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INTERPRETATION OF THE OPTICAL DEPHASING TIME AND LINESHAPE FUNCTION IN THE $S_0 \rightarrow T_1$ EXCITON TRANSITIONS OF 1,4 DIBROMONAPTHALENE

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DISCLAIMER

Interpretation of the Optical Dephasing Time and Lineshape Function

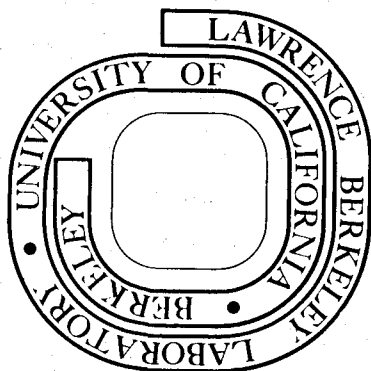in the $S_o \rightarrow T_1$ Exciton Transitions of 1,4 Dibromonapthalene.

by

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ABSTRACT

The lineshape function for the $S_o \rightarrow T_1$ absorption in 1,4 dibromo-napthalene is analyzed in terms of exchange theory. It is shown that the dominant optical dephasing mechanism for the electric dipole transition to the k=o state in the band is not due to Orbach or Raman scattering but results from the absorption and emission of a low energy optic phonon. This process dephases the optical absorption because of frequency differences of the optic phonon in the ground and excited state but does not cause the exciton to loose coherence because the phonon and exciton wavevectors are unchanged in the phonon absorption and emission process. In addition, it is shown how to extract the phonon absorption rate and the lifetime in the phonon promote state from the data. The promotion rate constants are $\sim 10^6 \sec^{-1}$ at 2°K and approach $\sim 10^{11} \sec^{-1}$ at 30°K. The lifetime in the phonon promoted state is 7 psec over the range 15-40°K.

I. INTRODUCTION

Recently there has been a considerable interest in the dynamics of exciton migration and the relationship of spectroscopic lineshapes[1-2], spin resonance[3-7] and transient optical experiments[8-10] to the coherent nature of the exciton states[5,11-15]. For Frenkel[16] excitons a simple explanation for the optical lineshape function has been presented[17] that is based on exchange theory[18,19]. It departs from existing theories and provides a clear picture of how various phonon exciton interactions contribute to optical dephasing times (homogeneous T_2 processes), absorption lineshape functions, and the k-scattering processes in the band states which, in turn, can lead to the loss of exciton coherence. It has been shown[17] that two mechanisms can account for the observed lineshape function for absorption to the k=0 state in the band, but only one mechanism leads to the loss of exciton coherence. The first mechanism is a multi phonon-exciton scattering process of the sort given by:

$$k_o + q \xrightarrow{W_+} (k_o q) \xrightarrow{W'} k' + q' \tag{1}$$

If $(k_o q)$ is taken as a real state, the scattering represents an Orbach process and if $(k_o q)$ is a virtual state then it is a Raman process. Both will cause linebroadening in the optical transition from the ground state, $\langle 00|$, to the k=0 state of the exciton band, $\langle k_o 0|$, with a temperature dependence which is related to the occupation number of the Planck distribution function evaluated at the energy ε_i of the optic phonon which is initially coupled to the exciton state. This mechanism, hence forth called mechanism I

should be the dominant channel for the loss of exciton coherence since a change in the exciton wavevector ($k_o \to k'$) is effected. Although mechanism I leads to line broadening it has been shown[17] that little or no frequency shift of the transition with temperature is to be expected in the range where the Planck function is small because the final exciton and phonon states are not coupled via an allowed electric dipole transition to the ground electronic state.

Although, Mechanism I is usually assumed [1,15,20] in the interpretation of optical dephasing times, it may not be the most important or significant contributor to line broadening at low temperature.   In this regard it was shown[17] that the simple absorption and emission of a phonon of the same wavevector q coupled to exciton $\langle k_o 0|$ state can also dephase the optical transition to the exciton band.   This mechanism (henceforth called mechanism II) is represented by:

$$k_o + q \underset{W_-}{\overset{W_+}{\rightleftarrows}} (k_o q) \tag{2}$$

and does not cause a loss of coherence of the exciton k=0 state because the exciton wavevector is unchanged.

From an experimental point of view the significant feature of mechanism II   is that the optical transition moment $\langle 00|\mu(t)|k_o 0\rangle$ can be "exchange averaged" with an allowed transition between the lowest phonon state, $\langle 0q|$, and the phonon-exciton state $\langle k_o q|$. This is illustrated in Figure 1. The manifestation of exchange averaging is to produce both a temperature dependent line broadening and frequency shift that reflects the Planck distribution function.

This will occur when the difference between the ground and excited state phonon energies $\delta\omega = (\varepsilon_i - \varepsilon_i')$ and the lifetime, τ, in $\langle k_o q|$ satisfy the condition

$$\delta\omega\tau \sim 1 \tag{3}$$

The important point to note in this range (intermediate exchange), is that the lineshape function reflects phase memory of the phonon absorption process (mechanism II) and not of the multiple phonon scattering process (mechanism I) and hence mechanism II can be distinguished from mechanism I in a given temperature range from the experimental value of $\delta\omega\tau$.

In this paper the optical absorption to the $k=o$ state in the triplet exciton bands of 1,4 dibromonapthalene[21,22] will be analyzed in terms of the above considerations. It will be shown (i) that the lines can be considered "homogeneous" above 7°K but that they are in intermediate exchange (exchange narrowed by the optic phonons) and hence the correct interpretation of optical dephasing times and phonon scattering or absorption mechanisms must come from an analysis of both the linewidth and frequency shift. Furthermore, (ii) it will be shown that the dominant dephasing mechanism for absorption to the $k=o$ state of the triplet exciton band in this crystal is the absorption and emission of a low energy optic phonon with little or no change in the phonon or exciton wavevector and that a quantitative measure of the phonon absorption rate, W_+ and lifetime in the state $\langle k_o q|$ can be obtained from the data. Finally, (iii) some general observations will be made about dephasing times of optical transitions that apply to band states as well to localized state in pure and mixed crystals.

II. Analysis of the Exciton Lineshape Function of 1,4 Dibromonapthalene

The work of Burland, Konzelmann, and Macfarlane[22] (BKM) has unequivocally established that (i) the triplet exciton absorption linewidth for both crystal sites[23] in 1,4 dibromonapthalene broaden in an non-exponential manner from 4°K to 40°K; (ii) both transitions are frequency shifted to _lower_ energy with increasing temperature. In addition they have determined that the lowest optic phonon has an energy of 17 cm^{-1} [24].

It has been shown[17] that the temperature dependent portion of the lineshape function can be given by a Lorentz lineshape function, $I(\omega)$, defined by an effective frequency, ω_e and relaxation time, T_{eff}^{-1}, where

$$I(\omega) = \left(1 + (\omega_e - \omega)^2 (T_{eff})^2\right)^{-1}, \qquad (4)$$

$$\omega_e = \omega_o + \left(\frac{\delta\omega\tau}{1 + (\delta\omega\tau)^2}\right) \cdot W_+, \qquad (5)$$

$$T_{eff}^{-1} = \left(\frac{(\delta\omega\tau)^2}{1 + (\delta\omega\tau)^2}\right) \cdot W_+. \qquad (6)$$

For scattering mechanism I, equations 5 and 6 converge[17] to:

$$\omega_e = \omega_o \qquad (7)$$

$$(T_{eff}^{-1}) = W \qquad (8)$$

where

$$W \sim \langle n(\varepsilon_i) \rangle \qquad (9a)$$

for an Orbach process, and

$$W \sim \langle n(\varepsilon_i)\rangle\langle n(\varepsilon_i) + 1\rangle \tag{9b}$$

for a Raman process. $\langle n(\varepsilon_i)\rangle$ is the Planck distribution function evaluated at the energy of the phonon responsible for scattering. For phonon absorption (mechanism II), at low temperatures equations (4) and (5) converge[17] to:

$$\omega_e = \omega_o + \Delta_{eff} \tag{10}$$

where

$$\Delta_{eff} = \delta\omega \left(\frac{1}{1 + (\delta\omega\tau)^2} \right) \cdot \langle n(\varepsilon_i)\rangle \tag{11}$$

and

$$T_{eff}^{-1} = \delta\omega \left(\frac{\delta\omega\tau}{1 + (\delta\omega\tau)^2} \right) \cdot \langle n(\varepsilon_i)\rangle \tag{12}$$

The importance of exchange broadening via mechanism II can be determined[17] from BKM's data from the ratio of the temperature dependent line broadening to the temperature dependent frequency shift. One notes that the ratio of the temperature dependent portion of the frequency shift Δ_{eff} and the linewidth (T_{eff}^{-1}), given by equation 11 and equation 12 respectively, is equal to:

$$T_{eff}^{-1}/\Delta_{eff} = \delta\omega\tau \tag{13}$$

This ratio is plotted vs. temperature from the data of BKM for both absorption origins in the 1,4 dibromonapthalene triplet exciton spectrum. These are illustrated for site I ($20,192$ cm^{-1}) and for site II ($20,245$ cm^{-1}) in figure 2a and 2b respectively. Although the error is large at 15°K and 20°K it is clear that both transitions reflect exchange narrowing as outlined above. The average value of $\delta\omega\tau$ is 0.63 for site I and 0.75 for site II. This establishes that the optical lineshape function for both sites are broadened by mechanism II. Moreover, the energy of the optic

phonon in the exciton triplet state is lower in the excited state
than in the ground state because the frequency shift of the transi-
tions are toward lower frequency with increasing temperature. A
quantitative estimate of τ and $\delta\omega$ can be arrived at by further
analysis.

Substitution of the values for $\delta\omega\tau$ for each site (I and II)
into equations 11 and 12 results in two equations for each site
which relate the frequency shifts and relaxation times to the
Planck distribution function,

$$\langle n(\varepsilon_i)\rangle = (e^{\varepsilon_i/kT} - 1)^{-1} . \tag{14}$$

For site I, in terms of Δ_{eff} and T_{eff}^{-1} in wavenumbers, these are:

$$(\Delta_{eff})_I = \delta\omega_I \cdot (0.72) \cdot \langle n(\varepsilon_i)\rangle \tag{15}$$

$$(T_{eff}^{-1})_I = 2 \cdot \delta\omega_I \cdot (0.45) \cdot \langle n(\varepsilon_i)\rangle \tag{16}$$

and for site II:

$$(\Delta_{eff})_{II} = \delta\omega_{II} \cdot (0.64) \cdot \langle n(\varepsilon_i)\rangle \tag{17}$$

$$(T_{eff}^{-1})_{II} = 2 \cdot \delta\omega_{II} \cdot (0.48) \cdot \langle n(\varepsilon_i)\rangle \tag{18}$$

In figure 3 the data for the temperature dependent portion of the
linebroadening, T_{eff}^{-1}, (FWHM) and the temperature dependent frequency
shift, Δ_{eff}, are plotted vs. $f \cdot \langle n(17 \text{ cm}^{-1})\rangle$ where ε_i has been taken
to be equal to the energy of the lowest optic phonon branch at
17 cm^{-1}[24]. f is the appropriate constant in equations 15
through 18. From the plots one obtains the value for the frequency
shift $\delta\omega$ given in the figures along with the standard error from
a least squares fit to the four plots. It is clear from figure 3

that the data fits the theory remarkably well. From the value

of $\delta\omega$ and the exchange function $\delta\omega\tau$ one can calculate the lifetime

τ in the phonon promoted state, $|k_o q\rangle$, for each site.

For site I,

$$\tau_I = 5.7 \pm 0.4 \text{ psec}$$

and for site II,

$$\tau_{II} = 8.7 \pm 1.5 \text{ psec}$$

In addition, the promotion rate W_+ from $\langle k_o 0|$ to $\langle k_o q|$ can be

obtained from the relationship that satisfies microscopic reversi-

bility, i.e.

$$W_+\tau = \langle n(\epsilon_i)\rangle / (\langle n(\epsilon_i)\rangle + 1) \tag{19a}$$

which for low temperatures is:

$$W_+\tau \simeq \langle n(\epsilon_i)\rangle \tag{19b}$$

If one uses an average value of 7 psec for τ in the range 14-40°,

W_+ can be extrapolated from BKM's data to lower temperatures.

Figure 4 illustrates the temperature dependence of W_+ in the range

2°-40°K. In the temperature range 2 - 4.2° there is an extremely

rapid increase in the homogeneous relaxation time due to mechanism

II. For 1,4 dibromonapthalene the relationship between W_+ and

homogeneous relaxation time including the effects of temperature

independent T_1 and other T_2 processes is given by

$$(T_2^*)^{-1} = (0.32) W_+ + (T_1)^{-1} + (T_2)^{-1} \tag{20}$$

The factor 0.32 was arrived at using an average value of $\langle\delta\omega\rangle$ and

$\langle\tau\rangle$ for both sites. Since the total radiative and non-radiative

decay of the triplet exciton state[25] is $\sim 10^{-4}$ seconds, T_1^{-1} is

very small relative to W_+ at temperatures above $2°$. If the optical
absorption in 1,4 dibromonaphathalene is inhomogeneously broadened
at low temperature then the decay of a photon echo vs. time should
measure a combination of W_+ and $(T_2)^{-1}$. Burland and coworkers[22]
have analyzed the question of impurity or isotope scattering in
this system as a contributor to $(T_2)^{-1}$ and arrived at a value of
0.2 cm^{-1} at $2°$K. If one considered this as a temperature inde-
pendent homogeneous mechanism for dephasing then the influence
of the phonon absorption and emission on the total homogeneous
linewidth would minimal below $6.8°$K. This is illustrated in figure
4 as the "impurity scattering limit", and is taken at a temperature
where $(T_2)^{-1} \sim (T_{eff})^{-1}$. The question of impurity scattering in
exciton states is a complicated one. It is not clear, at least
to this author, under what circumstances the interactions could
be considered homogeneous in nature as opposed to inhomogeneous
or static in character. Photon echo experiments below the impurity
scattering limit in 1,4 dibromonaphathalene could experimentally
resolve some of the ambiguity. If, for example, the interactions
were to be inhomogeneous in character, then echo decays should
reflect $(T_{eff})^{-1}$ as related to W_+ given in figure 4. For a homogeneous
interaction echos should not be seen below $7°$K.

III.   Discussion and Conclusions

Several features of the above analysis are particularly note-
worthy. First, a lifetime of 7 psec in the phonon promoted state
is consistant with vibrational relaxation lifetime measurements
in other systems. It has been shown by de Vries and Wiersma[26]
that the homogeneous linewidth (FWHM) at $2°$K of the vibronic

transition at 5700 Å of dimethyl-s-tetrazine in durene is 28.8 GHz. This results in a vibrational lifetime of 11 psec. From a spin resonance experiment van't Hof and Schmidt[27] have determined a lifetime of 3 psec for a phonon promoted triplet state in parabenzoquinone. The promoted state in these experiments[27] was between 12.5 cm^{-1} and 16.5 cm^{-1} above the electronic origin. What appears to be emerging from the analysis of the data in 1,4 dibromonapthalene, and from the other experiments, is that τ is similar from one system to another and may not depend strongly on whether the state is localized (as in mixed crystals) or delocalized (as in the phonon-promoted exciton band). If this turns out to be the case, and τ is between 1-10 psec, one can anticipate that many optical transitions to the lowest singlet and triplet states in both mixed and pure crystals will be in intermediate exchange with optic phonon transitions since small shifts (1-10 cm^{-1}) in the optic branch phonon spectra are to be expected from differences in the ground and excited state potentials.

A second feature which emerges from the above analysis is that the interpretation that Orbach or Raman scattering is the dominant mechanism for optical dephasing[28] in photon-echo and other experiments at low temperature may be erroneous. It is essential to look for frequency shifts with temperature in the systems that have been studied before final conclusions can be drawn about the mechanims responsible for dephasing. This is particularly important if one wishes to determine a quantitative measure of the phonon promotion or scattering rates.

Finally, it should be noted that the promotion rates from 2° - 4.2°K as illustrated in figure 4 for a 17 cm^{-1} optic phonon are very small. If they are representative of other triplet exciton bands, such as in 1,2,4,5 tetrachlorobenzene[5], then there can be little doubt as to the coherent nature of exciton migration in these systems at low temperature[5,7]. Indeed, the results presented in section II demonstrate that, in fact, the exciton coherence persists over most of higher temperature range studied because the phonon absorption mechanism for optical dephasing or linebroadening does not require a change of the exciton wavevector to any considerable extent.

IV. Acknowledgement

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Figure Captions

Figure 1: Schematic representation of the absorption and emission of an optic phonon exchange averaging the $\langle 00|\mu(t)|k_o 0\rangle$ electric dipole transition moment (exciton origin) with the $\langle 0q|\mu(t)|k_o q\rangle$ transition moment. Only half of the exciton bands $\langle k0|$ and $\langle kq|$ are illustrated for clarity.

Figure 2: The ratio of the temperature dependent portion of the linewidth and frequency shift in the exciton origins of 1,4 dibromo-napthalene (A) crystal site I $(20,192 \text{ cm}^{-1})$; (B) crystal site II $(20,245 \text{ cm}^{-1})$.

Figure 3: Experimental and theoretical fit of the temperature dependent linewidth (A: site I; C: site II) and frequency shift (B: site I; D: site II) to equations 15 thru 18.

Figure 4: Phonon absorption rate for optic phonons at 17 cm^{-1} in 1,4 dibromonapthalene from 2°K to 35°K.

Figure 1

XBL774-5293

RATIO OF THE TEMPERATURE DEPENDENT PORTION OF THE
LINEWIDTH AND FREQUENCY SHIFT IN THE EXCITON ORIGINS
OF 1,4 DIBROMONAPHTHALENE

(A) Site I

$T_{eff}^{-1}/\Delta_{eff} = 0.63$

(B) Site II

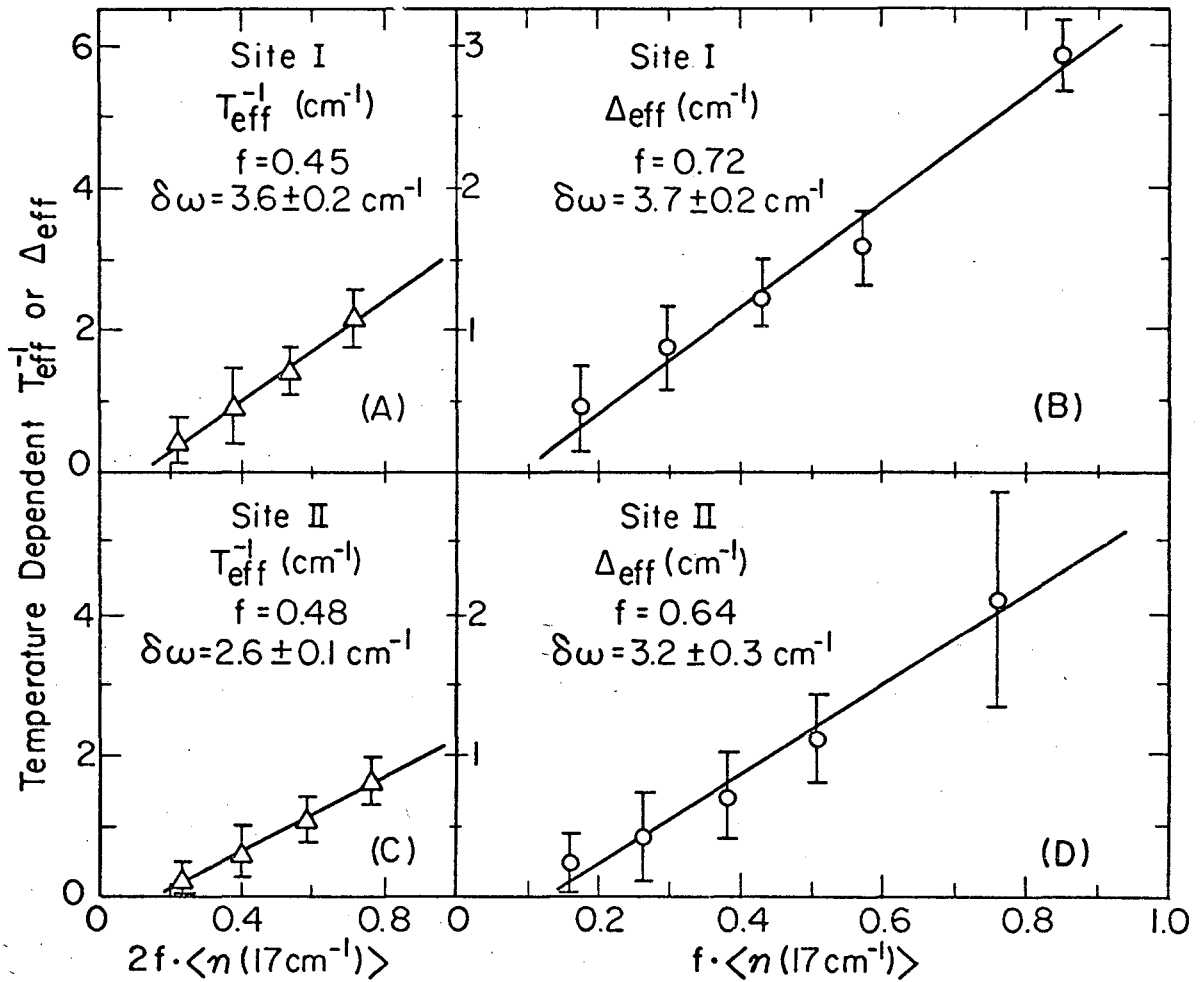$T_{eff}^{-1}/\Delta_{eff} = 0.75$

$\dfrac{T_{eff}^{-1}}{\Delta_{eff}}$
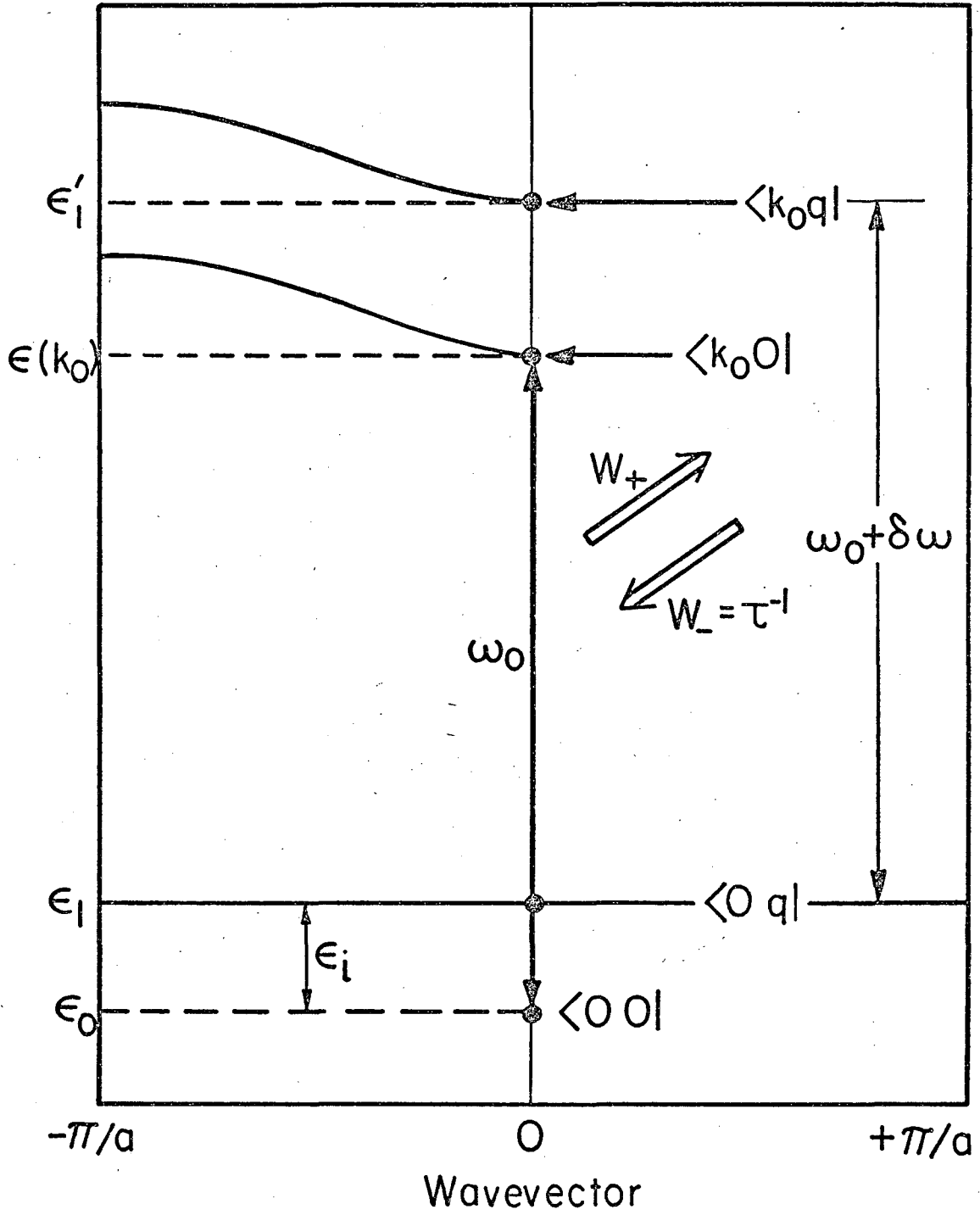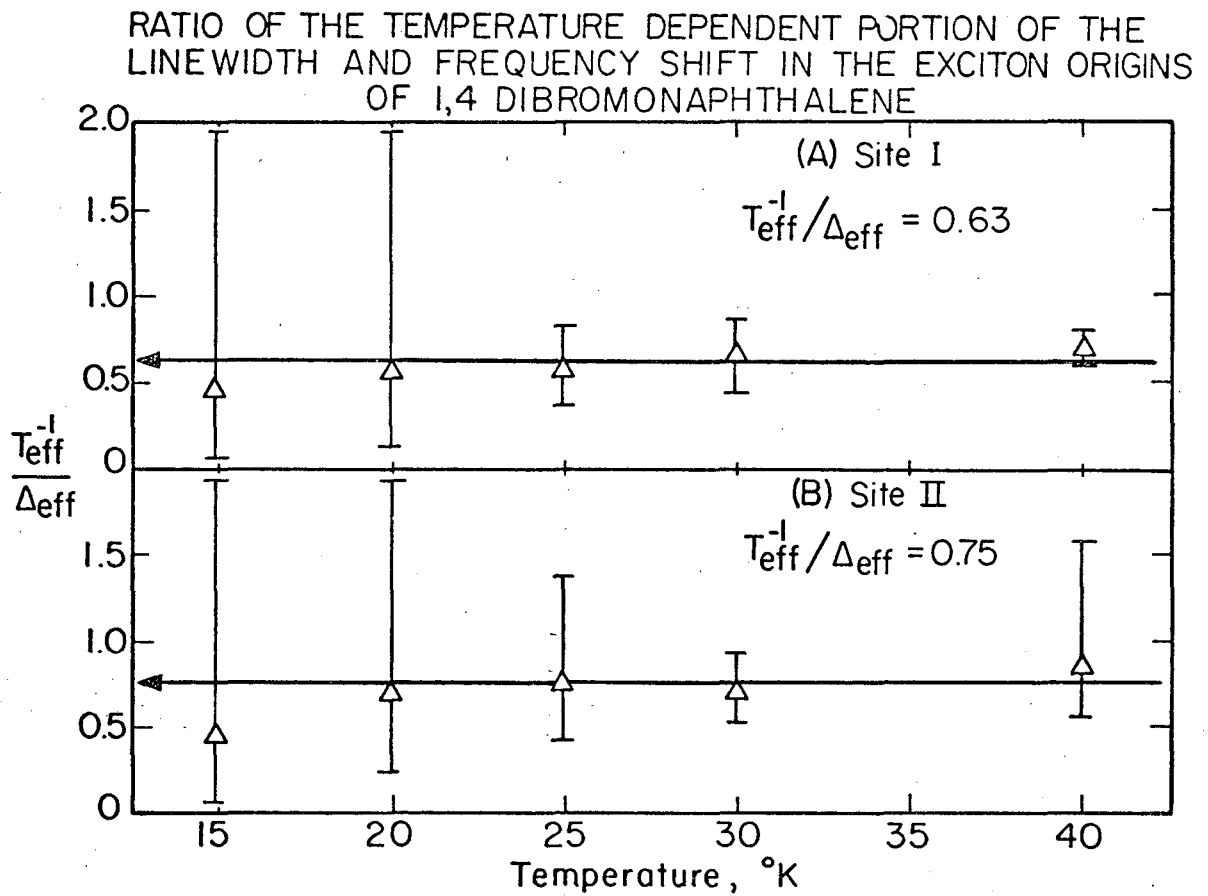
Temperature, °K

XBL774-5310

Figure 2

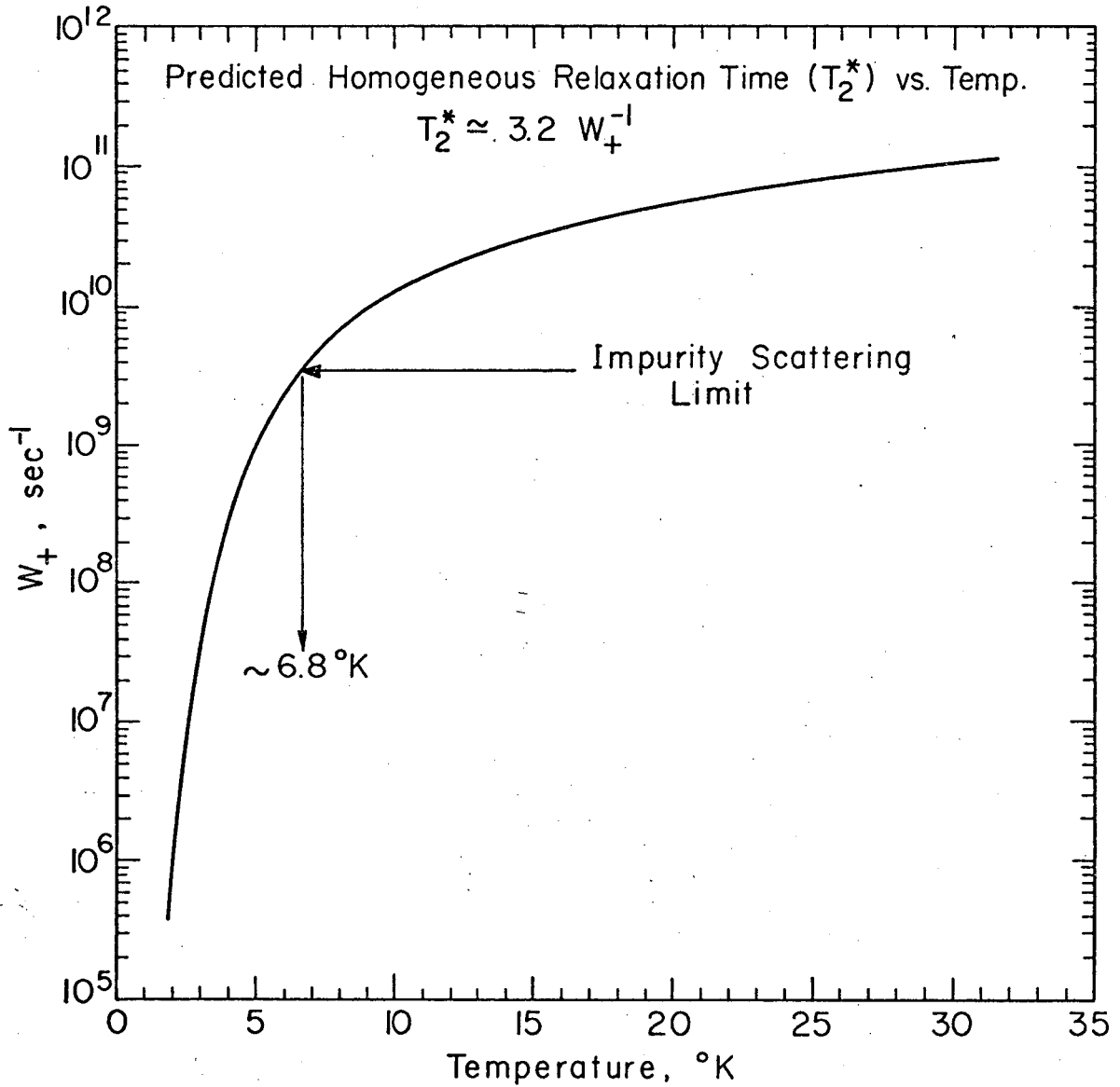LINEWIDTH AND FREQUENCY SHIFT ANALYSIS OF THE EXCITON ORIGINS IN 1,4 DIBROMONAPHTHALENE FROM 15°K TO 40°K

Figure 3

XBL774-5311

PHONON ABSORPTION RATE VS. TEMPERATURE FOR THE PROCESS $k_0 + q \underset{W_-}{\overset{W_+}{\rightleftharpoons}} (k_0 q)$ IN THE TRIPLET EXCITON BAND OF 1,4 DIBROMONAPHTHALENE

Figure 4.

XBL 7 74-5312