Apparent vibrational side-bands in \(\pi\)-conjugated systems: the case of distyrylbenzene

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The photoluminescence (PL) spectra of dilute solution and single crystals of distyrylbenzene show unique temperature dependent vibronic structures. The characteristic single frequency progression at high temperatures is modulated by a low frequency progression series at low temperatures. None of the series sideband modes corresponds to any of the distyrylbenzene Raman frequencies. We explain these PL properties using a time dependent model with temperature dependent damping, in which the many-mode system is effectively transformed to two- and then to a single "apparent" mode as damping increases.
Fourier transform of the time dependent auto-correlation function of the transition dipole moment, \( f(t) \),

\[
F(E) = \int_{-\infty}^{\infty} f(t) e^{iEt/h} \, dt .
\]  

(1)

![Image](image1)

**FIG. 1.** PL spectroscopy of DSB. (a) Solution spectra at 20 K and 200 K. The indices 0 and 1,2,3 in the 200 K spectrum denote the fundamental and vibronic replica transitions, respectively. The pairs of indices k,n (k=0,1,2,3) in the 20 K spectrum denote the complex modulated vibronic structure (see text). Inset: Chemical structure of DSB. (b) Fourier transform of the PL spectra shown in (a). Note the fast decrease at 200 K and the long period modulation at 20 K. The 200 K curve is vertically displaced for clarity. (c) Same as in (a) but for a DSB single crystal. Note the missing fundamental transition at 200 K and its finite, but small, intensity at 4 K.

Following Ref.\(^9\), we write the correlation function for a multi-mode system in the harmonic approximation and linear electron-phonon coupling as:

\[
f(t) = |P|^2 e^{-iE_0 t/h} - S_+ (t) + S_- (t) e^{-\Gamma |t|} ;
\]

\[
S_{\pm} (t) = \sum_j S_j w_j^{\pm} e^{i\omega_j t} ; S = \sum_j S_j (2n_j + 1) ,
\]

(2)

where \( P \) is the dipole matrix element for the relevant optical transition and \( E_0 \) is the bare optical transition energy. In Eq. (2), \( j \) is the mode index, \( w_j^+ = w_j^- + 1 = n_j + 1 \), where \( n_j = 1/[\exp(h\omega_j/k_B T) - 1] \) is the mode occupation number at temperature \( T \), \( S_j = \omega_j \Delta_j^2 / (2\hbar) \), and \( \Delta_j \) is its equilibrium (normal coordinate) displacement in the optically excited electronic state relative to the ground state. We emphasize here that it is the "electron temperature", \( T_e \), which determines the mode occupation, \( n_j \). \( T_e \) is determined by the photon excitation energy and the electron excess energy relaxation rate and may be considerably higher than the lattice temperature, \( T \).

We identify \( S \) with the system HR factor, which is the sum of the individual HR factors modified by the temperature (Eq. (2)). The time dependent term \( S_+ (t) \) in Eq. (2) is responsible for the red shifted vibronic side bands in the PL spectrum, while \( S_- (t) \) gives rise to blue-shifted side bands (due to excited vibrational level occupation), emphasizing the low frequency modes at relatively high \( T_e \). In Eq. (2), a simple mode-independent phenomenological damping, \( \Gamma \geq 0 \), is introduced; it represents losses due to natural line broadening and/or other degrees of freedom\(^8\). Note that \( f(t) \) in Eq. (2) is a product of various periodical functions, \( \exp(-i\omega_j t) \), each with a different period and amplitude. Thus, the effect of finite damping is to limit the effective time domain in the integral (Eq. (1)), emphasizing partial periodic recurrences in \( f(t) \) that result in apparent vibronic frequencies in the PL spectrum. The apparent mode (APM) frequencies need not be equal to one of the observed Raman modes, but are related to them in a non-trivial way\(^10\).

An example of this effect is shown in Fig. 3a, where \( f(t) \), calculated using the 11-mode system of DSB given in Table I, is plotted on a logarithmic scale. It is clearly seen, that even for low damping (Fig. 3a, top) \( f(t) \) is dominated by two APMs: a high frequency (short period), APM\(_H\), modulated by a low frequency (long period), APM\(_L\). The main effect of the damping is the faster decrease of the low frequency component (Fig. 3a, bottom).

The HR factors that determine the vibronic structure are closely related to the measured Raman spectrum, since the Raman process is enabled by the electron-phonon interaction. The \( T=0 \) intensity \( (I^0_j) \) of each Raman line measures its excited state displacement\(^8\): \( I^0_j \propto \omega_j^3 \Delta_j^2 \).

We then have:

\[
S_j / S(0) = \left[ \sum_{j'} (I^0_j / I^0) (\omega_j / \omega_{j'})^2 \right]^{-1} ,
\]

(3)

where \( S(0) \) is \( S \) at \( T=0 \) K. We note that the \( \omega_j^{-2} \) factor in \( S_j \) emphasizes the lower frequency Raman modes in the PL spectrum. This can be seen in Table I, where we list for DSB \( S_j / S(0) \), calculated using Eq. (3) and the Raman data (Fig. 2): the lowest frequency mode has the largest HR factor, although its intensity is \( \approx 1\% \) of the strongest line! We conclude then: (1) The apparent modes are the result of a "weighted beating" of all Raman frequencies. (2) The frequencies of the apparent modes are not, in general, the simple sum or difference of the Raman frequencies, and cannot therefore be predicted a priori. (3) The
relative intensities of the apparent vibronic structure of the PL spectrum is solely determined by the experimentally measured pre-resonant Raman spectrum. (4) The only fitting parameters needed are the overall damping and the absolute magnitude of the total HR factor.

| $j$ | $\nu_j$ (cm$^{-1}$) | $I_j/I_{10}$ (%) | $S_j/S$ |
|-----|---------------------|-----------------|---------|
| 1   | 131                 | 1.16            | 0.35    |
| 2   | 261                 | 0.45            | 0.039   |
| 3   | 640                 | 0.71            | 0.01    |
| 4   | 873                 | 0.77            | 0.01    |
| 5   | 1000                | 6.7             | 0.035   |
| 6   | 1181                | 50              | 0.19    |

Table I. The most intense Raman lines of crystalline DSB at 10 K. $\nu_j$, $I_j/I_{10}$ and $S_j/S$, respectively, denote the measured peak frequency, relative integrated intensity and the calculated relative HR factor (Eq. (3), for each mode.

FIG. 2. Raman spectrum of DSB single crystal at pre-resonant conditions.

The first excited state of isolated DSB molecules is optically allowed, making them strongly luminescent and useable as active media in light emitting devices$^4$. Typically, the PL spectrum of isolated DSB molecules consists of the fundamental (0-0) optical transition and a single frequency phonon side bands replica series. However, in DSB and other p-oligophenylene-vinylenes, as well as oligothiophens$^2$, in the form of solid films and crystals, the 0-0 band is strongly suppressed, whereas the phonon replica retain their intensity and dominate the PL spectrum$^5,11$. The 0-0 PL band in films and crystals is forbidden due to Davidov splitting associated with H-aggregates. The 0-0 intensity depends on the film morphology (or aggregate size) and/or crystal purity. In an inhomogeneous solid sample, the resulting emission spectrum may be composed of contributions from several domains, with various 0-0 to 0-n intensity ratio. We therefore discuss separately the emission spectra of solution and crystalline DSB.

FIG. 3. Model calculations of DSB PL spectra using the 11-mode system of Table I for $\Gamma$ as shown. (a) Normalized dipole auto-correlation function $f(t)$ (Eq. (2)) for $S(0)=2.5$, $T_e=4$ (200) K for the upper (lower) curve; note the log scale. (b) PL spectra obtained by the Fourier transform of $f(t)$ similar to that in (a), but for $S(0)=1.7$, $T_e=150$ (200) K for the upper (lower) curve. $E_0$ is the energy of the fundamental transition. (c) PL spectra obtained by the Fourier transform of $f(t)$ for parameters as in (a), but for the totally suppressed (bottom) and 85% suppressed (top) fundamental transition. Using the data of Table I we show in Fig. 3a the dipole auto-correlation function, $f(t)$, generated for low and high damping. It is visually striking that the 11-mode system is dominated by only two APM: a short period mode modulated by a long period mode. Moreover, the frequency associated with these two APMs does not coincide with any DSB normal mode. The data given in Table I is also used to generate the PL spectra shown in Fig. 3b. Here, the values of the electron temperature, $T_e$, HR factor $S$ and damping $\Gamma$ were chosen to best fit the frozen solution experimental data at low and high lattice temperatures, T (Fig. 1a). The higher damping spectrum that presumably occurs at $T=200$ K ($\Gamma = 42$ps$^{-1}$, $3.5$...
It is seen in the PL spectra of crystalline DSB (Fig. 1c), the crystalline PL spectra show similar characteristics to those seen in Fig. 3c a high temperature (200K, $\Gamma=36$ ps $^{-1}$). At low $\Gamma$ values, there appears a low frequency modulation (with $\Delta \omega \approx 17$ meV) of the high frequency vibronic series, as shown in Fig. 3b (top curve). The combined progression peaks are denoted as $(k,n)$, where $k=0,1,2,3$ denotes the APM$_L$ progression and $n=0,1,2...$ denotes the APM$_H$ modulation of APM$_H$. The PL spectrum in Fig. 3b (top curve) was calculated using $T_c = 150$K; it shows two blue shifted peaks, in very good agreement with the experimental data at $T=200$ K (Fig. 1a, top curve). We thus conclude that due to the non-resonant PL excitation, $T_c > T$.

The crystalline PL spectra show similar characteristics to the solution spectra: i.e., at high temperatures is dominated by a single APM, whereas at low temperatures this structure is modulated by a low frequency APM. As for the solution spectra, this behavior naturally results from a decreased damping at low temperatures. However, the crystalline spectra reveal an additional feature not observed in solutions.

It is seen in the PL spectra of crystalline DSB (Fig. 1c), that the band centered at $\approx 2.95$ eV appears at $T=4$ K but not at $T=200$ K. Measurements at intermediate temperatures reveal that its intensity monotonically decreases with increasing temperature; above $T=150$ K it cannot be observed any longer. We interpret this band as the fundamental optical transition that is suppressed by the crystal symmetry. However, the vibronic structure below $\approx 2.95$ eV is not affected.

In order to quantitatively account for the temperature dependent crystalline PL spectra, we have allowed the "0" transition to vary independently of all other phonon mediated transitions. First, we recognize that the $S_n(t)$ terms in Eq. (2) are responsible for all the red shifted spectral features associated with the electron-phonon interaction. The time independent term $S$ in Eq. (2) gives the intensity of the fundamental optical transition in the presence of the coupled vibrational modes. Second, assuming that the fundamental optical transition has a small finite width of $\hbar \Gamma_0$, we calculate its intensity (denoted $I_0(E)$) using Eq. (2) while taking into account only those modes whose frequency is smaller than $\Gamma_0^{-1}$. We then let $I_0$ to be partially suppressed, and write for the crystalline PL spectrum,

$$ F_{\text{cryst}}(E) = F(E) - \alpha I_0(E) ,$$

where $F(E)$ is given by Eq. (1), and $\alpha$ is the suppression parameter controlling $I_0$ in the crystalline spectrum. Using Eq. (4), the data of Table I, and $\hbar \Gamma_0=4$ meV we show in Fig. 3c a high temperature (200K, $\Gamma=36$ ps $^{-1}$) PL spectrum with totally suppressed fundamental transition, namely $\alpha=1$. This is in excellent agreement with the $T=200$ K crystalline spectrum (Fig. 1c).

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