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Optical line broadening of triplet excitons in dibromonaphthalene: Isotopic impurity and phonon scattering

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We present experimental data on the linewidths of the ground state to triplet exciton optical transition in 1,4-DBN at low temperatures. The linewidths are theoretically modeled by contributions due to ¹³C impurity scattering, defect scattering, deuterium impurity scattering, and one- and two-phonon scattering mechanisms. A consistent and complete description of the contribution of all these processes to the linewidths is achieved.

I. INTRODUCTION

The line shapes of exciton states in organic molecular crystals have been of interest for a number of years, both experimentally and theoretically. Because such crystals have highly anisotropic and variable intermolecular interactions, it is possible to test the theories of line shape in a variety of ways, such as the dependence of dimensionality (or anisotropy), exciton bandwidth, temperature (phonon scattering), and isotopic substitution. In this paper, we begin a detailed comparison of the predictions of the theory with experiment, by considering the very low temperature line shape of the ground state singlet to excited triplet 0.0 transition in 1,4-dibromonaphthalene (DBN).

This transition (and the excited triplet state) has been the object of a number of experimental and theoretical studies in the past.¹⁻¹⁰ We draw heavily on this work in this paper, in particular the work of Burland *et al.*⁸ in studying the linewidth. In the present paper, we present new experiments and a new calculation of the line shape, and show that there is quantitative agreement. Thus, the low temperature line shape in this system is understood.

This paper is laid out as follws: In Sec. II the experimental results are presented, including linewidths and line shapes as a function of temperature and isotopic doping. In Sec. III the coherent potential approximation is used to compute the line shape due to scattering by carbon-13 isotopic substitution, and by deuteration. In Sec. IV, we comment on the temperature dependence of the line shape, and conclude in Sec. V.

II. EXPERIMENT

DBN crystallizes in the $P2_1/a$ space group with eight molecules per unit cell.¹¹⁻¹³ These form two sets with four crystallographically equivalent molecules in each set. Since the dominant interactions (in the transition we are studying) are between *translationally* equivalent molecules, we can describe the crystal as made up of one-dimensional stacks of translationally equivalent molecules.

The ground state singlet to first excited triplet state optical transition in the crystal is split into two lattice components (corresponding to the two sets mentioned above), each lattice component is split in principle into two allowed Davydov components (and two unallowed Davydov components), and each of these is split into three triplet states.¹⁴ Whereas earlier workers did not resolve the Davydov or triplet components, since the splittings are so small, recently we succeeded in studying these in detail.¹⁵ However, for the present purpose the underlying substructure of the exciton transition can be neglected in most respects.

A. Experimental methods

The experimental results reported in this work were obtained by triplet photoexcitation spectroscopy. The excitation spectra were measured using a tunable cw dye laser (Coherent Mod. 599; dye Coumarin 102) in broad and narrow band version, at bandwidth of 0.5 and 0.001 cm⁻¹, respectively.

Sublimation grown crystal flakes we used, which developed in the *ac* plane with typical areas of about $1 \times 10 \text{ mm}^2$ and thickness between 1 and 10μ . The protonated and perdeuterated starting material has been zone refined in the Stuttgarter Kristallabor. By mass spectrometry a content of 11% DBN- d_5h_1 impurity in the DBN- d_6 material has been determined.

Crystal samples were held strainfree between paper masks. They were kept at constant temperature in a standard variable temperature helium cryostat and irradiated perpendicular to the ac plane with light polarized parallel to the crystal c axis.

B. Experimental results

The results reported in the present work are confined to measurements on the purely electronic $T_1 \leftarrow S_0$ 0-0 transition.

(1) Low temperature lines: In Fig. 1 are reproduced the 0–0 lines of both lattice components observed at 1.5 K in polarized light ||c. The lines TG I at 20 192 cm⁻¹ and TG II at 20 245 cm⁻¹ are essentially narrower than in other experi-

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FIG. 1. Low temperature line shape of the lower (a) and upper (b) lattice component of the DBN triplet exciton (light polarized $||c\rangle$).

ments and clearly differ with respect to both linewidth and line shape. The polarization ||c| has been specifically chosen to yield the narrowest line in zero field. Moreover, in this case, the measured linewidth of TG I (FWHM = 0.075 cm⁻¹), which is made up of a superposition of its Davydov subcomponents, is only slightly larger than the individual widths (FWHM = 0.065 cm⁻¹) actually observed in magnetic fields.¹⁵ The line shape of TG I is very sensitive with respect to crystal quality. For example, strongly asymmetric (toward high energy) line broadening is observed in samples of lower quality (Fig. 2). Thus the presence of inhomogeneities can lead to strongly asymmetric lines in some cases, in contrast to the usually assumed symmetric line broadening from inhomogeneities.



FIG. 2. Low temperature line shape of the lower lattice component TG I in two crystals of different crystal quality. The observed linewidths (FWHM) are 0.075 and 0.10 cm^{-1} , respectively.

Both the lines TG I and TG II are asymmetric (broader toward high energy) with asymmetry ratio (half-width to high energy divided by half-width to low energy) of $\gamma_2/\gamma_1 = 2$ for TG I and $\gamma_2/\gamma_1 = 1.3$ for TG II. To a good approximation the high energy side of both lines is Lorentzian, while the low energy side of both is Gaussian.

(2) Deuteration effects at low temperature: Sublimation grown samples of protonated 1,4-dibromonaphthalene (DBN- h_0) doped with its perdeuterated counterpart (DBN- d_6) reveal a drastic line broadening and line shift of TG I, which both increase proportional to the guest concentration. The asymmetry of the line shape, however, ($\gamma_2/\gamma_1 \approx 2$) is not changed upon doping. Examples are shown in Fig. 3(a).

For comparison the line TG I of a DBN- d_6 undoped crystal is given in Fig. 3(b), which is known to contain about 11% DBN- d_5h_1 isotopic impurities intrinsically. Both line shape and asymmetry are the same as above. The linewidth, however, is smaller than in the more highly doped sample of Fig. 3(a), in which the impurity concentration is compara-



FIG. 3. Deuteration effects on the low temperature lines of TG I: (a) 0%, 5%, and 10% DBN- d_6 in DBN- h_6 (b) natural DBN- d_6 , containing about 11% DBN- d_3h_1 impurity.

ble to the DBN- d_6 case. Apparently the amount of impurity induced line broadening is different for the barriers or the trapping centers.

(3) Temperature dependences: The temperature dependences of lines TG I and TG II are given in Fig. 4 for the temperature range between 1.6 and 25 K. Both lines develop from the asymmetric low temperature shape into symmetric Lorentzians as the temperature increases. The line positions are red shifted with increasing temperature at $T \ge 10$ K. The shift of line I is greater than that of line II.

In Fig. 5 are plotted separately the respective linewidth contributions γ_2 and γ_1 of higher and lower energy tails from Fig. 4, which develop differently with temperature.

III. THEORETICAL DESCRIPTION OF THE T=0 LINE SHAPE

A. Scattering by ¹³C isomers

As pointed out by Burland et al.,8 the natural abundance of carbon-13 will mean that $\sim 11\%$ of the DBN molecules has been isotopically substituted in one position. This will change the transition energy by a small amount ($\sim 2 \text{ cm}^{-1}$), but because the exciton bandwidth B is only $\sim 25 \text{ cm}^{-1}$ wide, this change will have an observable effect on the line shape. Earlier calculations of this effect used a two component model; i.e., they assumed that every isotopically substituted molecule has a transition energy shift of $+2 \text{ cm}^{-1}$ regardless of the position of the substituted carbon in the naphthalene skeleton. From experiments on the singlet-triplet transition of naphthalene substituted with ${}^{13}C$ in the α , β , or γ position, ¹⁶ we know that the shift in transition energy is in fact dependent on substitution position: the shifts are 3.5, 1.7, and 2.1 cm⁻¹, respectively. In DBN, the α and β shifts depend on which side of the naphthalene skeleton they are¹⁵; we will, however, ignore this effect. Thus, at this level of approximation the DBN crystal contains four components, three ¹³C substituted guests and the unsubstituted host.

We use the coherent potential approximation (CPA)¹⁷ to calculate the line shape. The Hamiltonian for this crystal is taken to be a tight-binding model:

$$H = \sum_{n} \epsilon_{n} |n\rangle \langle n| + \sum J_{nm} |n\rangle \langle m|, \qquad (1)$$

where $|n\rangle$ is the state representing a single, localized excitation on site n, ϵ_n is the excitation energy on site n, and J_{nm} is the matrix element for the transfer of excitation from site nto site m. For DBN, only the matrix element for nearest neighbors down the stack is appreciable. In what follows then, we take a one-dimensional model for the exciton band, although it is only a computational matter to include some interactions in other directions. We also assume that J_{nm} is independent of the isotopic species. For this Hamiltonian, the line shape as a function of energy (E) is given by I(E),

$$I(E) = \operatorname{Im} \langle G(\mathbf{k} = 0, E) \rangle_{c}, \qquad (2)$$

where the brackets represent an average over all configurations of the mixture of guest and host molecules consistent with the concentrations, and

$$G(k,E) = \langle k | (E - H - i\epsilon)^{-1} | k \rangle, \qquad (3)$$

where ϵ is a small positive number which is taken to be zero after the calculation, and $|k\rangle$ is the exciton state

$$|k\rangle = N^{-1/2} \sum_{n} e^{ikn} |n\rangle.$$
(4)

The effect of the guest molecules is to spread intensity from the zeroth order k = 0 level to other energies in the band, by the mixing of the zeroth order k = 0 state into other states. One way this can be represented is to do the configurational average of the inverse operator in Eq. (3):

$$\langle (E - H + i\epsilon)^{-1} \rangle_c = [E - H_{\text{eff}}]^{-1}, \qquad (5)$$

where the effective Hamiltonian is now a complex function of E. The line shape is then

$$I(E) = \operatorname{Im}\{\langle k | [E - H_{eff}(E)]^{-1} | k \rangle\}.$$
 (6)

In the CPA, a particular form for H_{eff} is assumed.

We assume that H can be written as the effective Hamiltonian, H_{eff} and a residual perturbation V given by

$$H_{\text{eff}} = \left[\bar{\epsilon} + \sigma(E)\right] \sum_{n} |n\rangle \langle n| + \sum_{n,m} J_{nm} |n\rangle \langle m|,$$
$$H_{\text{eff}} = \sum_{n} \left[\bar{\epsilon} + \sigma(E) + J(k)\right] |k\rangle \langle k|, \tag{7}$$



FIG. 4. Temperature dependence of the TG I and TG II lines in the range between 1.6 and 25 K.





FIG. 5. Temperature dependent linewidths of the higher and lower energy sides γ_2 and γ_1 of TG I and TG II; experimental values and best fitting curves (see Sec. IV).

$$V = \sum_{n} \left[\epsilon_{n} - \bar{\epsilon} - \sigma(E) \right] |n\rangle \langle n| \equiv \sum v_{n} |n\rangle \langle n|, \qquad (8)$$

where

$$\bar{\epsilon} = \sum_{\alpha=1}^{N} C_{\alpha} \epsilon^{(\alpha)} \text{ and } J(k) = \sum_{n \neq 0} e^{ikn} J_{n0}$$
(9)

and $\epsilon^{(\alpha)}$ is the excitation energy of species α and C_{α} is the number fraction of species α . The complex self-energy σ will depend on the energy E in a nontrivial way. From this form of H_{eff} and the form for I(E), we find

$$I(E) = \frac{\operatorname{Im} \sigma(E)}{\left[E - \overline{\epsilon} - J(0) - \operatorname{Re} \sigma(E)\right]^2 + \left[\operatorname{Im} \sigma(e)\right]^2}.$$
(10)

In the CPA, the form of $\sigma(E)$ is found by demanding that

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the configurationally averaged site diagonal
$$t$$
 matrix ele-
ment vanish, ensuring that the first correction is fourth or-
der. The site diagonal t matrix element is given by

$$t_n = \frac{v_n}{1 - v_n \langle G_{nn}^{(0)} \rangle_c},\tag{11}$$

where

$$\langle G_{nn}^{(0)} \rangle_c = \langle n | (E - H_{\text{eff}})^{-1} | n \rangle.$$
(12)

The configurational average of t_n is set to zero:

$$\sum_{\alpha=1}^{N} C_{\alpha} t^{(\alpha)} = 0$$
 (13)

or

$$\sum_{\alpha=1}^{N} \frac{C_{\alpha} v^{(\alpha)}}{1 - v^{(\alpha)} \langle G_{nn}^{(0)} \rangle} = 0$$

A simple manipulation gives

$$\sum_{\alpha=1}^{N} \frac{C_{\alpha}}{1 - v^{(\alpha)} \langle G_{nn}^{(0)} \rangle} = 1.$$
 (14)

Since both $v_{(\alpha)}$ and $G_{nn}^{(0)}$ contain $\sigma(E)$, this self-consistent equation must be solved numerically.

These equations for σ and I(E) have been solved for the energies and concentrations of the DBN crystal, assuming a one-dimensional array. The relevant parameters (bandwidth B and ¹³C shifts) are taken from the above discussion. The calculated line shape is given in Fig. 6. If the four component system is replaced by an equivalent two component system (i.e., a single guest with energy shift such that the average energy shift is the same as in the four component system), the line shape is given by the other curve in Fig. 6. As expected, the line shape is highly asymmetric. The halfwidth at half-maximum, on the high energy side in the four component system is 0.048 cm^{-1} and in the two component system 0.056 cm^{-1} ; the HWHM on the low energy side for the four component case is 0.015 cm^{-1} and for the two component case, 0.012 cm^{-1} . Thus the results are very similar for the four or two component systems. In Fig. 7 the two line shapes are plotted on top of one another with identical peak intensities in order to compare them. In addition, a Lorent-



FIG. 6. Calculated line shape of TG I for 13 C scattering in the CPA. Solid line: four components; broken line: two components (see the text). The unit of energy is 1/2 the exciton bandwidth. The intensity is in arbitrary units.

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FIG. 7. Comparison of calculated line shapes of TG I for ¹³C scattering in the CPA together with a Lorentzian. Solid line: four components; dot-dash line: two components; broken line: Lorentzian. Note that the four component line is nearly Lorentzian on the positive energy side. The unit of energy is 1/2 the exciton band width. The intensity is in arbitrary units.

zian of same height and high energy width is plotted. The two component line has a longer tail than does the four component line or the Lorentzian. Note that the four component line is quite Lorentzian on its high energy side.

When we compare the four component computed line with the experimental line shape, Fig. 1, we find good agreement in shape and overall width. In fact, when this computed line shape is compared to the experimentally observed *individual TG I subcomponents* (as observed in magnetic fields), the agreement for the linewidth is almost perfect. This agreement along with the observation of the effect of crystal quality on shape and width (Sec. II) lead to the conclusion that the zero temperature line shape is due almost exclusively to ${}^{13}C$ scattering and not to defect scattering as sometimes stated in the literature.⁹

B. Scattering by deuterated molecules

As we noted in Sec. II, when DBN- d_6 is introduced into the lattice, the low temperature line broadens and shifts as the concentration of deuterated molecules increases. The excitation energy of DBN- d_6 is ~65 cm⁻¹ above that of DBN h_6 , so that the deuterated molecules act as energy *barriers* for the excitation. Since the energy defect is ~2.6 times the bandwidth, we may take, in the first approximation, the barrier to be infinite. Then the deuterated molecules split the linear stack into noninteracting short stacks of DBN- h_6 molecules. We calculate the spectral intensity of each of these short stacks and add these together to obtain the total intensity.¹⁸

Consider a stack of N host molecules with *nearest neighbor* matrix element J (= -6.25 cm⁻¹ for DBN). The eigenfunctions for this stack are

$$\psi(k,N) = \left(\frac{2}{N+1}\right)^{1/2} \sum_{n=1}^{N} \sin\left(\frac{k\pi n}{N+1}\right) |n\rangle , \quad (15)$$

where *n* labels the site and *k* runs from 1 to *N*. The transition dipole moment from the ground state $|g\rangle$ is given by

$$\begin{aligned} \mu(k) &= \left\langle g \left| \sum_{n=1}^{N} \hat{\mu}_{n} \right| k, N \right\rangle \\ &= \left(\frac{2}{N+1} \right)^{1/2} \sum_{n=1}^{N} \sin\left(\frac{k\pi n}{N+1}\right) \langle g | \mu_{n} | n \rangle \\ &= \mu \left(\frac{2}{N+1} \right)^{1/2} \sum_{n=1}^{N} \sin\left(\frac{k\pi n}{N+1}\right) \\ &= \mu \left(\frac{2}{N+1} \right)^{1/2} \cot\left(\frac{k\pi}{2(N+1)}\right) \cdot \left[\frac{1-(-1)^{k}}{2} \right], \end{aligned}$$
(16)

where $\mu = \langle g | \mu_n | n \rangle$ is the transition dipole moment for the molecule at site *n*. The eigenvalue of state $|k,N\rangle$ is

$$\epsilon(k,N) = \epsilon_0 + 2J \cos\left(\frac{k\pi}{N+1}\right). \tag{17}$$

Thus the total intensity of the stack of N molecules is

$$I_N(a\omega) = \left(\frac{2\mu^2}{N+1}\right) \sum_{\substack{k=1\\\text{odd}}}^N \cot^2\left[\frac{k\pi}{2(N+1)}\right]$$
$$\cdot \frac{\gamma/\pi}{\left[\omega - 2J\cos(k\pi/N+1)\right]^2 + \gamma^2}, \quad (18a)$$

where we have taken $\epsilon_0 = 0$ and have assumed that every state $|k,N\rangle$ has a Lorentzian line shape of width γ .

The total intensity of the entire stack is

$$I(\omega) \propto \sum_{N=1}^{\infty} (1-C)^{N} I_{N}(\omega).$$
(18b)

In Fig. 8(a) we plot $I(\omega)$ for concentrations (c) of 5%, $7\frac{1}{2}$ %, and 10% using this model for $\gamma = 0.002 J \approx 0.0125$ cm⁻¹.

This calculation predicts linewidths in reasonable agreement with experiment when γ is fairly large; however, the calculated energy shifts are not as the experimental values. This suggests that other terms in the Hamiltonian beyond our approximate form (i.e., nearest neighbor interactions and *J* independent of deuteration) may play a role in describing the experiment. In Fig. 8(b), we also plot the line shape predicted by the CPA, which is *not* expected to be quantitatively accurate for very large barriers, as in this case. As expected, the CPA results are in poor agreement with the experiment.

IV. TEMPERATURE DEPENDENCE

The temperature dependence of the line shape is given in Fig. 4. The line broadens and becomes more and more symmetric as the temperature rises. These results are qualitatively similar to those of Burland *et al.*,⁸ although the widths are substantially smaller for the present samples. The theory of the temperature dependence of an exciton linewidth due to phonon scattering is well known¹⁹; the theory for the exciton linewidth in the case of phonon scattering vs impurity and defect scattering is less understood, in particular in those cases in which they are of comparable magnitude. In the present case, the thermal effects soon overwhelm the simple approximation that the width due to thermal scattering $\Gamma(T)$ and that due to impurity and defect scattering Γ_0 and so that the full width Γ_{tot} , is given by

$$\Gamma_{\rm tot} = \Gamma_0 + \Gamma(T). \tag{19}$$



FIG. 8. (a) Calculated line shapes of TG I for deuteration scattering in the infinite barrier model. The curves are for 5% (top), $7\frac{1}{2}$ % (middle), and 10% (bottom) concentrations of deuterated molecules. The unit of energy is 1/2 the bandwidth; the intensity is in arbitrary units, and $\gamma = 0.002$ J ≈ 0.025 cm⁻¹. (b) Calculated line shapes of TG I for deuteration scattering in the CPA for 5% and 10% deuterated impurities in DBN- h_6 . The solid line is 5%, dot-dash line is 10%. The energy unit is 1/2 the bandwidth; the intensity is in arbitrary units.

The major mechanisms of phonon scattering of the exciton transition are one phonon and two phonon (Raman) events. In a one phonon event, the exciton at $\mathbf{k} = 0$ is scattered by annihilation of a phonon wave vector q to the exciton state at $\mathbf{k} + \mathbf{q}$, with conservation of energy and wave vector. For acoustic phonons in DBN, these conservation laws rule out intraband scattering in a one phonon event. An interband one phonon (either acoustic or optical) event from TG I to TG II in DBN will have a rate given by

$$\Gamma^{(1)}(T) = G_1 \cdot \bar{n}(\omega_0) \equiv G_1 \cdot e^{-\beta\omega_0} (1 - e^{-\beta\omega_0})^{-1}, \quad (20)$$

where ω_0 is the phonon (either acoustic or optical) frequency and G_1 is the square of the matrix element multiplied by a density of states factor. Since TG II is $\sim 53 \text{ cm}^{-1}$ higher in energy, $\omega_0 \approx 53 \text{ cm}^{-1}$. Note that the scattering from the TG II k = 0 state down to TG I will have a rate,

$$\Gamma_{II}^{(1)}(T) = G_2 \cdot [\bar{n}(\omega_0) + 1], \qquad (21)$$

where we expect G_2 in this expression to be approximately equal to G_1 in the former equation for optical phonons but not necessarily for acoustic phonons. The *two phonon events* at low temperature can be described as the creation of a phonon of wave vector \mathbf{q}_1 , the annihilation of a phonon of wave vector \mathbf{q}_2 and the scattering of the exciton from $\mathbf{k} = 0$ to $\mathbf{k} = \mathbf{q}_2 - \mathbf{q}_1$ (*intraband*). Many such events can contribute, since the conservation laws do not lead to severe restrictions here. For *acoustic* modes, with Debye temperature T_D , this leads to a $T^{7, 19(b)}$ dependence of the rate at low T and T^2 at high T:

$$\Gamma_{\rm ac}^{(2)}(T) = G_3 \cdot f_{\rm ac} \left(T/T_D \right)$$

= $G_3 \left(T/T_D \right)^7 \int_0^{T_D/T} \frac{x^6 e^x}{(e^x - 1)^2} dx.$ (22)

For optical modes (e.g., librations), the rate will be

$$\Gamma_{\rm op}^{(2)}(T) = G_4 \bar{n}(\omega_{\rm op}) \left[\bar{n}(\omega_{\rm op}) + 1 \right].$$
⁽²³⁾

In the work of Burland *et al.*,⁸ the temperature dependence of the linewidth could be fit equally well with either a one phonon *interband* process with $\omega_0 = 50 \text{ cm}^{-1}$ or a two optical phonon *intraband* scattering with $\omega_0 = 17 \text{ cm}^{-1}$. These



FIG. 9. Temperature dependent part of the linewidth contributions γ_2 and γ_1 of TG I and TG II plotted as a function of $\bar{n}(\omega_0)$ [$\bar{n}(\omega_0) + 1$] with $\omega_0 = 53 \text{ cm}^{-1}$ (top) and $\omega_0 = 39 \text{ cm}^{-1}$ (bottom), respectively. Circles: TG I, high energy side; triangles: TG I, low energy side; squares: TG II, low energy side; crosses: TG II, high energy side. Note that straight lines cannot be drawn through the sets of points for either TG I or TG II.

authors were not able to decide which mechanism was preferred.

Note that if the one phonon *interband* process is the dominant process and if, as we expect, the exciton band shape and exciton phonon coupling matrix elements for the lower lattice component and upper lattice component are approximately equal $(G_1 \approx G_2)$, then by detailed balance, we expect the upper lattice component to have a width governed by Eq. (21). Thus an upper bound of G_1 can be derived from the difference in the low T linewidths of these two components after subtracting Γ_0 from both linewidths.

The present data cannot be fit accurately either by a one phonon interband process alone or by a two phonon intraband process alone. As an example of the latter, we plot the experimental values of $\Gamma(T)$ in Fig. 9 for the high and low energy sides of the lines for TG I and TG II vs $\bar{n}(\omega_{op})$ $[\bar{n}(\omega_{op}) + 1]$ for $\omega_{op} = 53$ cm⁻¹ and for $\omega_{op} = 39$ cm⁻¹ (both frequencies are seen in the Raman spectrum of DBN crystals at low temperature). The higher temperature behavior of $\Gamma(T)$ (Fig. 9) clearly rules out the possibility of the former.

The final result of this is that in order to fit the experimental data $\Gamma_{tot}(T) = \Gamma_0 + \Gamma(T)$ of both TG I and TG II we must use the form

$$\Gamma_{\rm I}(T) = G_1 \bar{n}(\omega_0) + G_3 f_{\rm ac}(T/T_D), \qquad (24)$$

$$\Gamma_{\rm II}(T) = G_2 [\bar{n}(\omega_0) + 1] + G_3 f_{\rm ac}(T/T_D)$$

with $\omega_0 = 53 \text{ cm}^{-1}$, $G_1 = G_2 = 0.1 \text{ cm}^{-1}$, $T_D = 90 \text{ K}$, and $G_3 = 85 \text{ cm}^{-1}$.

The fit is given in Fig. 5. Note the excellent agreement between experiment and this model; in addition, if the asymmetric contribution of Γ_0 is subtracted from $\Gamma_{tot}(T)$, we find symmetric lines with confirmation of the above assumption that $G_1 \cong G_2$. The difference in linewidths of TG I and TG II in the limit $T \rightarrow 0$ can be understood only by the spontaneous emission term in Eq. (24) for TG II.

It would be possible, of course, to fit the data with more complicated superpositions of all phonon scattering processes discussed above; however, we believe that the present fit is the most simple and sufficiently convincing description of the observed temperature dependences.

V. CONCLUSION

In this paper, we have presented the first complete analysis of the different contributions to the optical linewidths in an exciton transition in a molecular crystal.

In the zero temperature limit, the linewidth is dominated by scattering by intrinsic residual impurities (${}^{13}C$ containing molecules) and is highly asymmetric. Deuterium substitution produces a different type of impurity scattering, which also leads to asymmetric lines with broader high energy tails, and can be treated theoretically by the methods of Lifshitz.¹⁷ Defect scattering can be avoided by careful preparation of thin crystals. In the data analyzed here, this type of broadening can be neglected. However, in this sytem, which is a quasi-one-dimensional exciton, the experimental results clearly show that defect scattering can lead to asymmetric line shapes, in agreement with CPA models. The explanation for the asymmetric lines due to defects lies in the microscopic nature of the defect scattering. That is there are two limiting kinds of defects: microscopic and macroscopic, by which we mean point-like scattering centers and domainlike defects. These lead to different broadening effects and hence to different line shapes. Microscopic defects lead (in one-dimensional systems) to asymmetric lines, macroscopic defects to symmetric lines. Clearly, there is a continuum of possibilities between these limits.

Finally, we have analyzed the experimental temperature dependence of the optical linewidths and have accurately fit the data by a superposition of two different phonon scattering mechanisms, a one phonon interband contribution and a two phonon Raman contribution. By examining both lattice components, TG I and TG II, we were able to show consistency with a single set of parameters.

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