

Method of Heavily Doped Isotopic Mixed Crystal for Determination of Exciton Splittings and Normal Modes: Raman Spectra of Naphthalene*

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Recent developments on concentrated mixed crystal exciton spectra enabled us to develop new qualitative and quantitative criteria for the identification of vibrational exciton splittings: Observation of an appropriately structured spectrum in the exciton $\mathbf{k} \neq 0$ gap. This is especially useful for Raman Spectra where the *ideal mixed crystal* approach is not very useful due to the low intensity of very dilute solid solutions and where the classical pure crystal polarization criterion is difficult to use, especially at low temperatures. The conflicting literature assignments of Raman exciton splittings for naphthalene are resolved: the eight major splittings ($\geq 4 \text{ cm}^{-1}$) found here have been missed before, while all major "Davydov" splittings ($\geq 4 \text{ cm}^{-1}$) recently reported are invalidated. The clarification of exciton splittings leads to some clarification of the normal mode assignments in the naphthalene molecule. A helpful criterion is utilized here as well: isotopic substitution has mild and predictable effects on the exciton bandwidth and splitting.

INTRODUCTION

Raman active modes of naphthalene have been studied recently by a number of workers.¹⁻⁵ While even the assignment of the fundamentals is still in some dispute, the assignment of the Davydov splittings is in a state which we can only describe as complete disagreement. On one hand, Hanson and Gee,² from their study on single crystals of naphthalene- h_8 , concluded that the Davydov splitting of Raman active modes is small (within 1 cm^{-1}). Stenman,³ in his study on Raman active modes of a powdered naphthalene- h_8 sample, agreed with the assignments suggested by Hanson and Gee. In addition, he saw some new bands which he assigned as combination bands. However, in view of the fact that the vibrational exciton structure of a molecular crystal is seldom determined by dipole-dipole interactions there is no obvious reason to expect the exciton splitting for Raman active modes to be small. Theoretical calculations^{6,7} based on atom-atom interactions do, in fact, predict a few Davydov splittings larger than 1 cm^{-1} . On the other hand, Kondilenko *et al.*⁴ claim numerous Davydov splittings and seem to have assigned most of the doublets seen in the Raman spectrum of naphthalene- h_8 to exciton splittings. We also note that Raman active modes of naphthalene- d_8 have received much less attention^{5,8} and that Davydov splitting of naphthalene- d_8 modes has not been reported so far.

The vibrational spectrum of a molecular crystal is complicated by: (i) Davydov splitting, (ii) crystal-field splitting of degenerate modes, (iii) combination bands, often intensified due to crystal-state induced Fermi resonance, (iv) presence of lattice phonons. A doublet in the crystal spectrum can arise because of any of the above effects. In this paper we demonstrate the effectiveness of isotopic mixed crystal studies for determining the nature of the splitting and show that the doublet (or multiplet, in general) structure of the neat

crystal is perturbed severely in the isotopic mixed crystal only for the first case, i.e., Davydov splitting. A careful study of mixed crystal systems, combined with the results from neat crystals, can thus reveal the correct nature of the Davydov splitting. However, in contrast to electronic and infrared exciton studies, the *ideal mixed crystal* approach, utilizing very dilute isotopic solid solutions, is not practical for Raman studies, and the use and understanding of heavily doped mixed crystals is almost mandatory. Also, while polarization studies of neat crystals give an excellent criterion for the establishment of Davydov splittings in principle, in practice difficulties arise due to low intensity, low temperature crystal cracking, etc.

We present an isotopic mixed crystal study on naphthalene. Our result is not consistent with any of the previous works in regard to the assignments of Davydov splittings. We have seen Davydov splittings of about $4-5 \text{ cm}^{-1}$ on four fundamentals, for both naphthalene- h_8 and naphthalene- d_8 , in qualitative agreement with the theoretical calculation by Pawley and Cyvin.⁶ We also contribute below towards a final assignment of the naphthalene molecule normal modes.

EXPERIMENTAL

Single crystals of naphthalene- h_8 (zone refined and potassium treated) and its various concentration mixtures with naphthalene- d_8 were grown in a capillary under vacuum by the Bridgman technique. The capillary containing the crystal was inserted in the Raman spectrometer. It was cooled by a flow of cold nitrogen vapor which provided a temperature of about 100°K . The spectra were recorded photoelectrically on a Ramalog-Spex double spectrometer model 1401. The excitation was provided by a Coherent Radiation Laboratory argon ion laser. The 4880 \AA laser emission, selected by a suitable interference filter, was used as the excitation line. The intensity problem at very small slitwidths did not permit us to investigate splittings

less than 3 cm^{-1} . The naphthalene- d_8 samples were from ICN (International Chemical and Nuclear Corporation, Irvine, California), 99.5% atom deuterium.

RESULTS

Except for the modes of naphthalene- h_8 in the regions $380\text{--}475\text{ cm}^{-1}$ and $930\text{--}960\text{ cm}^{-1}$, and modes of naphthalene- d_8 in the regions $340\text{--}430\text{ cm}^{-1}$ and $820\text{--}840\text{ cm}^{-1}$, the spectra of the mixed crystals could be explained, *within the available spectroscopic resolution*, as a superposition of naphthalene- h_8 and naphthalene- d_8 spectra. Specifically, no new band appeared in the mixed crystal spectra that was not present in the spectra of either of the pure components.

The results on modes in the region $380\text{--}475\text{ cm}^{-1}$ of both naphthalene- h_8 neat crystals and mixed crystals are shown in Figs. 1 and 2. In the mixed crystal with 10% naphthalene- h_8 we see single sharp modes at 392

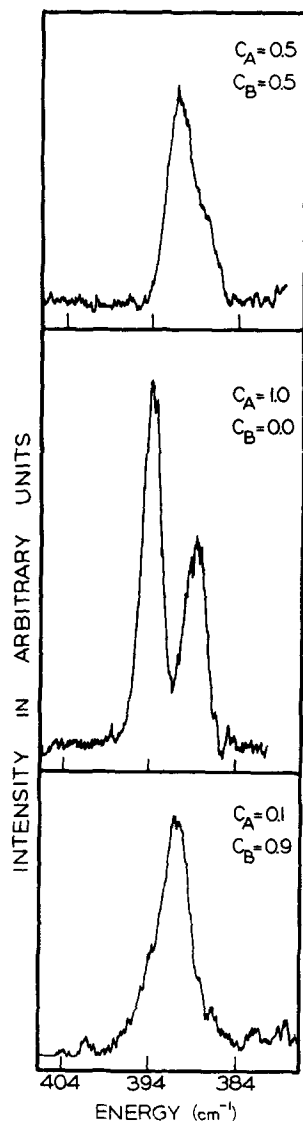


FIG. 1. Raman spectrum of the 392 cm^{-1} fundamental of naphthalene- h_8 in both the neat and the isotopic mixed crystals. C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

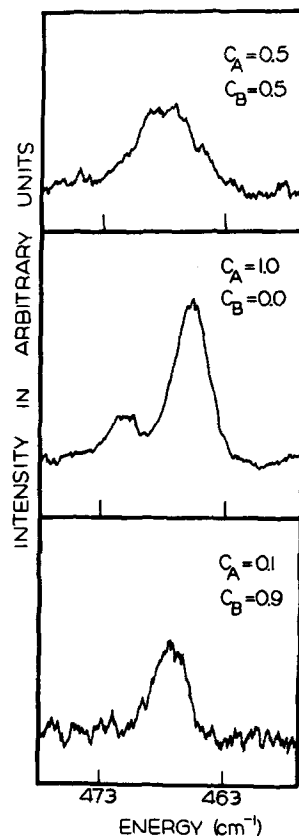


FIG. 2. Raman spectrum of the 467.5 cm^{-1} fundamental of naphthalene- h_8 in the neat and the isotopic mixed crystals. C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

and 467.5 cm^{-1} . In the neat crystal of naphthalene- h_8 these bands split to give doublets at frequencies 388, 394 and $466, 471\text{ cm}^{-1}$, respectively. In the crystal with a 50%–50% mixture of naphthalene- h_8 and naphthalene- d_8 the doublet structures of both these bands disappear and the spectra consist of broad bands with peaks at 392 and 468.5 cm^{-1} . Figure 3 displays the Raman spectra of naphthalene- h_8 in the region $930\text{--}960\text{ cm}^{-1}$ for both the neat crystal and the mixed crystal. Because of the intensity problem we do not have the spectrum of a 10% naphthalene- h_8 mixed crystal. In the neat crystal of naphthalene- h_8 we see doublets at frequencies 933.5, 937.5 and 947, 951 cm^{-1} . In the 50% naphthalene- h_8 mixed crystal the doublet features of both these bands are replaced by broad bands with peaks at 935 and 949.5 cm^{-1} .

It is interesting to compare our results with those obtained by Hanson and Gee.² In the region of 390 cm^{-1} they see two modes, of frequencies 388 and 392 cm^{-1} at room temperature, and assign them as b_{2g} and b_{1g} fundamentals, respectively. They see only one mode near 466 cm^{-1} at room temperature and assign this as a b_{2g} mode. The interpretation of Suzuki *et al.*¹ differs on the 388 cm^{-1} b_{2g} mode. They put it at 878 cm^{-1} . Stenman³ agrees with the interpretation of Hanson and Gee.² In addition he sees a doublet near 466 (465 and 470 cm^{-1}). He assigns the new mode seen at 470 cm^{-1} as a combination of the 392 cm^{-1} fundamental and a lattice vibration. Hanson and Gee report only

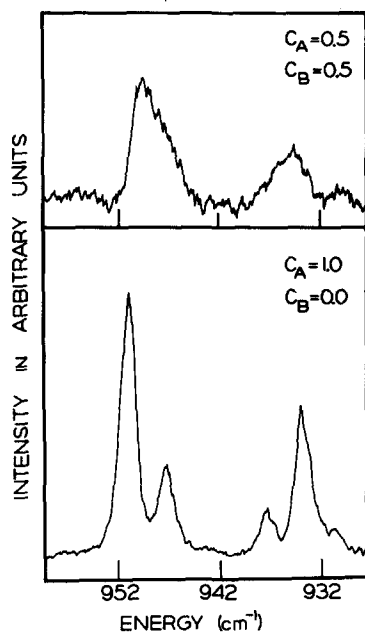


FIG. 3. Raman spectrum of naphthalene- h_8 in the region 930–960 cm^{-1} for both the neat and the mixed crystals. C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

one mode, at 950 cm^{-1} , for the Raman spectrum in the region 930–960 cm^{-1} . They assign this as a b_{1g} fundamental. A vibrational mode observed at 938 cm^{-1} in the crystal fluorescence^{9,10} of naphthalene- h_8 and at 936 cm^{-1} in the vapor spectrum^{8,11,12} has been assigned as a b_{3g} fundamental. Stenman³ sees a doublet at 950 cm^{-1} (947, 951 cm^{-1}), but only one transition at 936 cm^{-1} . He agrees with the Hanson and Gee assignment of the 951 cm^{-1} transition as a b_{1g} mode and suggests that the additional line at 947 cm^{-1} can be assigned as an overtone of the 475 cm^{-1} b_{1u} fundamental.

The results on the modes of naphthalene- d_8 in the regions 340–430 cm^{-1} are presented in Figs. 4 and 5. In the mixed crystal with 10% naphthalene- d_8 , single transitions are observed at 348.5 and 417 cm^{-1} , which in the neat crystal split to form doublets with frequencies 345.5, 349.5 and 415, 420 cm^{-1} , respectively. In the 50% mixture we see only two broad bands with peaks at 348 and 416 cm^{-1} . The spectra for the region 820–840 cm^{-1} are displayed in Fig. 6. In the spectrum of 10% naphthalene- d_8 mixture we see two peaks, at 828.5 and 834 cm^{-1} . The spectrum of neat naphthalene- d_8 itself is not very clear, but it can be seen that there are four transitions at frequencies 826, 831 and 834, 838 cm^{-1} whereas in the 50% mixed crystal we see only two broad bands at frequencies 829 and 834 cm^{-1} . Naphthalene- d_8 Raman active vibrations are not well understood and normal mode assignments have not been well established. The recent Raman investigation of Bree and Kydd⁵ on single crystals of naphthalene- d_8 reports lines at 348, 410, 831, and 838 cm^{-1} . They assign the modes at 348 and 410 cm^{-1} as b_{1g} and b_{2g} fundamentals. They agree with the previous assignments of the vibration at 831 cm^{-1} by McClure¹³ and Hollas,⁸ as a b_{3g} fundamental and confirm the

assignment of the 838 cm^{-1} mode by Luther *et al.*¹⁴ as an a_g fundamental.

DISCUSSION

The fact that the infrared active modes do not seem to appear in the Raman spectrum of a dilute (10%) isotopic mixed crystal and the fact that Raman spectral singlets do not broaden in the mixed crystal (10%–90%) suggest that the site symmetry is preserved in the mixed crystal, within the sensitivity of the method. The preservation of the “mutual exclusion rule” between infrared and Raman active bands even in the heavily doped systems (like 50%) is consistent with the restricted-Davydov-Frenkel limit, in which only near neighbor dynamic interactions are important¹⁵ as well as with a coherent-potential-approximation model based on the above limit and on a static crystal field that preserves the site symmetry.¹⁶ In other words, a model based on (1) static field site symmetry, (2) restricted-Frenkel limit, and (3) coherent potential approximation, while ignoring configuration interaction (intermolecular Fermi resonance), would be

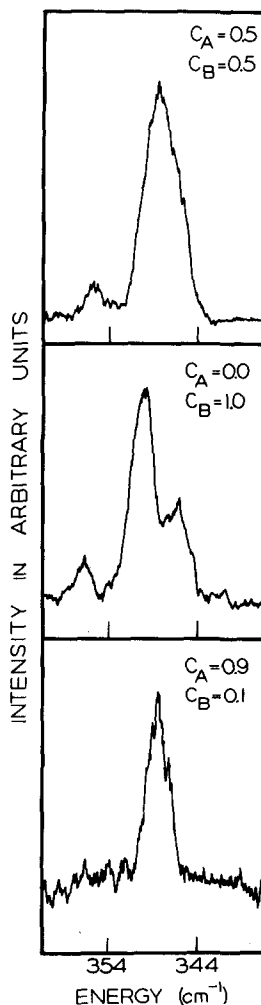


FIG. 4. Raman spectrum of the 348.5 cm^{-1} fundamental of naphthalene- d_8 in the neat crystal and the mixed crystals. The transition at 356.5 cm^{-1} is, perhaps, due to isotopic impurities ($C_{10}D_7H-\alpha$ and $-\beta$). C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

consistent with our results. However, our results do not prove the correctness of such a model.

Before analyzing our results we would like to present a detailed discussion about the correlation of a doublet structure in the neat crystal spectrum with the spectrum of an isotopic mixed crystal. Such a doublet (or multiplet) structure in the neat crystal can arise as a result of (i) static crystal field splitting of a degenerate mode, (ii) crystal field shifts which might bring two normal modes close in energy, (iii) a fundamental near a combination band, where the latter may be intensified due to crystal induced Fermi resonance, (iv) presence of lattice phonons; (v) Davydov splitting.

Crystal field splitting of a degenerate mode arises because the molecular symmetry is usually reduced in the crystal to the site symmetry. The naphthalene symmetry (D_{2h}) is too low for necessary degeneracies, but there may be accidental ones. According to our previous discussion the site symmetry remains preserved in the isotopic mixed crystal. Thus, a crystal field splitting of degenerate modes in the neat crystal should not change much in the isotopic mixed crystal. The same argument holds for a doublet produced by two normal modes which are brought close to each other by static crystal field shifts. For combination bands that involve an intramolecular combination of normal modes, the previous consideration is again applicable; the neat crystal doublet feature should again be retained in the isotopic mixed crystal.

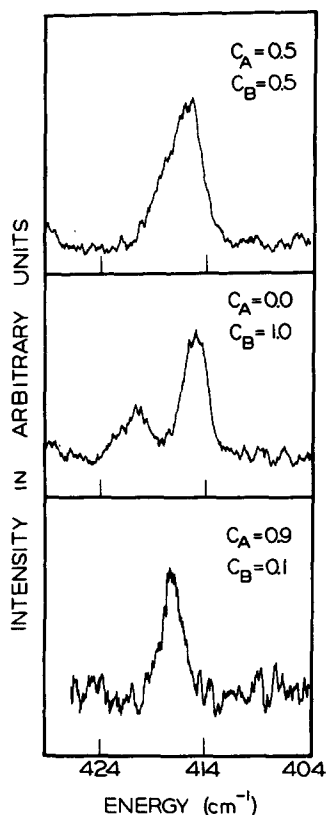


FIG. 5. Raman spectrum of the 417 cm^{-1} fundamental of naphthalene- d_8 in both the neat and the mixed crystals. C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

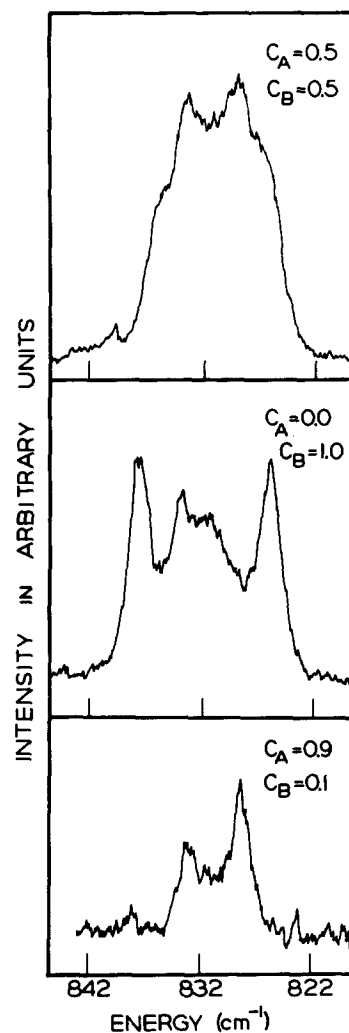


FIG. 6. Raman spectrum of naphthalene- d_8 in the region $820\text{--}840\text{ cm}^{-1}$ for both the neat and the isotopic mixed crystals. C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

The case of phonon (intermolecular vibrations) participation requires a more careful consideration. Our work¹⁷ on phonons in isotopic mixed crystals shows that the phonon bandwidths in these crystals are large compared to the deuteration shifts of the phonon frequencies. The isotopic mixed crystal system in this respect represents the *amalgamation limit*. In this limit the phonon spectrum changes in nearly a linear fashion with concentration of the isotopic component. In view of this, except for some frequency shifts, the phonon structures should be retained in the isotopic mixed crystal. Finally, we would like to consider the structures due to exciton splitting. The exciton (interchange, factor group, Davydov) splitting for a vibrational excitation is generally much smaller than the corresponding isotopic (deuteration) shift. For this reason the vibrational excitation of the isotopic mixed crystal system falls into the *separated band limit*. This limit implies that the $\mathbf{k}=0$ selection rules break down in the mixed crystal and that transitions to all crystal levels (previously the \mathbf{k} levels of the neat crystal) become accessible. This leads to both broadening and coalescing

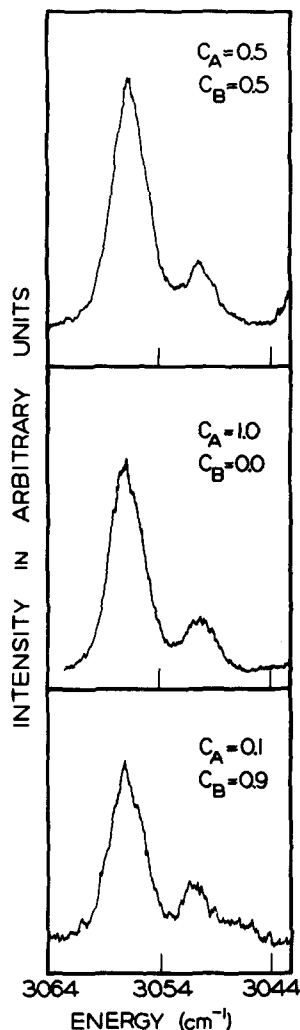


FIG. 7. Raman spectrum of the 3057 cm^{-1} fundamental region of naphthalene- h_8 in the neat and the isotopic mixed crystals. C_A and C_B are, respectively, the concentrations of naphthalene- h_8 and naphthalene- d_8 .

of the doublet structure in going from the neat crystal to the heavily doped mixed crystal. Also, in the separated band limit, only a major single peak corresponding to the monomer level will appear in the limit of low concentration (practically up to 10%) of the component being studied. We conclude from the above consideration that the doublet structure of the neat crystal may be perturbed severely in the isotopic mixed crystal only if it is due to Davydov splitting (case v above).

In light of the discussion presented above, our spectrum clearly shows that the previous assignments^{2,3} of the doublets seen near 394, 466, and 950 cm^{-1} in the spectrum of the neat naphthalene- h_8 crystal are erroneous and establishes that these doublets (for both naphthalene- h_8 and naphthalene- d_8) are due to Davydov splitting. A summary of our results is presented in Table I.

The assignment of the 388 cm^{-1} frequency by Hanson and Gee² as a b_{2g} fundamental cannot be correct. An attempt will be made in the future to completely assign the normal mode vibrations of naphthalene, based on Raman studies along with data on the fluorescence and

phosphorescence of naphthalene in mixed crystals. Some naphthalene- d_8 results follow below.

To compare the nature of the doublets reported above with that of some other doublets seen in the neat crystal spectra we present the results of our isotopic mixed crystal study on the doublet near 3057 cm^{-1} (3051 and 3057 cm^{-1}) in Fig. 7. It can be seen that this doublet feature remains unperturbed in the isotopic mixed crystals, revealing that it is not due to Davydov splitting. Hanson and Gee² have assigned the transition at 3057 cm^{-1} to an a_g fundamental. The transition at 3051 cm^{-1} could be another fundamental. Considering that the 3000 cm^{-1} region is rich in possible vibrations, it is difficult to make an unambiguous assignment, and it could be a combination band too. We would like to comment here on the Davydov splittings reported by Kondilenko *et al.*⁴ They report splittings $\geq 4\text{ cm}^{-1}$ on three fundamentals, at 514 cm^{-1} ($514, 510\text{ cm}^{-1}$), 761 cm^{-1} ($761, 755\text{ cm}^{-1}$), and at 3062 cm^{-1} ($3062, 3055\text{ cm}^{-1}$). The doublet $514, 510\text{ cm}^{-1}$ has been established^{2,18} to be due to two fundamentals (a_g and b_{3g} respectively), which may be brought closer to each other by crystal field effects. Our results reported above show clearly that the doublet $3062, 3055\text{ cm}^{-1}$ (our values are 3057 and 3051 cm^{-1}) is not due to Davydov splitting. We have also investigated the doublet $761, 755\text{ cm}^{-1}$ and the result shows that this feature is again not a Davydov splitting. Therefore, none of the larger doublets reported in Ref. 4 are due to Davydov splitting. As we have mentioned earlier, the intensity problem did not allow us to investigate with confidence splittings $\leq 3\text{ cm}^{-1}$. For this reason we cannot comment at this stage on other splittings ($\leq 3\text{ cm}^{-1}$) reported in Ref. 4, though, on statistical grounds, they are more likely to be genuine exciton splittings. The single modes seen in the crystals with 10% guest concentration are the guest monomer transitions and give approximately the centers of the exciton band. These are listed in the fifth column of Table I. We use the word "approximately" in the sense that we assume the static *site shift*¹⁹ term to be the same for a naphthalene- h_8 or naphthalene- d_8 environment. This is supported by our previous observation about unbroadened singlets in concentrated mixed crystals.

The difference between the mean frequency of the Davydov components and the center of the band could be because of the interactions between translationally equivalent molecules¹⁹ (*translational shift*). This difference is listed in Col. 6 of Table I and for most of the bands is near 1 cm^{-1} . Considering the resolution available to us, we are not sure whether this difference is real. However, if such difference exists, it is in accord with the theoretical results of Harada and Shimanouchi,²⁰ who have shown that in the case of *gerade* modes one has to include the interaction between translationally equivalent molecules in order to get a better fit with the experimental result. Alternative explanations for this difference may involve *band mixing*, due to higher

TABLE I. Some normal modes and crystal splittings of naphthalene- h_8 and naphthalene- d_8 .

Component studied	Neat crystal frequencies (cm ⁻¹)		Davydov splitting (cm ⁻¹)		A = Mean of the observed Davydov splitting (cm ⁻¹)	B = Monomer transition 10% guest solution (cm ⁻¹)	The difference A - B (cm ⁻¹)	Peak positions in 50% mixture (cm ⁻¹)	Interchange equivalent pairwise interaction (cm ⁻¹)
	Exptl	Calc ^a	Exptl	Calc ^a					
Naphthalene- h_8	388	417	6	4	391	392	+1	392	0.75
	394	421							
	466	481	5	9	468.5	467.5	-1	468.5	0.63
	471	490							
	933.5	940	4	0	935.5			935	0.50
	937.5	940							
	947	953	4	1	949			949.5	0.50
	951	954							
Naphthalene- d_8	345.5		4		347.5	348.5	+1	348	0.50
	349.5								
	415		5		417.5	417	-0.5	416	0.63
	420								
	826		5 ^b		828.5	828.5	0	829	0.63 ^b
	831 ^b								
	834		4		836	834	+2	834	0.50
	838								

^a G. S. Pawley and S. J. Cyvin, J. Chem. Phys. **52**, 4073 (1970).

^b It is difficult to get an accurate value as the band at 831 cm⁻¹ is very broad.

order interactions, or the previously neglected environment dependence of the *site shift*. The last column of Table I gives the values for the interchange equivalent pairwise molecular interaction term,¹⁹ on the assumption of only nearest neighbor interactions.

Next we would like to compare our results with the calculations of Pawley and Cyvin⁶ on naphthalene- h_8 . To our knowledge no such calculation has been done for Davydov splittings in naphthalene- d_8 . Such comparisons of the calculated values with our experimental findings are made in the two subcolumns of Cols. 1 and 2 of Table I. In their calculation, Pawley and Cyvin used a 6-exp potential model for crystal interactions and only considered interactions between atoms with separations up to 5.5 Å. It can be seen that the correlation between the experimentally observed Davydov splittings and the calculated Davydov splittings is not very good. Our results on the bands at 392 and 467.5 cm⁻¹ are only in qualitative agreement with their predictions. The results show a larger Davydov splitting for the band at 392 cm⁻¹ compared with that for the band at 467.5 cm⁻¹. This seems to follow the order of the relative exciton bandwidths, rather than the Davydov splittings, given by the calculation of Pawley and Cyvin.²¹ The agreement between the calculated Davydov splitting and its observed value for the in-plane b_{3g} mode at 935.5 cm⁻¹ is very bad. However, a qualitative agreement with their calculation is that the latter predicts for almost all other bands Davydov splittings less than 4 cm⁻¹.

Several attempts^{5,8,13,14} have been made in the past

to assign the fundamentals of naphthalene- d_8 and correlate them with those of naphthalene- h_8 . There seems to be a general consensus for the assignment of the 348.5 and 417 cm⁻¹ modes as the b_{1g} and b_{2g} fundamentals, respectively, and that they correlate with the 392 cm⁻¹ (b_{1g}) and 467.5 cm⁻¹ (b_{2g}) fundamentals of naphthalene- h_8 . If we compare the magnitude of the Davydov splittings of these modes of naphthalene- d_8 with those of the corresponding modes of naphthalene- h_8 we see that they are very similar. This is in agreement with what would be expected from a simple minded theory. Another interesting similarity to be noticed is the relative intensity of the Davydov components for these two fundamentals. This feature of the naphthalene- d_8 spectrum mimics the behavior of the naphthalene- h_8 spectrum. On the basis of these two similarities we feel that the region 820–840 cm⁻¹ of the naphthalene- d_8 spectrum correlates with the region 930–960 cm⁻¹ of the naphthalene- h_8 spectrum. This suggests that the 828.5 and 834 cm⁻¹ modes of naphthalene- d_8 correspond, respectively, to the 935.5 cm⁻¹ (b_{3g}) and 949 cm⁻¹ (b_{1g}) fundamentals of naphthalene- h_8 . This assignment of the 828.5 cm⁻¹ line as a b_{3g} fundamental of naphthalene- d_8 agrees with the assignments made by McClure¹³ and Hollas.⁸ However, a discrepancy arises with previous assignments of the 834 cm⁻¹ line as an a_g mode^{5,8,14}. We have not seen a splitting more than 3 cm⁻¹ on any a_g modes of naphthalene- h_8 or any other a_g modes of naphthalene- d_8 . In view of all these facts we suggest that the 834 cm⁻¹ mode is, perhaps, a b_{1g} fundamental²² of naphthalene- d_8 and

corresponds to the 949 cm^{-1} b_{1g} fundamental of naphthalene- h_8 . In this crowded region of naphthalene- d_8 ($820\text{--}840\text{ cm}^{-1}$) it is also likely that some interband perturbation (exciton configuration interaction) is operative. This might be indicated by the anomalous isotope effect on the Davydov splitting of the 828 cm^{-1} band (Table I) and deserves further study, along the lines outlined before for exciton-Fermi resonance interactions.²³ It should be emphasized that, in general, the assignment of normal modes is greatly helped by the criterion²³: isotopic substitution has mild and predictable effects on the restricted¹⁵ Frenkel exciton bandwidth and splitting.

Finally, we would like to comment on the theoretical conclusion reached by Ting²⁴ about the relative intensity of Davydov components. He predicted that only the symmetric combination A_g factor group state should appear in the crystalline Raman spectra. Our result clearly shows that such a view is incorrect. Though in most cases studied here there is a difference in intensity between the two components, it can be seen that in the cases of the 392 cm^{-1} mode of naphthalene- h_8 and the 348.5 cm^{-1} mode of naphthalene- d_8 , the relative intensities are not very different. Ting's point of view has already been criticized by Hanson and Gee.²

CONCLUSION

While our study on Davydov splittings is not complete, due to instrumental difficulties, it suffices to demonstrate the utility and simplicity of the *heavily doped isotopic mixed crystal method* for the identification of such splittings, and thereby of exciton bands. Also, while our present normal mode assignment is only fragmentary, it also suffices to show the utility of Davydov splittings for such an assignment, and thereby the utility to normal mode assignments of the same heavily doped isotopic mixed crystal method.

ACKNOWLEDGMENT

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²⁰ I. Harada and T. Shimanouchi, *J. Chem. Phys.* **44**, 2016 (1966).

²¹ Their calculation shows that though the Davydov splitting is only 4 cm^{-1} , the exciton band is about 12 cm^{-1} wide for the first mode.

²² It should be noted that this is the only a_g assigned mode by Bree and Kydd (Ref. 5) that *cannot* "be identified from the strength and depolarization ratios." Actually their observed depolarization is typical of a b_{1g} mode. However, because of the spectral crowding in this region one cannot exclude the a_g assignment: a b_{2g} fundamental may be complicating the situation—note the gas phase b_{2g} frequency (829 cm^{-1}) of D. B. Scully and D. H. Whiffen, *Spectrochim. Acta* **16**, 1409 (1960); *J. Mol. Spectry* **1**, 257 (1957). This assignment of two high energy b_{2g} modes ($760, 829\text{ cm}^{-1}$) for naphthalene- d_8 agrees also with our observation that there is no b_{2g} naphthalene ($-h_8$ or $-d_8$) mode below 400 cm^{-1} . It also agrees with the statement by Bree and Kydd that for naphthalene- d_8 "two high-energy (b_{2g}) modes have not been identified, and these must either be too weak to be found or must be hidden under stronger lines."

²³ R. Kopelman, *J. Chem. Phys.* **44**, 3547 (1966).

²⁴ C. h. Ting, *Spectrochim. Acta* **24A**, 1177 (1968).