The 5.6-eV absorption in the anthracene crystal has been attributed to a transition which is derived from a molecular transition from the ground state to an excited state, which is again a linear combination of two configurations[11,30]:

$$\psi_{\mathrm{mol}}{}^{+} = (1/\sqrt{2})\,(\chi_{5\to 10} + \chi_{6\to 9}), \qquad (14)$$

and the transition at 6.5 eV has been attributed to the $\psi_{\mathrm{mol}}{}^{-}$ combination in (14). The appearance of these transitions should thus lead to decreases or inflection points in the photocurrent yield where these transitions set in.

Similar considerations apply to tetracene, except that none of the excited states are exactly degenerate. The different configurations making up the linear combinations of the excited states are therefore not equally weighted as they are in anthracene.

It is thus shown that when the autoionization mechanism is invoked, the appearance of photoconductivity peaks on the low-energy portion of spectral absorption peaks can be explained, even though there is no specific dependence of the photocurrent on the absorption coefficient.

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Electronic States of Mixed Molecular Crystals: Singlet Excited States of Isotopic Impurities in Crystalline Benzene and Naphthalene

BAT-SHEVA SOMMER AND JOSHUA JORTNER
Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel

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In this paper the one-particle Green's-function method has been applied for the study of singlet excited states of isotopically mixed crystals of benzene and naphthalene. Calculations of energy levels, of excitation amplitudes, and of line-shape functions were performed, considering both bound and virtual impurity energy levels. The present treatment relates experimentally observable properties for the dilute mixed crystals with the exciton density-of-states function of the pure crystal. The available experimental data for mixed crystals can be adequately accounted for using empirical data for the exciton density-of-states functions derived from hot-band spectroscopy. The theoretical density of states for naphthalene based on the transition-octupole coupling terms provide only qualitative agreement with the experimental mixed-crystal data. We consider the applicability of simple perturbation expressions by using a moments-expansion method of the Green's function. Finally, we discuss the information on the intermolecular interactions derived from the moments of the density-of-states functions.

I. INTRODUCTION

During recent years, it has become apparent that in view of the inherent difficulties involved in the theoretical calculations of the electronic states of solids, *a priori* theoretical calculations based on the Hartree–Fock scheme are not practical at present. In many-band structure calculations, errors of several electron volts are involved in the location of the energy levels; these errors are considerably larger than the actual level spacing. The current interpretation of the optical spectra of metals and of semiconductors is currently focused on the application of general theoretical ideas, rather than on *a priori* theoretical computations. Theoretical concepts such as pseudopotential theory[1] or the nature of the interband density-of-states function and its analytical singularities[2] have been very fruitful in providing a coherent semiquantitative description of the electronic excited states of solids.

The theoretical interpretation of the electronic states of molecular crystals of organic molecules[3] still lags far behind the experimental data which are available. The theoretical calculations within the framework of the tight-binding Frenkel exciton limit are based on the implicit assumption that the molecular wavefunctions are known. Reasonably good theoretical results were obtained for optically allowed singlet excited states where a major contribution to the intermolecular interaction arises from long-range dipole–dipole interactions[3b,3c] and for triplet exciton states where the interactions are dominated by short-range electron

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exchange interactions.[3c] The situation is far less satisfactory concerning the first singlet excited states of naphthalene and benzene crystals, which have a unique parentage in the α free-molecule excited state ($^1B_{2u}$ state in benzene and $^1B_{3u}$ state in naphthalene).[4–7] Because the transition dipole moments to the α singlet states are very small, a description of these crystal states within the framework of the tight-binding Fraenkel exciton limit implies that the intermolecular interactions are dominated by transition-octupole–transition-octupole coupling.[4–6] However, the transition-octupole moments required to fit the Davydov splittings and the polarization ratios in crystalline naphthalene and benzene are considerably larger than those predicted by π-electron theory.[5,6] Because of the poor quality of the available molecular wavefunctions, the disagreement between the theoretical and the fitted octupole moments may not really indicate a serious discrepancy between theory and experiment. Nevertheless, this apparent discrepancy motivated the suggestion[7] to include charge-delocalization effects by examining the configuration interaction between Fraenkel exciton states and charge-transfer states. A recent critical reexamination of the possible location of charge-transfer states in molecular crystals[8] which are close to the positions predicted by a classical analysis[9] (i.e., appreciably higher in energy than assumed before[7]) indicates that the effect of charge-transfer interactions is much less dramatic than originally assumed. According to this analysis,[8] octupole–octupole (and possibly higher monopoles) interactions contribute about two-thirds of the Davydov splittings and determine the polarization ratios of the Davydov components. In view of these difficulties inherent in the theoretical analysis, it is tempting to attempt to bypass *a priori* calculations of the intermolecular interactions based on the molecular wavefunctions, and to seek alternative sources of theoretical and experimental data which will provide physically meaningful information on the interactions in singlet exciton states of these molecular crystals.

Up to date, most of the theoretical and experimental effort in the studies of the excited states of molecular crystals of organic molecules were centered on $\mathbf{k}\approx 0$ crystal states. It was recently pointed out that new information concerning the exciton band structure and the intermolecular interactions can be derived from two sources:

(a) Information on the exciton band structure can be obtained from hot-band spectroscopy in molecular crystals, that is, transitions from an extremely narrow vibrational exciton band, corresponding to the ground electronic state, to an electronic exciton band.[10–12] This method, first proposed by Rashba,[10] was studied in detail by Colson, Kopelman, and Robinson.[11] It was pointed out by Colson *et al.*[11] that when the intermolecular interactions are dominated by short-range interaction, the diagonal matrix elements of the crystal energy matrix for each $\mathbf{k}$ are approximately equal. This situation of accidental degeneracy leads to the conclusion that the transition moments for the hot band are approximately independent of $\mathbf{k}$, so that the hot absorption band is proportional to the exciton density of states function. The first experimental data for hot-band spectroscopy in crystalline naphthalene at 77°K were reported by Shpak and Sheka.[3a,13] A careful study of the temperature dependence of these transitions by Colson *et al.*[12] indicates that phonon contributions are not negligible and that only below 30°K can phonon broadening be eliminated. The beautiful experimental work of Colson, Hanson, Kopelman, and Robinson yields reliable experimental data for the exciton density of states function. (In what follows, we shall refer to these densities of states as the experimental density-of-states functions.)

(b) The optical properties of dilute mixed crystals of isotopically substituted molecules can be related to the exciton density of states functions of the pure crystal.[14,15] This treatment, based on the one-particle Green's-function method, rests on the implicit assumption that the perturbation induced by the introduction of an isotopically substituted molecule is local. Experimental data for impurity energy levels in isotopically mixed crystals of naphthalene/deuteronaphthalene[16] and in benzene/deuterobenzene[17] are at present available, and experimental results for the excitation amplitudes[18] in isotopically mixed naphthalene crystals were also reported. With the availability of theoretical data for the density-of-states function derived from octupole–

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octupole interactions in naphthalene,[19] and the experimental density of states in naphthalene and in benzene,[12] the energy levels of dilute mixed crystals are now amenable to a theoretical study.

In the present work, we consider the theory of isotopically mixed crystals, using the Green's-function method.[15] Previous studies of the problem by Philpott and Craig[19] and by Ross and Body[20] utilized the original Koster–Slater recipe,[21] which requires the knowledge of the exciton-energy-dispersion curve. Body and Ross[20] also derived approximate relations using the second moment of the exciton density of states which was related to the intermolecular interactions. The present treatment directly relates experimentally observable quantities for dilute mixed crystals with the exciton density-of-states function. The latter can be obtained either from theory or from experiment. The energy levels of dilute mixed crystals are rather sensitive to the exciton density-of-states function, and will in some cases provide useful complementary information concerning the nature of the intermolecular interactions which determine the band structure in the pure crystal. In particular, the first and second moments of the distribution of states in the pure crystal are of interest. Finally, we consider the nature of bound and virtual impurity states[15] and present theoretical predictions concerning the location and the line shape expected for virtual scattering states in these systems.

II. IMPURITY ENERGY LEVELS IN BENZENE AND IN NAPHTHALENE CRYSTALS

Consider an infinitely dilute mixed crystal consisting of guest and host molecules which differ by isotopic substitution. Furthermore, we shall assume that:

(a) The pure crystal is characterized by a center of symmetry.

(b) The guest molecules substitute the host molecules without any change in molecular orientation.

(c) Crystal-field effects on the density of states of the pure crystal exciton band are negligible. The calculations of Craig *et al.*[3b,5] indicate that the effects of crystal-field mixing on the energy levels in the first singlet exciton bands of benzene and naphthalene are small.

(d) The isotopic impurity is characterized by a local perturbation. The perturbation strength, U_0, is given by[3c,19]

$$U_0=\Delta\epsilon^f_{\text{guest}}-\Delta\epsilon^f_{\text{host}}+D^f_{\text{guest}}-D^f_{\text{host}}, \qquad (1)$$

where $\Delta\epsilon^f_{\text{guest}}$ and $\Delta\epsilon^f_{\text{host}}$ correspond to the gas-phase excitation energies of the impurity molecule and the molecules constituting the pure crystal, respectively. D^f_{guest} and D^f_{host} are the environmental D^f terms of the guest molecule in the mixed crystal and of the host molecule in the pure crystal, respectively. These are given by

$$D^f_{\text{guest}}=\sum_{i\neq p}\langle|\,\phi_i^0\,|^2\,|\,v_{ip}\,|\,|\,\psi_p^f\,|^2-|\,\psi_p^0\,|^2\rangle + \text{dispersion terms},$$

$$D^f_{\text{host}}=\sum_{i\neq j}\langle|\,\phi_i^0\,|^2\,|\,v_{ij}^0\,|\,|\,\phi_j^f\,|^2-|\,\phi_j^0\,|^2\rangle + \text{dispersion terms}, \qquad (1')$$

where ψ_p^0 and ψ_p^f are the ground-state and the excited-state molecular wavefunctions of the impurity molecule (located at the crystal site p) while ϕ_i^0 and ϕ_i^f correspond to the ground-state and to the excited-state molecular wavefunctions of a host molecule (located at site i). v_{ij}^0 and v_{pj} represent the host–host and the guest–host Coulomb interaction potentials, respectively. Thus, U_0 corresponds to the change in the molecular excitation energy between the guest and the host molecules in the host crystal. It was recently pointed out by Colson[17] that in the case of isotopically mixed benzene crystals the term $D^f_{\text{guest}}-D^f_{\text{host}}$ in Eq. (1) should be taken into account. As the D^f_{host} term for the first singlet states of crystalline naphthalene and benzene is of the order of -200–-400 cm^{-1},[17,18] a diagonal contribution to the local perturbation strength of a few centimeters^{-1}, arising from the term $(D^f_{\text{guest}}-D^f_{\text{host}})$, is possible.

(e) In the case of isotopic substitution, other contributions to the general perturbation matrix[15] $\mathbf{V}$ are small, relative to the contribution of the local perturbation U_0. Two types of such terms have to be considered[3c,19]: changes in the resonance interactions and corrections to environmental shifts. The changes in the intermolecular coupling terms induced by the presence of the impurity are given by[3c,19]

$$m_{pj}=\langle A\psi_p^f\phi_j^0\,|\,v_{pj}\,|\,\psi_p^0\phi_j^f\rangle-\langle A\phi_p^f\phi_j^0\,|\,v_{pj}^0\,|\,\phi_p^0\phi_j^f\rangle, \qquad (2)$$

and appear as off-diagonal matrix elements in the general perturbation matrix[15] $\mathbf{V}$. Contributions of the order of $m_{pj}\sim 1$ cm^{-1} are expected to reveal only a negligibly small second-order effect on the impurity level. The second contribution to the perturbation matrix $\mathbf{V}$ arises from the corrections to the environmental shifts of the host molecules in the presence of the guest,[3c,19]

$$d_{pi}=\langle|\,\psi_p^0\,|^2\,|\,v_{pi}\,|\,|\,\phi_i^f\,|^2-|\,\phi_i^0\,|^2\rangle-\langle|\,\phi_p^0\,|^2\,|\,v_{pi}^0\,|\,|\,\phi_i^f\,|^2 - |\,\phi_i^0\,|^2\rangle+\text{dispersion terms}. \qquad (2')$$

The d_{pi} terms appear as diagonal matrix elements in the perturbation matrix $\mathbf{V}$. These terms, which are of considerable importance for the case of chemical substitution, are not expected to exceed a few centimeters^{-1} in the case of isotopic substitution. In the latter case, the d_{pi} terms are again expected to lead to a negligibly small second-order contribution to the impurity level. Model calculations on a system where the exciton band struc-

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ture is determined by short-range interactions have demonstrated that the effect of the m_{pj} and the d_{pi} terms (in the range of interest) is indeed small. To conclude, it is safe to assume that the case of isotopic substitution can be adequately described in terms of a local perturbation.

For the case of isotopic substitution, the impurity level, E, is obtained from the relation

$$1/U_0 = F(E), \tag{3}$$

$$F(E) = P\int \frac{g_0(E')\,dE'}{E-E'}, \tag{3'}$$

where P stands for the Cauchy principal part of the integral. In the weak vibronic coupling limit, $g_0(E)$ corresponds to the density of states in the first vibronic band. Equations (3) and (3') represent a useful form of the Koster–Slater relations.

In the case of a molecular crystal where three-dimensional intermolecular interactions determine the exciton band structure, these physically significant cases can be distinguished, corresponding to (1) an extremely weak perturbation where no solutions to the energy equation (3) are available, (2) a virtual scattering level in the band, and (3) a localized bound impurity level found outside the band. At this point it will be useful to define the critical values of the perturbation strength[15] which gives rise to Cases (1)–(3) outlined above. Let U_c^- and U_c^+ be the critical values of the perturbation strength at which virtual states appear, so that when $|U_0| < |U_c^-|$ (when $U_0<0$) and when $U_0<U_c^+$ (when $U_0>0$) the change in the density of states is a monotonic function of the energy in the range of the unperturbed exciton band.[15] The limiting values of the perturbation strength required for the appearance of localized states are U^- and U^+. These states will be observed when $|U_0| > |U^-|$ ($U_0<0$) and $U_0>U^+$ ($U_0>0$). Virtual states will be observed when $|U_c^-| < |U_0| < |U^-|$ (for $U_0<0$), and when $U_c^+<U_0<U^+$ (for the case $U_0>0$).

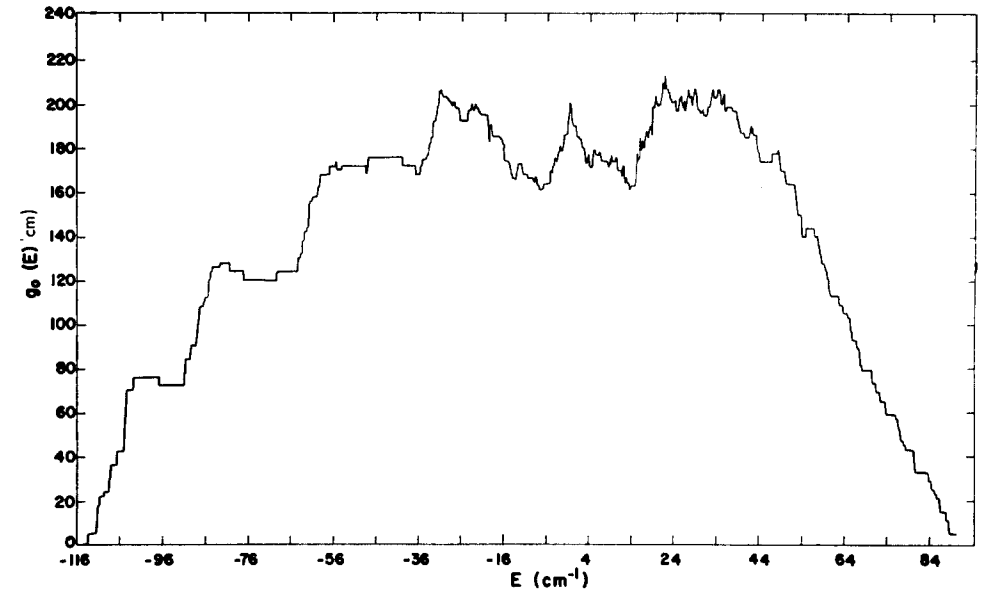
We shall now turn our attention to the calculation of impurity states in isotopically dilute crystals of naphthalene and benzene. The input information involves the density of exciton states in the pure crystal, which for the case of naphthalene crystal can be obtained from two sources:

(a) Theoretical data: The crystal energy levels for naphthalene were calculated by Philpott and Craig,[19] fitting the transition-octupole moments.[3b,5] Using these detailed energy-level data, kindly made available to us by Craig and Philpott, the density-of-states function was calculated using 20 000 points in the Brillouin zone. These energy points were interpolated using the Philpott–Craig original data. The resulting density-of-states function and the corresponding F function are displayed in Fig. 1. It should be noted that the present results for the density-of-states function is characterized by the same width as the approximate density function presented by Philpott and Craig,[19b] but differ from it in some details. In particular, a critical point resembling a logarithmic singularity reported in Fig. 5 of Ref. 19b was not reproduced by our calculations. A Van Hove critical analytical point revealing a logarithmic singularity is characteristic of a two-dimensional band structure. As the octupole model for the intermolecular interactions predicts that the intermolecular interactions outside the *ab* monoclinic crystal plane are of considerable importance,[3b,5,19,20] the critical points in the band structure are expected to reveal square-root singularities, as exhibited by the result presented in Fig. 1. The density-of-states and the F function presented herein correspond to the total electronic contribution, and in order to obtain the corresponding data for the first vibronic band, one has to scale the energy scale by a vibrational overlap factor of[19] 0.87. The calculations of the density-of-states function, the F function, and all the other numerical computations reported in the present paper were performed using the 1604 CDC computer and the "Golem" computer at the Weizman Institute of Science.

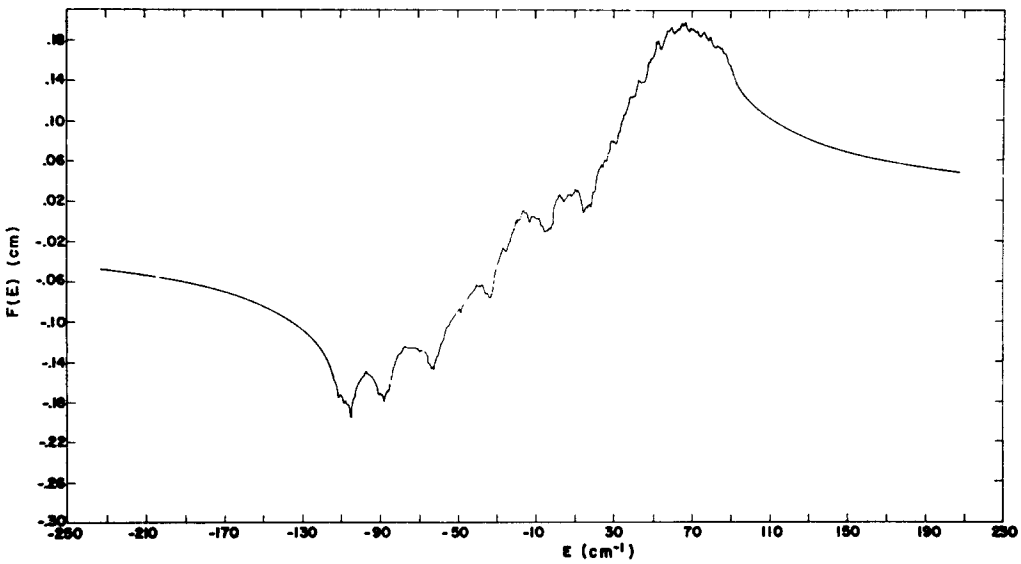
(b) Experimental data: The hot band of the naphthalene crystal measured at 77°K reported by Shpak and Sheka[13] and recently used by Broude *et al.*[16b] provides a zero-order approximation to the exciton density of states, and was used for model calculations previously reported.[15c] In the present work the band-structure data obtained by Hanson *et al.*[12] from absorption and emission data in the region 30°–77°K were applied. These experimental data are approximate, as they involve a phenomenological correction of the temperature-dependent phonon component in the observed line shape. The F function calculated from these data is displayed in Fig. 2.

We now turn our attention to the estimate of the perturbation strength U_0 [Eq. (1)] for isotopic impurities in crystalline naphthalene. Provided that the intermolecular coupling terms are equal for the guest and host molecules, U_0 can be estimated from the shift of the Davydov components in the pure host and the pure guest crystals.[19] If the $(D^f_{\text{guest}} - D^f_{\text{host}})$ term is negligible, one can, of course, set $U_0 = \Delta\epsilon^f_{\text{guest}} - \Delta\epsilon^f_{\text{host}}$. From the available data for crystalline naphthalene and crystalline perdeuterated naphthalene,[19] the low-energy *ac*-polarized component is shifted by 115 ± 4 cm^{-1} in naphthalene d_8 relative to naphthalene h_8, while the *b*-polarized component is shifted by 115 ± 4 cm^{-1} in naphthalene d_8 as compared to naphthalene h_8. From the gas-phase data,[19] $\Delta\epsilon^f(d_8) - \Delta\epsilon^f(h_8) = 118$ cm^{-1}. Thus, in the case of naphthalene it appears that the intermolecular coupling terms and the D^f terms are practically identical for the guest and host molecules.

In Fig. 3, we compare the predicted energy levels of impurity states in crystalline naphthalene derived from the theoretical data and from the experimental density-



(a)



(b)

FIG. 1. (a) The density-of-states function for naphthalene calculated from the theoretical transitional-octupole coupling model of Whalmsley and Craig.[5] Zero energy was taken at the center of gravity of the band. (b) The theoretical F function for naphthalene as calculated from the theoretical density-of-states function.

of-states function of Hanson *et al.*[12] A number of experimental data are available for mixed naphthalene crystals for both $U_0<0$ (h_8/d_8, $h_8/\beta d_8$, and $h_8/\alpha d_8$) and for $U_0>0$ (d_8/h_8).[16,18] (We are using here the abbreviated notation: guest/host for the mixed crystal.) In Table I, we compare the experimental energy levels with the theoretical predictions. The perturbation strengths were taken from the work of Philpott and Craig.[19] The energies are measured from the bottom of the exciton band, where the *ac*-polarized $\mathbf{k}=0$ Davydov component is located,[19b,20] as inferred from low-temperature emission studies.[3a] As pointed out by Philpott and Craig,[19] their theoretical data (which were rederived herein by a somewhat different manner) reproduce the gross features of the impurity energy levels. The experimental band-structure data for the density of states obtained from hot-band spectroscopy yield impurity levels which are in good agreement with experiment.

In Table II, we have displayed the critical values of the perturbation strengths for naphthalene. The values of U^+ and U^- are compared with the experimental estimates of Broude *et al.*[16b] The present calculations

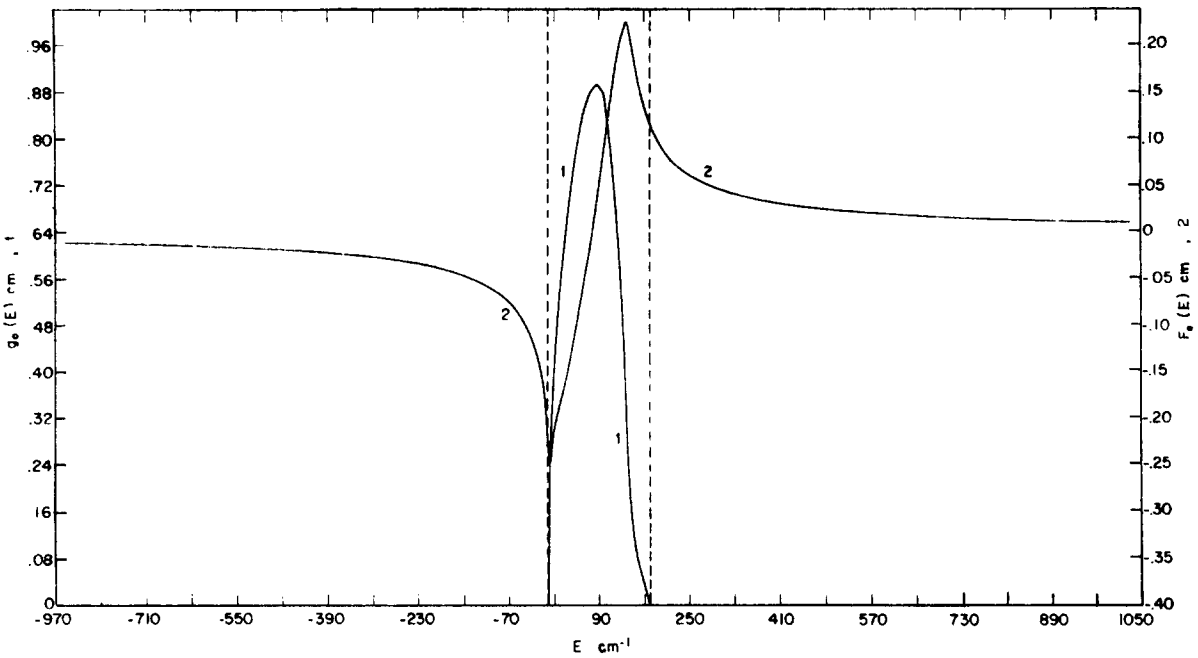


FIG. 2. The experimental density-of-states function for naphthalene (curve 1) obtained by Hanson *et al.*[12] (see Text). Zero energy was taken at the bottom of the band. This band structure was applied for the calculation of the F function (curve 2).

indicate the range of the perturbation strength for which virtual scattering states can be detected in the band region. Practically no virtual states for $U_0<0$ are expected, while for $U_0>0$ virtual states will occur in the energy range 40 $cm^{-1} \leq U_0 \leq 80$ cm^{-1}. To date, no experimental evidence for virtual impurity states in naphthalene has been reported.

We now turn our attention to the mixed crystals of benzene and deuterated benzenes. The experimental band-structure data were recently reported by Colson, Hanson, Kopelman, and Robinson.[12] In Fig. 4, we present the calculated F function, which makes possible the evaluation of the impurity levels E with respect to the band edge. The theoretical curve is presented in Fig. 5. It should be noted that, in view of the small exciton bandwidth $\sim$60 cm^{-1} in crystalline benzene, the dependence of E on U_0 is practically linear except for small deviations near the exciton band edges. We shall return later to this point. The critical energy values which determine the lower limits of U_0 required for the appearance of virtual and of localized states are displayed in Table II. Unlike the case of naphthalene, virtual states are expected to occur for both positive and negative values of U_0. The lowest a-polarized $\mathbf{k}=0$ exciton component in crystalline benzene is located at the bottom of the exciton band, as demonstrated by the

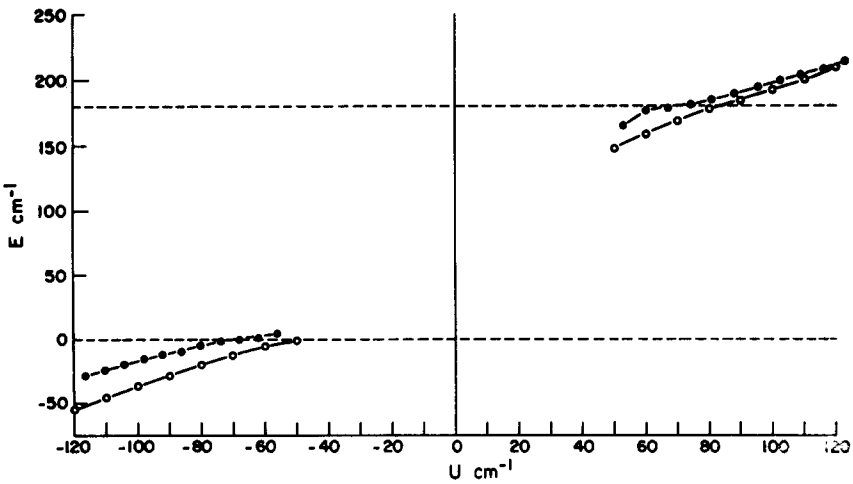


FIG. 3. The dependence of the energy of naphthalene mixed crystal on the perturbation strength U. ⊙: results obtained using the theoretical density-of-states function of Whalmsley and Craig. ○: results obtained using the experimental density-of-states function. The dashed lines represent the band edges.

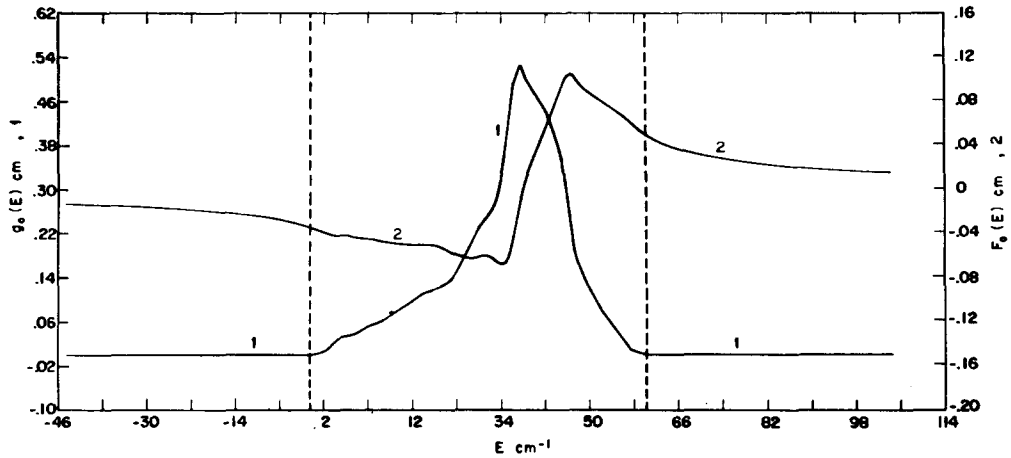


FIG. 4. The experimental density-of-states function of benzene as reported by Colson *et al.* (curve 1). Curve 2 represents the F function calculated from these data. Energy scale chosen relative to the band edge.

low-temperature emission data of Vatulev *et al.*[22] The available spectroscopic information on the energy of the bottom of the exciton band E_B^- (i.e., the position of the a component) and on the 0–0 gas-phase excitation energies, $\Delta\epsilon^f$, of the isolated molecules is summarized in Table III.

The determination of the perturbation strength for the case of isotopically mixed benzene crystals is fraught with difficulties in view of the following observations:

(a) As concluded by Colson,[17] the $D^f_{\text{guest}}-D^f_{\text{host}}$ term is nonvanishing, being determined by the isotopic composition.

(b) The values of $\Delta\epsilon^f-E_B^-$ presented in Table III reveal a systematic trend[23] which is consistent with Colson's arguments.

(c) The Craig–Philpott method[19c] which was successfully applied for the evaluation of U_0 in the case of naphthalene fails for the case of benzene. There is[17] a difference of 6 cm^{-1} between the relative displacements of the higher and of the lower Davydov component in C_6H_6 as compared to C_6D_6.

(d) The values of $\Delta\epsilon^f_{\text{guest}}-\Delta\epsilon^f_{\text{host}}$ derived from the gas-phase data are reliable only within a few centimeters^{-1} in view of the spacings between the maximum of the rotational envelopes and vibronic origin.[17] In view of these inherent difficulties we shall adopt the following approximate procedure for extracting new physical information from the benzene mixed-crystals data: (a) we shall set $U_0=\Delta\epsilon^f_{\text{guest}}-\Delta\epsilon^f_{\text{host}}$ as taken from the gas-phase data; (b) as in the case of naphthalene we shall present the guests' energies relative to the host exciton band, which is of course the natural procedure suggested by the theoretical treatment. For the cases which involve partial deuteration, this procedure will partially compensate for the isotopic dependence of the term D^f_{guest}, leading only to a small contribution to $D^f_{\text{guest}}-D^f_{\text{host}}$. In view of these approximations, the theoretical data on this system are uncertain within a range of about ± 5 cm^{-1}.

TABLE I. The energy levels of naphthalene mixed crystals.[a]

System guest/host	U_0 (cm^{-1})	E_1[b] (cm^{-1})	E_2[c] (cm^{-1})	E_3[d] (cm^{-1})
h_8/d_8	−115	−46	−33	−49
$h_8/\beta d_4$	−78	−19	−5	−18
$h_8/\alpha d_4$	−55	−7	Virtual state	−5
d_8/h_8	+115	+205	+209	+205

[a] All energies measured relative to the bottom of pure host crystal exciton band.
[b] E_1: experimental value (experimental uncertainty ± 2 cm^{-1}).
[c] E_2: Craig–Philpott calculation.
[d] E_3: present calculation.

In Tables IV and V we compare the recent experimental data of Colson[17] with the predictions of the approximate theoretical treatment. All energies E are referred to the bottom of the host exciton band. The most important feature of these results is that the impurity energy levels, E, exhibit a linear dependence on the strength of the local perturbation U_0, as is evident from the theoretical curve presented in Fig. 5. Reasonable agreement between theory and experiment applies both for positive and negative values of U_0. One discrepancy should be noted. The theory predicts that for the C_6D_5H/C_6H_6 system where $U_0\approx -29$ cm^{-1} a bound state located very close to the bottom of the exciton band will be observed. Colson reports this impurity level to be located at $E=-9$ cm^{-1}, while the theory predicts $E=-0.6$ cm^{-1}.

[22] V. N. Vatulev, N. L. Sheremet, and N. R. Shpak, Opt. Spektrosk. **16**, 577 (1964) [Opt. Spectrosc. **16**, 315 (1964)].
[23] We wish to thank the anonymous referee for this comment.

TABLE II. Critical U_0 values for the appearance of virtual and localized states in naphthalene and benzene mixed crystals.

System	Theory				Experimental estimate	
	U_c^+ (cm^{-1})	U_c^- (cm^{-1})	U^+ (cm^{-1})	U^- (cm^{-1})	U^- (cm^{-1})	U^+ (cm^{-1})
Naphthalene	+41	−41	83	−46	−44	+95
Benzene	+9.4	−14.3	+20	−29	...	...

From the analysis of the theoretical data, we conclude that:

(a) From the theoretical point of view, the experimental density-of-states functions derived by Hanson *et al.*[12] are adequate for the calculation of impurity levels. It is evident that these density functions do reproduce faithfully the gross features of the exciton density of states. It should, however, be pointed out that the experimental density functions do not reproduce the Van Hove-type analytical singularities within the band. However, these are of minor importance for the interpretation of the mixed-crystal data.

(b) From the experimental point of view, the detection of virtual impurity states will be of considerable interest. In the case of naphthalene crystals, only positive perturbations should be investigated. In this context the system $\beta h_4 d_4/h_8$ ($U_0 \approx +78$ cm^{-1}) will be of considerable interest. On the other hand, the appearance of a virtual state in the $\alpha h_4 d_4/h_8$ system ($U_0 = +55$ cm^{-1}) is uncertain as the perturbation strength is very close to U_c^+. No virtual states will be observed for the $h_5 d_3/h_8$, $h_6 d_2/h_8$, and $h_7 d/h_8$ systems. In the case of the benzene crystal, virtual states are expected to be observed in the range 10 $cm^{-1} < U_0 < 20$ cm^{-1} and -20 $cm^{-1} > U_0 > -30$ cm^{-1}. For the case of this narrow exciton band, even a single hydrogen–deuterium substitution leads to a too-large perturbation, pushing the impurity state outside the band. Virtual states in this system can be observed by using $^{13}C \leftrightarrow {}^{12}C$ substitution. It was reported by Bernstein *et al.*[24] that for the $^{13}C^{12}C_5H_6/{}^{12}C_6H_6$ system, $U_0 = +3.7$ cm^{-1}. This positive perturbation is too small and will not result in a virtual state, leading only to continuous modification of the exciton density of states. Indeed, this natural abundance (about 6%) of $^{13}C^{12}C_5H_6$ in $^{12}C_6H_6$ may lead to impurity-induced (distinct from phonon induced) background absorption broadening of the exciton lines and to the appearance of background absorption in organic crystals in the exciton band region. It would be extremely interesting to study the systems $^{13}C_3{}^{12}C_3H_6/{}^{12}C_6H_6$ ($U_0 \approx 11$ cm^{-1}), $^{13}C_4{}^{12}C_2H_6/{}^{12}C_6H_6$ ($U_0 \approx 15$ cm^{-1}), and $^{13}C_5{}^{12}CH_6/{}^{12}C_6H_6$ ($U_0 \sim 19$ cm^{-1}), where virtual states are expected to be observed.

TABLE III. Gas-phase excitation energies and lowest crystal exciton state for deuterated benzenes.

Molecule	$\Delta\epsilon^f$ [a] (cm^{-1})	E_B^- [b,c] (cm^{-1})	$\Delta\epsilon^f - E_B^-$ (cm^{-1})
C_6H_6	38 089	37 803	286
C_6H_5D	38 124	37 840	284
p-$C_6H_4D_2$	38 155	(37 875)	(280)
sym-$C_6D_3H_3$	38 186	(37 909)	(277)
m-$C_6D_4H_2$	38 222	(37 945)	(277)
C_6D_5H	38 260	(37 983)	(277)
C_6D_6	38 289	38 012	277

[a] Data from Broude, Ref. 26.

[b] Data from crystalline C_6H_6 and C_6D_6 from Ref. 17 and for C_6H_5D from V. L. Broude and S. M. Kochnbei, Opt. Spectrosc. **13**, 494 (1962).

[c] Data in parenthesis represent approximate evaluation of the bottom of the exciton band from the gas-phase data, and the crystal data for C_6H_6 and C_6D_6.

III. APPLICATION OF THE MOMENT-EXPANSION METHOD

The general energy expression [Eq. (3)] which relates the energy of the impurity level and the host density of exciton states provides an important consistency check on the accuracy of the $g_0(E)$ function. It is interesting to inquire whether for some limiting cases some further energetic information can be derived, for instance, what is the net effect of the configuration interaction between the impurity level and the manifold of states in the exciton band, on the energetic shift of the impurity level. A qualitative answer to this problem was provided by Nieman and Robinson,[25] who claimed that a simple perturbation equation can be applied for the impurity level

$$E_{NR} = \Delta\epsilon^f{}_{guest} + D^f + \delta_{NR}, \tag{4}$$

where

$$\delta_{NR} = 4\beta^2/U_0. \tag{4'}$$

It has been recently stressed by Colson[17] that one should set $D^f = D^f{}_{guest}$ [see Eq. (1')] in Eq. (4) and that this term depends on the nature of the isotopic substituent. Philpott and Craig[19] and Body and Ross[20] drew atten-

[24] E. R. Bernstein, S. D. Colson, and D. S. Tinti, reported in Ref. 12.

[25] G. C. Nieman and G. W. Robinson, J. Chem. Phys. **39**, 1298 (1963).

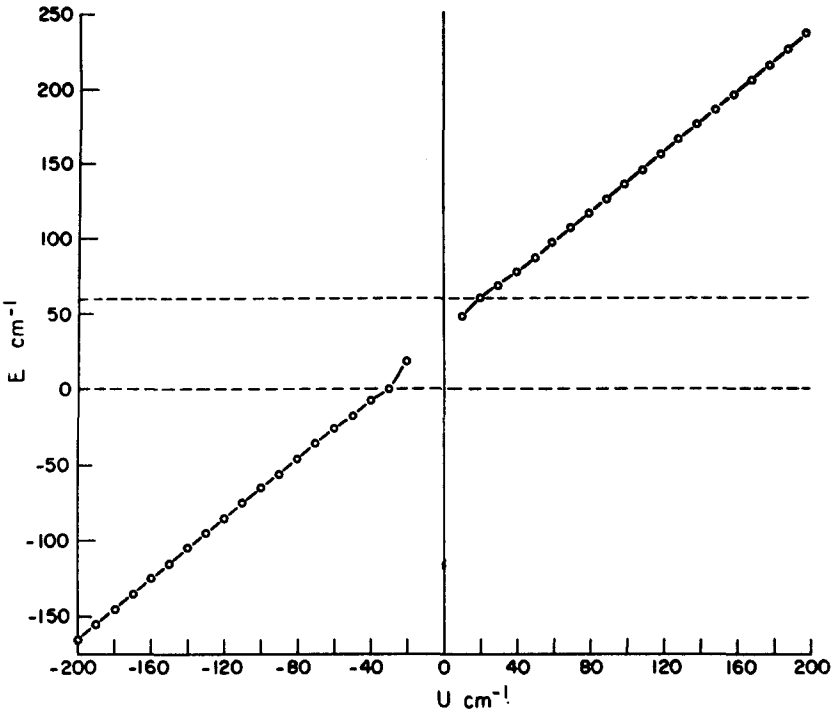


FIG. 5. The predicted dependence of benzene mixed-crystal energies on the perturbation strength U_0. The dependence E on U_0 is practically linear except near band edges.

tion to the limiting validity of the perturbation expansion (4), pointing out that this simple result is expected to hold only when the strength of the local perturbation considerably exceeds the exciton bandwidth. The application of the moments-expansion method for the F function previously outlined by us[15c] makes it possible to derive some approximate relations for the impurity level.[20] It will be of some interest to establish more precise criteria for the validity of perturbation expansions of various degrees of sophistication. The $F(E)$ function now defined on an energy scale relative to the ground state of the crystal can be expanded in an infinite power series provided that $E>E'$ for all E' values within the band,

$$F(E)=\sum_{I=0}^{\infty}\frac{m^{(I)}}{E^{I+1}}, \tag{5}$$

where $m^{(I)}$ is the Ith moment of the density-of-states

TABLE IV. Energy levels of benzene mixed crystals.

Host	Guest	E (guest) (Crystal)[a] (cm^{-1})	U_0 (cm^{-1})	E^a exptl (cm^{-1})	E^b calc (cm^{-1})
C_6H_6	C_6H_6	37 803	...	...	...
C_6D_6	C_6D_6	38 012	...	...	...
C_6D_6	C_6H_6	37 853	−200	−159	−165
C_6D_6	C_6H_5D	37 884	−165	−128	−130
C_6D_6	p-$C_6D_2H_4$	37 913	−134	−99	−100
C_6D_6	sym-$C_6D_3H_3$	37 949	−103	−63	−66
C_6D_6	m-$C_6D_4H_2$	37 981	−67	−31	−32
C_6D_6	C_6D_5H	38 003	−29	−9	−0.58
C_6H_6	C_6D_6	38 033	+200	+230	+232
C_6H_6	C_6D_5H	38 001	+171	+198	+205
C_6H_6	m-$C_6D_4H_2$	37 971	+133	+168	+169
C_6H_6	C_6DH_5	37 877	+35	+74	+73

[a] Experimental data from Colson, Ref. 17.

[b] Energies measured relative to the bottom of the host exciton band.

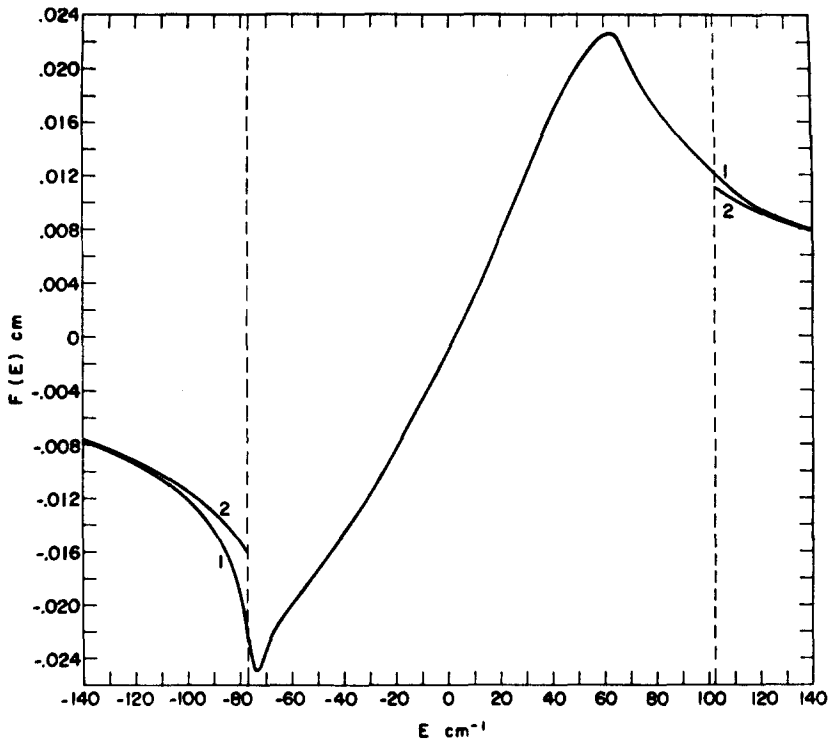


FIG. 6. The calculated F function for the first singlet exciton band of naphthalene using Eq. (2a) (curve 1) and a moments expansion using only the first two moments of the density of states function (curve 2).

function

$$m^{(I)}=\int (E')^I g_0(E')\,dE'. \tag{6}$$

Consider now the first moment $m^{(1)}$ corresponding to the center of gravity of the exciton density of states. Applicability of the diagonal sum rule immediately leads to the result

$$m^{(1)}=\Delta\epsilon^I{}_{\text{host}}+D^I{}_{\text{host}}. \tag{6'}$$

Let us now redefine the moments of the distribution of the density of states in the form

$$M^{(I)}=\int (E'-m^{(1)})^I g(E')\,dE'. \tag{7}$$

On the energy scale $\tilde{E}=E-m^{(1)}$ (defined so that $M^{(1)}=0$) we display the F function in the form

$$F(\tilde{E})=\tilde{E}^{-1}+\sum_{I=2}^{\infty}\frac{M^{(I)}}{\tilde{E}^{I+1}}. \tag{8}$$

Defining the energies corresponding to the top and the bottom of the exciton band by $E_B{}^+$ and $E_B{}^-$, respectively, the infinite power series expansion (5′) converges provided that

$$|E|>(E_B{}^+-m^{(1)}) \quad \text{or} \quad (m^{(1)}-E_B{}^-).$$

At the risk of triviality, we point out that virtual impurity states cannot be treated by the power-expansion method, and only bound states can be considered. To gain information on the convergence of the power series (8), we present in Fig. 6 an approximation for the F function for the first singlet exciton band of naphthalene using only two moments in the expansion. A calculation using 10 moments practically coincides with the exact F function. The lowest moments calculated from the experimental density-of-states functions in crystalline benzene and naphthalene are displayed in Table VI. It should be noted that for the case of crystalline naphthalene when only the $M^{(2)}$ term is retained, there is an error of about 2% in the F function

TABLE V. Energy levels for C_6H_6 and C_6D_6 impurities in crystals of deuterated benzenes.

Host	Guest	U_0 (cm^{-1})	E^a exptl (cm^{-1})	E^b theory (cm^{-1})
C_6D_6	C_6H_6	−200	−159	−165
C_6D_5H	C_6H_6	−171	−131	−135
m-$C_6D_4H_2$	C_6H_6	−133	−95	−97
sym-$C_6D_3H_3$	C_6H_6	−97	−59	−63
p-$C_6D_2H_4$	C_6H_6	−66	−34	−32
C_6DH_5	C_6H_6	−35	−9.5	−4
C_6DH_5	C_6D_6	+165	+197	+200
p-$C_6D_2H_4$	C_6D_6	+134	+167	+170

[a] Experimental data from Colson, Ref. 17.
[b] Energies measured relative to the bottom of the host exciton band.

TABLE VI. Moments of density-of-states function.

System	$m^{(1)}$ [a] (cm^{-1})	$M^{(2)}$ [b] (cm^{-2})	$M^{(3)}$ [b] (cm^{-3})	$M^{(4)}$ [b] (cm^{-4})
Benzene	35.35	1.10×10^{2}	-8.9×10^{2}	4.0×10^{4}
Naphthalene	77.37	1.41×10^{3}	1.3×10^{3}	4.3×10^{6}
Naphthalene[c]	91.2	1.79×10^{3}	-5.2×10^{4}	

[a] Zero energy located at lowest band edge.
[b] Zero energy located at center of gravity of the band.
[c] Moments derived from the Craig–Philpott theoretical-density-of-state curve and scaled by a vibrational overlap factor of 0.87.

for $E\sim120$ cm^{-1}, which will result in an error of about 20% for δ in that energy region.

Turning our attention to bound impurity states, Eqs. (3) and (8) lead to the relation

$$\tilde{E}=U_0+\sum_{I=2}^{\infty}\frac{M^{(I)}}{U_0^{I-1}}\left(\frac{U_0}{\tilde{E}}\right)^I \tag{9}$$

and

$$\delta=\tilde{E}-U_0,$$

resulting in an alternative relation for the effect of the exciton states on the bound impurity energy levels. To obtain the bound energy levels of interest, Eq. (9) has to be solved numerically for $\tilde{E}$, truncating the series after a finite number of terms. The Nieman–Robinson formula can be obtained by performing two successive approximations which lead to mutually canceling errors:

(a) Neglecting all terms above that which contain the second moment results in

$$\tilde{E}=U_0+(M^{(2)}/U_0)\,(U_0/\tilde{E})^2. \tag{9'}$$

The solution of the resulting quadratic equation was suggested by Ross and Body[20] as an adequate approximation for $\tilde{E}$. The reasonably good results obtained by them[20] for isotopically mixed naphthalene crystals are due to the fact that the third odd moment is small in this case. However, as a sizeable contribution may arise from higher even moments in Eq. (9), so in general this approximation will lead to an underestimate of $\tilde{E}$ and of the resulting δ term.

(b) Setting in Eq. (9') $U_0=\tilde{E}$, leads to

$$\tilde{E}=U_0+(M^{(2)}/U_0), \tag{10}$$

resulting in

$$\delta_{\mathrm{NR}}\approx M^{(2)}/U_0. \tag{10'}$$

This second approximation in turn leads to an overestimate of the $\tilde{E}$ value as compared to the result of Eq. (9').

In Tables VII and VIII, we exhibit the singlet impurity energy levels calculated using the exact method, the moment-expansion method, and the empirical relation (10). The results for the naphthalene crystal clearly demonstrate that it is unjustified to truncate the series expansion of F after the $M^{(2)}$ term. However, a striking fortuitous agreement is obtained between the exact value of δ and the δ_{NR} term, calculated from Eq. (10') with $M^{(2)}$ taken from Table VI. It is amusing to note that even for virtual states, where the expansion (9) does not converge, the empirical relation (10) yields δ values which are in accidental agreement with the result of the exact calculations. From the results, we conclude that:

(a) The applicability of the Nieman–Robinson empirical formula [Eqs. (3) and (10)] over a surprisingly wide energy region, where the simple perturbation expansion completely breaks down, is due to mathematical artifacts, resulting in mutual cancellation of errors.

(b) In the cases of a virtual state and a bound shallow-trap limit, i.e., when $U_0\sim M^{(2)}/U_0$, the general Koster–Slater relation (3) must be applied.

(c) In the case of an intermediate trap when $0.3>M^{(2)}/U_0^2\gtrsim0.1$, the experimental δ value combined with the empirical relation (10') will lead to an estimate of $M^{(2)}$ for the exciton band which is reliable within 10%–20%.

(d) In the limit of a deep trap when $M^{(2)}/U_0^2<0.1$, Eq. (10) becomes, of course, a legitimate theoretical result. In this limit, the experimental uncertainties prohibit the estimate of $M^{(2)}$ from the experimental data.

IV. INFORMATION ON ENERGY LEVELS FROM MOMENTS EXPANSIONS

We shall consider now the implications of the moments-expansion method, and enquire what new information on the intermolecular interactions in the pure crystal can be obtained from the energy levels of the mixed crystals. From the experimental studies of the $k=0$ Davydov components, only the sum of interaction between translationally inequivalent molecules can be extracted. The missing information concerning the D term can be obtained from the first moment of the density-of-states function. Further information concerning intermolecular interactions between translationally equivalent molecules is contained in the second moment. The following comments are now in order:

(a) In the benzene crystal $M^{(2)}=110$ cm^{-2}, obtained from the experimental density of states. Hence, even for the lowest value of the perturbation strength corresponding to a deuterated impurity $U_0\sim30$ cm^{-1}, $M^{(2)}/U_0^2\sim0.1$. Hence, all the states of dilute mixed crystals of benzene-deuterated benzenes correspond to the deep-trap limit. This conclusion is in agreement with the recent considerations of Colson and Robinson,[17] who have modified some of the preliminary conclusions of Nieman and Robinson. In view of the small value of the second moment of the density-of-states function, it cannot be extracted from the mixed-crystals data.

TABLE VII. The effect of the exciton band on the energy shift of the isotopic impurity in naphthalene.[a] All energies given in centimeters^{-1}. Energies $\tilde{E}$ measured relative to the center of gravity of the exciton density of states. $\delta = E - U_0$.

	Exact solution [Eq. (4)]		Moments expansion						
			2 Moments		10 Moments		30 Moments		
U_0	E	δ	$\tilde{E}$	δ	E	δ	$\tilde{E}$	δ	δ_{NR} [Eq. (4)]
120	132.2	12.2	130.0	10.0	132.2	12.2	132.2	12.2	11.7
110	123.4	13.4	120.6	10.6	123.3	13.3	123.4	13.4	12.8
100	115.0	15.0	111.3	11.3	114.8	14.8	115.0	15.0	14.1
90	107.2	17.2	102.1	12.1	106.6	16.6	107.2	17.2	15.6
−50	−78.9	−28.9	−66.1	−16.1	−76.8	−26.8	−81.7	−31.7	−28.1
−60	−83.9	−23.9	−75.0	−25.0	−83.2	−23.2	−85.2	−25.2	−23.4
−70	−90.4	−20.4	−84.0	−14.0	−90.2	−20.2	−90.7	−20.7	−20.1
−80	−97.8	−17.8	−93.0	−13.0	−97.7	−17.7	−97.8	−17.8	−17.6
−90	−105.8	−15.8	−102.1	−12.1	−105.8	−15.8	−105.8	−15.8	−15.6
−100	−114.2	−14.2	−111.3	−11.3	−114.2	−14.2	−114.2	−14.2	−14.1
−110	−122.9	−12.9	−120.6	−10.6	−122.9	−12.9	−122.9	−12.9	−12.8
−120	−131.8	−11.8	−130.0	−10.0	−131.8	−11.8	−131.8	−11.8	−11.7

[a] Band edges: −77.4 cm^{-1}, +102.6 cm^{-1}.

(b) The experimental data of Colson[17] on the mixed-benzene–deuterobenzene systems can be adequately fitted by a linear relation $E = U_0 + (35 \pm 5)$ cm^{-1}, where the energy is measured relative to the center of gravity of the host exciton band. As apparent from Table VIII, the δ values are of the order of the experimental uncertainty (± 1 cm^{-1}) and cannot be extracted from the experimental data. The information available from the impurity spectra in this system is $m^{(1)}(\text{exptl}) = 35 \pm 5$ cm^{-1}, which is in excellent agreement with the first moment calculated directly from the experimental density-of-states function ($m^{(1)} = 35.3$ cm^{-1}) of Colson *et al.*

(c) These results provide two independent methods for locating the center of gravity of the first exciton band in crystalline benzene. The center of gravity is located 35 cm^{-1} above the bottom of the band, which corresponds to the a-polarized Davydov component. Thus for

TABLE VIII. The effect of the exciton band on the energy shift of the isotopic impurity in benzene.[a] All energies given in centimeters^{-1}. Energies E measured relative to the center of gravity of the exciton density of states. $\delta = E - U_0$.

	Exact solution [Eq. (4)]		Moments expansion [Eq. (9)]				
			2 Moments		30 Moments		
U_0	E	δ	E	δ	E	δ	δ_{NR} [Eq. (4)]
200	200.5	0.5	200.5	0.5	200.5	0.5	0.6
150	150.7	0.7	150.7	0.7	150.7	0.7	0.7
100	101.0	1.0	101.1	1.1	101.0	1.0	1.1
50	51.9	1.9	52.0	2.0	51.9	1.9	2.2
40	42.4	2.4	42.4	2.4	42.4	2.4	2.8
30	33.1	3.1	33.0	3.0	33.2	3.2	3.7
−40	−43.7	−3.7	−42.4	−2.4	−43.7	−3.7	−2.7
−50	−52.7	−2.7	−52.0	−2.0	−52.7	−2.7	−2.2
−100	−101.2	−1.2	−101.1	−1.1	−101.2	−1.2	−1.1
−150	−150.8	−0.8	−150.7	−0.7	−150.8	−0.8	−0.7
−200	−200.5	−0.5	−200.5	−0.5	−200.6	−0.6	−0.6

[a] Band edges: −35.35 cm^{-1}, +24.64 cm^{-1}.

C_6H_6 $\Delta\epsilon^f+D^f=37\,803+35=37\,838$ cm^{-1}. This estimate is in excellent agreement with the previous estimates of Broude[26] and of Colson[17] based on vibronic analysis of the pure-crystal data. From the $0\rightarrow 0+2\nu_{16}'(e_{2g}\cdot a_{1g})$ vibration in crystalline benzene (which does not reveal any splitting), Colson estimated $\Delta\epsilon^f+D^f=37\,838$ cm^{-1}, while Broude's previous analysis[26] of the $0\rightarrow 0+\nu_6'$ transition (which is split by 9 cm^{-1}) led to the result $\Delta\epsilon^f+D^f=37\,835$ cm^{-1}. Thus, three independent methods, the vibronic analysis, the direct evaluation of the first moment of $g_0(E)$, and the analysis of the electronic levels of dilute isotopically mixed crystals, lead to perfect agreement concerning the first moment of the density states, which is just the $\Delta\epsilon^f+D$ term. This result makes possible a reliable evaluation of the D term. Taking for C_6H_6 $\Delta\epsilon^f=38\,089$ cm^{-1}, one gets $D^f=-251$ cm^{-1}.

(d) The result obtained for the environmental shift in the first exciton band in benzene enables us to make a rough estimate of the sum of the interaction terms over translationally equivalent molecules, I_{eq}, in this system. We may now consider an estimate of the center of gravity of the *Davydov* components, although, as the method used by Colson, the accuracy of our estimate will be limited to a few centimeters^{-1}. From the band structure of Colson, the upper limit for the forbidden Au component in crystalline benzene is 37 863 cm^{-1}, which corresponds to the top of the band. Assuming for the moment that this is the location of Au exciton state, then the center of gravity of the four Davydov components (the three experimental observed levels located at 37 803, 37 842, 37 847 cm^{-1} and the fourth forbidden level at 37 863 cm^{-1}) is located at 37 838 cm^{-1}, which coincides with the value of $\Delta\epsilon^f+D^f$. Hence the sum of the interaction terms over equivalent molecules in this system is very close to zero.

(e) As pointed out by Nieman and Robinson[25] and by Colson,[17] the knowledge of the $M^{(2)}$ term ($4\beta^2$ in his notation) can provide an independent estimate for the sum of the squares of the short-range interaction terms. This quantity cannot be obtained from the impurity states in benzene; however, the second moment can be easily evaluated from the experimental density-of-states function, which leads to $M^{(2)}=110$ cm^{-2}. Using the Nieman–Robinson[25] assumptions concerning the dominating role of short-range interactions and Colson's interaction terms,[17]

$$J_a=J_b=J_c=0; \qquad J[\tfrac{1}{2}(\mathbf{a}+\mathbf{b})]=-1.55;$$
$$J[\tfrac{1}{2}(\mathbf{b}+\mathbf{c})]=3.93; \qquad J[\tfrac{1}{2}(\mathbf{a}+\mathbf{c})]=3.28.$$

Application of Eq. (7) leads to

$$M^{(2)}=\sum_j J_j^2, \tag{7'}$$

where J_j is the pair-interaction matrix element between the reference molecule and that located at site j. For the case under consideration, one gets

$$M^{(2)}=2(J_a^2+J_b^2+J_c^2)+4\{J^2[\tfrac{1}{2}(\mathbf{a}+\mathbf{b})]+J^2[\tfrac{1}{2}(\mathbf{b}+\mathbf{c})]+J^2[\tfrac{1}{2}(\mathbf{a}+\mathbf{c})]\}=114 \text{ cm}^{-2},$$

which is in agreement with the second moment $M^{(2)}=110$ cm^{-2} directly derived from the experimental density-of-state function. This result provides a consistency check that indeed the terms $|I_a|$, $|I_b|$, and $|I_c|$ are smaller than 1 cm^{-1}, so that $I_{eq}\sim 0$ in this system.

(f) The impurity states in crystalline naphthalene–deuteronaphthalenes correspond to the shallow and to the intermediate trap limits as $M^{(2)}=1400$ cm^{-2}. These states have to be treated by the general relation (3). This is consistent with the results of Body and Ross.[20]

(g) The adequacy of the experimental density-of-states function for predicting the impurity levels inspires some confidence in the reliability of the distribution moments derived from it. Hence, the first moment in naphthalene is $m^{(1)}=77$ cm^{-1}, so that $D^f+\Delta\epsilon^f_{host}=31\,475+77=31\,552$ cm^{-1}, and using the gas-phase value $\Delta\epsilon^f_{host}=32\,020$ cm^{-1} for C_8H_{10}, we get $D^f=-468$ cm^{-1} for the first exciton band. Now the center of gravity of the two Davydov components in crystalline naphthalene is located at $31\,550\pm 4$ cm^{-1}, and hence $I_{eq}=-2\pm 4$ cm^{-1}. This value is somewhat lower than a previous estimate $I_{eq}\approx 10$ cm^{-1} derived recently by Greer *et al.*[8] from the analysis of the shifts of the centers of gravity of the two Davydov manifolds arising from the 0–0 ($A_{1g}\rightarrow B_{3u}$) and the $0\rightarrow 0+438$ ($A_{1g}\rightarrow B_{3u}\cdot b_{1g}$) totally symmetric vibronic component, which also exhibits a Davydov splitting. A more careful study of the D^f term in various vibrational states is required. It should be noted, however, that the theoretical calculation of Craig, Walmsley, and Philpott[5,19] leads to the value $I_{eq}=-16\pm 4$ cm^{-1}, which is outside the region of the experimental estimates.

V. EXCITATION AMPLITUDES

The applicability of general perturbation techniques for the mixed crystal implies that the impurity wavefunction ψ can be expanded in terms of the localized basis set for the pure crystal, so that[14,15,19,20]

$$\psi=\sum_{n,\alpha} u(n\alpha)\,a_{n\alpha}^f, \tag{11}$$

where $a_{n\alpha}^f$ is a localized excitation on the lattice site $n\alpha$ and $u(n\alpha)$ are the expansion coefficients. The excitation amplitude $|u(0)|^2$ for the impurity molecule (located at site 0) is amenable to a direct experimental observation,[18] by the study of the ratio of the fluorescence intensity emitted by the host and by the guest molecules in the dilute mixed crystal. This excitation amplitude is given in the form[14,15]

$$|u(0)|^2=1/U_0^2[-F'(E_r)], \tag{12}$$

where E_r is the energy of the impurity level. This result

[26] V. L. Broude, Usp. Fiz. Nauk **74**, 577 (1961) [Sov. Phys.—Usp. **4**, 584 (1962)].

can be displayed in an alternative form[16b,18,20]

$$|u(0)|^2=(dE_r/dU_0), \qquad (12')$$

which relates the excitation amplitude to the theoretical (or experimental) localized impurity energy level in the mixed crystal.

In Tables IX and X, we display the excitation amplitudes for isotopically mixed naphthalene and benzene crystals, calculated from the experimental density-of-states functions. From these results, we conclude that:

(a) The excitation amplitudes for the mixed naphthalene crystals which correspond to the shallow and to the intermediate trap limit vary in the range 0.4–0.9.

TABLE IX. The expansion coefficient $|u(0)|^2$ of an impurity molecule in benzene.

U_0 (cm^{-1})	$\|u(0)\|^2$
−200	0.9969
−150	0.9944
−100	0.9865
−50	0.9291
−40	0.8664
−30	0.5995
+30	0.9011
+40	0.9450
+50	0.9642
+60	0.9746
+70	0.9810
+100	0.9903
+150	0.9955
+200	0.9974

The experimental data (for $U_0<0$) which are displayed in Table XI are in qualitative agreement with these expectations. The agreement between theory and experiment is, however, not as good as might be expected. We are inclined to blame this discrepancy on the accuracy of the experimental emission data.[18] It will, nevertheless, be interesting in this context to consider possible effects of crystal-field mixing of higher exciton levels.

(b) For the case of positive values of the perturbation strength, the impurity level located above the band will decay into the manifold of the crystal exciton levels located at lower energies. Thus, at low temperatures, the system will exhibit fluorescence from the bottom of the host exciton band. At higher temperatures, however, the thermal population of this impurity level can be accomplished. Thus, for example, in the $C_{10}D_8/C_{10}H_8$ system where $E_r=207$ cm^{-1} (above the bottom of the exciton band), the population of the impurity level at 50°–100°K can be achieved, and emission from this state will be observed. Such fluorescence studies will provide information on impurity states located above the band which will be complementary to the results obtained from absorption studies.

TABLE X. The expansion coefficient $|u(0)|^2$ of an impurity molecule in naphthalene.

U_0 (cm^{-1})	$\|u(0)\|^2$
+120	0.8879
+110	0.860
+100	0.8176
+90	0.7320
+80	0.7232
−50	0.3914
−60	0.5852
−70	0.6987
−80	0.7713
−90	0.8205
−100	0.8554
−110	0.8810
−120	0.900

(c) As we have already concluded from the study of the impurity energy levels in benzene, this system corresponds practically to the deep trap limit for all isotopic substitutions. The examination of the excitation amplitudes indicates that indeed for $U_0<-40$ cm^{-1} ($U_0<0$) one gets values of $|u(0)|^2$ in the range 0.9–1.0. However, for $U_0\approx-30$ cm^{-1} the impurity excitation amplitude is about 0.6. Thus the experimental study of the fluorescence from the dilute mixed crystals C_6H_6/C_6DH_5 ($U_0=-35$ cm^{-1}) and C_6D_5H/C_6D_6 ($U_0=-29$ cm^{-1}) will lead to the observation of simultaneous emission from both the guest and the host levels.

VI. IMPURITY INDUCED ABSORPTION

We shall now proceed to consider the optical absorption induced by the impurity in the region of the exciton states of the host crystal.[15] We have previously demon-

TABLE XI. Experimental expansion coefficients from emission studies in mixed naphthalene crystals.

Host	Guest	U_0 (cm^{-1})	$\|u(0)\|^2$ exptl	$\|u(0)\|^2$ theory
d_8	h_8	−115	0.9	0.89
d_8	αDH_7	−104	0.7	0.87
d_8	βDH_7	−95	0.6	0.83
βH_4D_4	h_8	−78	0.5	0.75

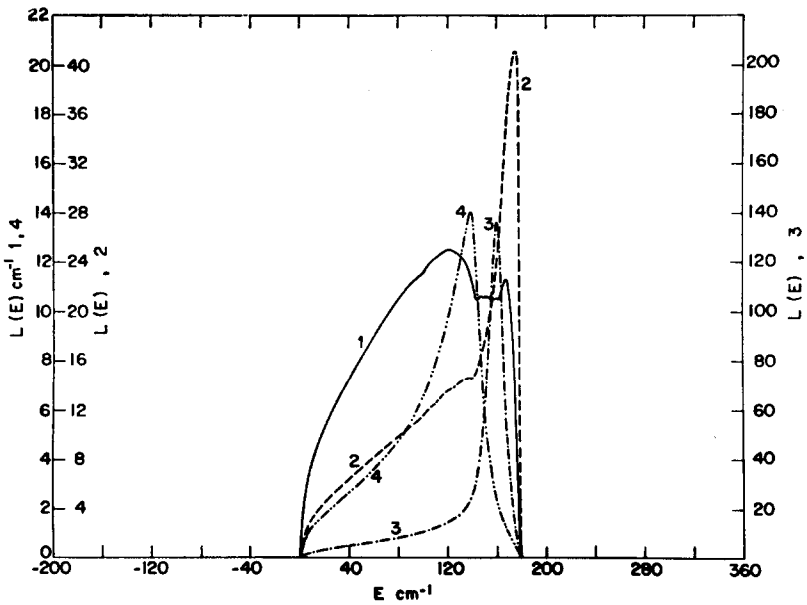


FIG. 7. The line-shape function for naphthalene mixed crystal calculated from the band structure displayed in Fig. 2. Curve 1: $U_0=+120$ cm^{-1}; curve 2: $U_0=+90$ cm^{-1}; curve 3: $U_0=+60$ cm^{-1}; curve 4: $U_0=+30$ cm^{-1}. From the analysis of Fig. 3 and Table II, we note that curves 1 and 2 correspond to bound states and yield a large contribution to $L(E)$ throughout the whole region of the exciton band. Curve 3 corresponds to a virtual state, leading to an appreciable contribution to $L(E)$ only near the band edge. Curve 4 corresponds to a very small perturbation leading to a $L(E)$ function which is close to the shape of $g_0(E)$.

strated[15] that the impurity-induced dipole strength, $d(E)$, defined per unit energy, can be displayed in the form

$$d(E)=L(E)T(E), \tag{13}$$

where $L(E)$ is the line-shape function which is determined by the diagonal matrix element of the perturbed density-of-states function[15]

$$L(E)=g_0(E)U_0^2/[1-U_0F(E)]^2+\pi^2U_0^2g_0(E), \tag{14}$$

and the term $T(E)$ is determined by the transition moments $\mathbf{M}(j)$ to the jth exciton band, and by the energy levels $E_j(0)$ corresponding to the $\mathbf{k}=0$ energy level for the jth exciton band. The $T(E)$ term can be displayed in the form

$$T(E)=\sum_j \{M(j)/[E-E_j(0)]\} \times \sum_{j'} \{M(j')/[E-E_{j'}(0)]\}. \tag{15}$$

From the analysis of the line-shape function[15] it follows that for the case of a localized state, the line-shape function will exhibit a delta-function behavior, $\delta(E-E_r)$, outside the band and will be characterized by a continuous contribution throughout the whole band region. In the case of a virtual state, there is an appreciable contribution to $L(E)$ only close to the exciton band edge. In the limit of an extremely weak perturbation, whereupon no virtual state can be formed, the line-shape function reveals again a continuous contribution throughout the whole band region, which is roughly proportional to $g_0(E)$. In Figs. 7 and 8, we display the line-shape functions in the exciton band region for naphthalene and for benzene, calculated again from the experimental density-of-states functions.[12] The impurity-induced dipole strengths for these two systems are presented in Figs. 9 and 10. These results demonstrate the expected behavior for bound states, virtual states, and the case of an extremely weak perturbation. Both the bound-state limit and the extremely weak perturbation case induce a continuous absorption throughout the exciton band, leading to the broadening of the Davydov components. The virtual state exhibits a well-defined asymmetric Lorentzian absorption band within the exciton band.

To date, no experimental data are available to test these theoretical predictions. The spectral data of Broude *et al.*,[16b] seem to reveal a broadening of the Davydov components in mixed naphthalene/deuteronaphthalene crystals, when a bound impurity level is located outside the band. However, these spectra were obtained by a photographic technique, so that no further analysis can be performed. We strongly recommend the experimental study of the optical properties of virtual impurity states, whose location was discussed in Sec. II of the present paper.

VII. DISCUSSION

In the present work, the one-particle Green's-function method has been applied for the study of singlet excited states of isotopically mixed crystals of benzene and of naphthalene. It has been demonstrated that the same theoretical methods which were successful for the understanding of phonon states, electron traps, and spin-wave states in perturbed solids are very successful in the quantitative interpretation of Fraenkel-type excited states in mixed molecular crystals. It has been claimed[20] that "a shortcoming of the theories which cumulate in a Green's function is that they are impossible to apply to many real problems, save by graphical or numerical methods." Indeed, the original Koster–Slater relations

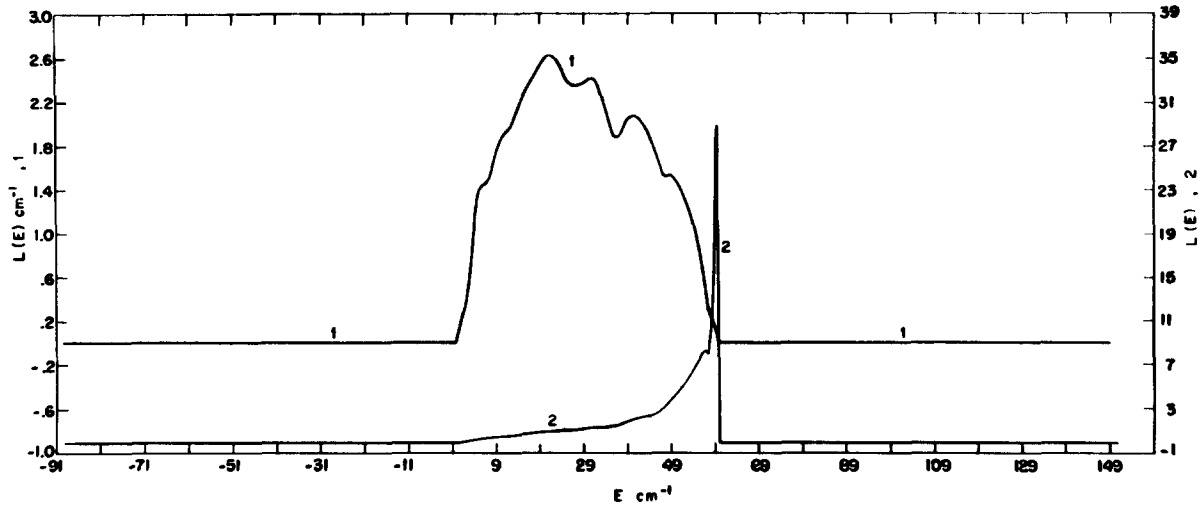


FIG. 8. The line-shape function for benzene mixed crystal calculated from the band structure displayed in Fig. 4. Curve 1: $U_0=+200$ cm^{-1}; curve 2: $U_0=+20$ cm^{-1}. Again, from the analysis of Fig. 5 and Table II, curve 1 corresponds to a bound state and curve 2 to a virtual state.

require a complete theoretical information on the exciton-energy-dispersion curve. On the other hand, the relation between the Green's function and the exciton density of states in the pure crystal leads to simple, manageable expressions which can be easily handled. The application of experimental data for the density-of-states functions obtained from hot-band spectroscopy[12] makes it possible to account semiquantitatively for the optical properties of mixed dilute molecular crystals. From the analysis presented herein, it is evident that simple perturbation techniques, in spite of their intuitive appeal to the chemist, cannot be applied for many cases of physical interest.

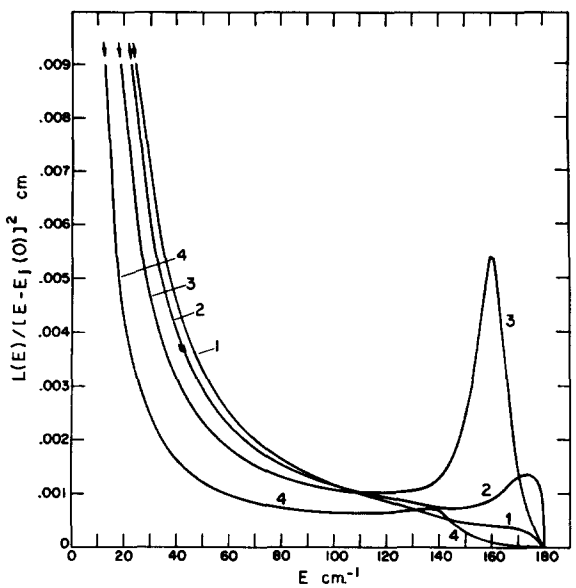


FIG. 9. Impurity-induced electronic absorption in the isotopically mixed naphthalene crystal. The first Davydov component is located at $E_1(0)=0$, and the absorption function

$$L(E)/[E-E_1(0)]^2$$

was calculated for this polarization. Curve 1: $U_0=+120$ cm^{-1}; curve 2: $U_0=+90$ cm^{-1}; curve 3: $U_0=+60$ cm^{-1}; curve 4: $U_0=+30$ cm^{-1}.

The theoretical study of the energy levels and the excitation amplitudes in mixed crystals provides a consistency check concerning the adequacy of the exciton density-of-states functions. The latter can be then used for the calculation of the first and second moments of the distribution of exciton states, which provide important information on the intermolecular interactions in excited states. In particular, from the first moment $m^{(1)}$ and the experimental fluorescence data,[3a,23] which locate one $\mathbf{k}=0$ Davydov component at the bottom of the band, the term $\Delta\epsilon^f+D^f$ can be derived, leading to an independent estimate of the interaction term I_{eq}.

The implications of the present treatment concerning the current theoretical calculations of intermolecular interactions in the first singlet exciton states in naphthalene and in benzene are somewhat discouraging. The theoretical density-of-states curves for naphthalene derived in the Fraenkel limit using the transition octupole coupling model[3b,5] do not reproduce faithfully the energy levels of mixed naphthalene/deuteronaphthalene crystals, in particular the states close to the band edge, which are sensitive to the details of the density-of-states function. Furthermore, the experimental density-of-states function leads to $I_{eq}\approx 0\pm 4$ cm^{-1}, while the value obtained from the octupole model is $I_{eq}\approx -16\pm 4$ cm^{-1}. Similar difficulties arise in the case of benzene, where according to the calculation of Thirunamachandran[6] the sum of excitation transfer

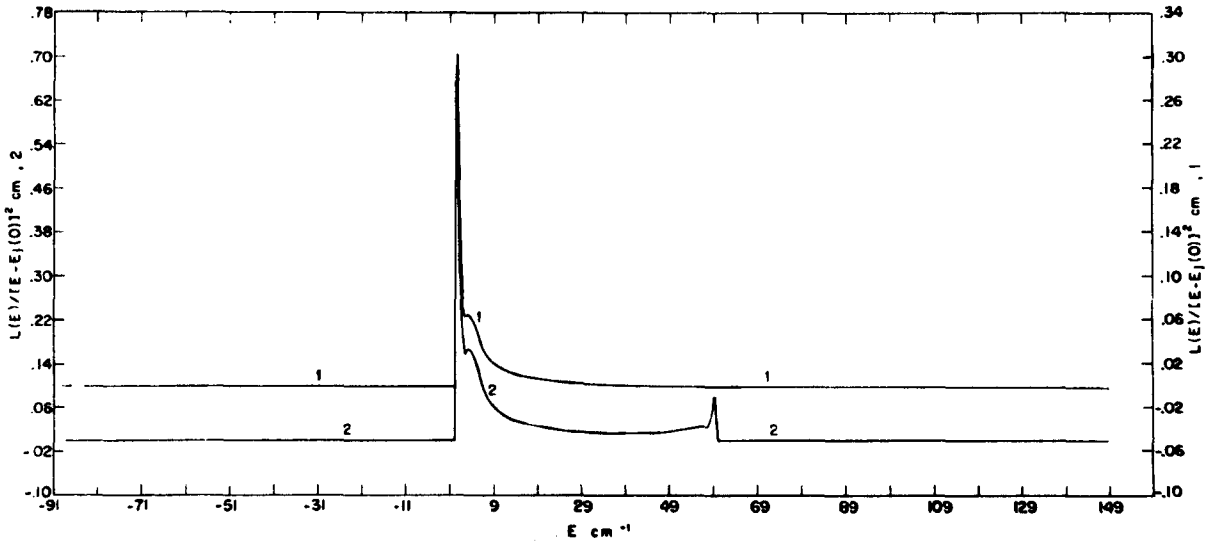


FIG. 10. Impurity-induced electronic absorption in the isotopically benzene mixed crystal. The lowest Davydov component is located at $E_1(0)=0$ and the absorption function $L(E)/[E-E_1(0)]^2$ was calculated for this polarization. Curve 1: $U_0=+200$ cm^{-1} (bound state); curve 2: $U_0=+20$ cm^{-1} (virtual state).

integrals over translationally equivalent molecules leads to a prediction of a negative contribution $I_{eq}=-0.003Q^2$ cm$^{-1}\approx-4$ cm^{-1}, while the first and second moment lead to $I_{eq}\approx0$. This discrepancy is not serious; however, it should be pointed out[17] that the short-range interaction terms with translationally inequivalent molecules derived from the experimental density-of-states function[17] $J[\frac{1}{2}(\mathbf{a}+\mathbf{b})]=-1.55$ cm^{-1}, $J[\frac{1}{2}(\mathbf{b}+\mathbf{c})]=3.93$ cm^{-1}, and $J[\frac{1}{2}(\mathbf{a}+\mathbf{c})]=3.28$ cm^{-1} are inconsistent with the results of the octupole model,[6] and cannot be obtained by scaling the transition octupole model Q (only one nonvanishing component exists for the B_{2u} state of benzene). It is apparent that at present the most profitable line of attack on the nature of the intermolecular interactions in the first singlet excited states of naphthalene and benzene and of the properties of the corresponding mixed crystals involves the application of empirical physical information derived from the experimental density-of-states functions.

Finally, it should be pointed out that the present treatment of mixed crystals rests on the simplest version of the Fraenkel tight-binding model. The apparent success of this treatment implies that the role of configuration interaction with higher crystal excited states is not of considerable importance. In particular, the role of charge-transfer states is not dominating.[8,17] This conclusion is consistent with the results of a recent analysis[8] of the crystal-shift terms in these systems.

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