimers by two orders of magnitude. In addition, the much denser band at 0.75 has much more of a "delocalization" effect on such cluster states (and thus more "washing out" power on their absorption lines). We emphasize that adding just one set of next nearest (interchange equivalent) pairwise interactions (say,  $M_{I II}$ ) to the effective exciton interaction topology (on an equal footing to the  $3 \text{ cm}^{-1} M_{I III}$  term) would result in a three-dimensional topology with coordination number eight (effectively *bcc*) and thus require a critical percolation concentration at about [46,65] 0.24. This would give rise to a band type exciton spectrum (i.e. quasi-Davydov components [43]). However, it would be inconsistent with the observation of only monomer-type and cluster-type spectra at 0.31 and 0.33 mole fraction (fig. 2 and Hall's fig. 21). The spectra are even inconsistent with the addition of just a pair of out-of-plane translationally equivalent interactions on an equal footing with  $M_{I III}$ , as this would give an effective *sc* (simple cubic) lattice with percolation at [64] 0.31.

Finally we note the qualitative similarity between the *heavily doped* mixed crystal spectra and those of the liquid [21]. Because of the practical absence of crystal selection rules at those intermediate concentrations [69] (i.e. near the percolation concentration), it is actually better to compare the spectra of the solid and the liquid at such a concentration rather than for the pure material, where selection rules dominate the behaviour of the crystal spectrum but not that of the liquid, even if the liquid microstructure were identical to that of the solid [40]. Preliminary results, based on  $-5^\circ\text{C}$  heavily doped crystal spectra,

indeed show a striking similarity in linewidth (and bandshape) to those of the ambient temperature liquid spectra [21].

## 5. Conclusions

Because of the excellent agreement between experiment and theory, it is indicated that the "cluster model" is correct. In spite of the relatively strongest transition dipole associated with the umbrella mode, the main exciton interactions are *not* due to long-range transition-dipole-transition-dipole terms but involve short-range interactions, probably due to 6-12 or 6-exp like potentials [16,70]. We emphasize that we get a very satisfactory agreement with the simplest possible short-range model, involving only nearest neighbor (interchange equivalent) pairwise exciton interactions. Thus, we can conclude that (1) the assumption of a square lattice topology [57] is a good approximation; (2) the molecular pairwise exciton interaction parameter used here is correct and agrees with the value found by Bernstein and Robinson [12]; (3) the calculated density-of-states for the pure benzene crystal [62] is a good representation. In addition, we seem to observe a coexistence of extended (band) and localized or pseudolocalized (cluster) states in the vicinity of the critical percolation concentration, in accordance with the cluster distribution [49,64,71,72]. Finally, our model of the umbrella mode exciton band in the liquid [21], based on short-range order and short-range interactions, is consistent with the behavior of the cluster exciton states in the solid.

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