Spectroscopy of dimerization in organic mixed-stack compounds and tetramethyl-p-phenylene-diamine chloranil

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The onset of dimerization in organic mixed-stack compounds allows the appearance of the otherwise symmetric phonons in the absorption spectra. A general theoretical framework shows that the most sensitive effect arises when symmetric and antisymmetric modes have nearby frequencies; the growth of dimerization then leads to gradual transfer of absorption intensity, from the antisymmetric mode to the symmetric one. Absorption data on tetramethyl-p-phenylene-diamine chloranil show this feature and thereby demonstrate the onset of dimerization below ~ 250 K. The transition involves a small and continuous change in ionicity.

Most organic charge-transfer solids are composed of donor (D) and acceptor (A) molecules in a mixed stack configuration,[1] i.e., A and D molecules stack alternately on top of each other. The discovery of phase transitions in a large variety of these compounds[2,3] has stimulated a renewed interest in them. The transitions are induced by pressure and in some cases also by temperature.

The transitions were considered as "neutral-ionic" transitions, related to a change in the average D to A charge transfer.[4] An alternative description of this phase transition predicted[5] the onset of lattice dimerization, i.e., the D-A separations have alternating values below the transition. This ordering does not change translation symmetry since the unit cell contains D-A pairs in both phases. Instead, inversion symmetry at the center of a donor (or acceptor) molecule is broken.

Breaking of inversion symmetry is readily observed by phonon spectroscopy. When inversion symmetry is present the phonon normal modes can be classified as symmetric or antisymmetric. Absorption data show only antisymmetric modes, while Raman scattering shows only symmetric modes. This selection rule is violated when inversion symmetry is broken; the same frequencies appear then in both absorption and Raman scattering, as was indeed observed in tetramethyl-p-phenylene-diamine chloranil.[6,7] More recently dimerization was also seen directly by x rays.[8]

In the present work we first derive a general formulation for phonons in mixed stack compounds allowing for a broken inversion symmetry in the dimerized phase. We allow for a coupling between symmetric and antisymmetric modes via electron degrees of freedom. The resulting relation between electron-phonon couplings and the eigenfrequencies modifies previous analysis considerably.[6,7] In particular, we focus on an effect which we term as the "intensity transfer" syndrome. This effect arises when symmetric and antisymmetric modes have nearby frequencies. The growth of dimerization yields a gradual transfer of absorption intensity from the antisymmetric mode to the symmetric one. This feature is extremely sensitive to the presence of dimerization and can be observed even if the

relevant electron-phonon couplings are very weak.

Second, we present what we believe to be the first observation of dimerization-induced intensity transfer as manifested in tetramethyl-p-phenylene-diamine chloranil (TMPD-CA). This compound is known to exhibit a transition near 250 K as seen by ESR in the pioneering work of Pott and Kommandeur.[9] Our data imply that dimerization sets in at this transition. We also find that the ionicity change is continuous and very small.

The following theoretical formulation assumes the adiabatic limit, namely, the phonon frequencies ($\lesssim 0.2$ eV) are small compared with the electronic gap [~ 1 eV (Ref. 9)]. No other assumptions are made; in particular, no assumption on the form of electron-electron interactions is necessary.

Electrons couple to phonons in two ways. First, the difference in D-ionization potential and A-electron affinity can be modulated by phonons. Since on-site potentials are modulated, the relevant phonons must be symmetric under inversion. Define these "site" phonon coordinates by Δ_n^s, $n = 1, 2, \ldots, N_s$, and $\Delta_s = \sum_n \Delta_n^s$ is the combined potential change felt by the electrons. (The electron phonon coupling is absorbed into Δ_n^s so that they have dimension of energy).

The second type of electron-phonon coupling is a modulation of the electron transfer integral between the D and A molecules. We are interested in bond modulations which induce dimerization; the coupled phonons are therefore antisymmetric. Define these "bond" phonon coordinates by Δ_n^b, $n = 1, 2, \ldots, N_b$, and $\Delta_b = \sum_n \Delta_n^b$ modulates the D-A transfer integral t_0 into $t_0 \pm \Delta_b$. Obvious members in this class are intermolecular "acoustic" modes and out-of-plane intramolecular modes. In general, however, even in-plane modes mix with acoustic modes and acquire coupling with the electrons.

We define the electron's free energy as $-F_e(\Delta_s, \Delta_b)\pi t_0$; this includes the electron kinetic energy, electron-phonon interactions, and unspecified electron-electron interactions. The total free energy is obtained by adding the ion elastic energies. The adiabatic limit implies that F_e is a function of $\Delta_s(t)$ and $\Delta_b(t)$ and not of their time deriva-

tives. To find the small oscillations of the ground state we need

$$A_s = 2\lambda_s \partial^2 F_e(\Delta_s, \Delta_b)/\partial \Delta_s^2 \ ;$$

$$A_b = 2\lambda_b \partial^2 F_e(\Delta_s, \Delta_b)/\partial \Delta_b^2 \ , \qquad (1)$$

$$B = \partial^2 F_e(\Delta_s, \Delta_b)/\partial \Delta_s \partial \Delta_b \ ,$$

with the derivatives evaluated at the ground state. Dimensionless electron-phonon couplings λ_n^s, λ_n^b are defined such that $(\Delta_n^s)^2/4\pi t_0 \lambda_n^s$ and $(\Delta_n^b)^2/4\pi t_0 \lambda_n^b$ are the elastic energies of nth s or b mode, respectively. In Eq. (1) $\lambda_s = \sum_n \lambda_n^s$ and $\lambda_b = \sum_n \lambda_n^b$.

An external electric field $E(t)$ couples to the electronic dipole $P(\Delta_s, \Delta_b)$. Its derivatives in the $E = 0$ ground state are

$$P_s = \pi t_0 \partial P(\Delta_s, \Delta_b)/\partial \Delta_s \ ;$$

$$P_b = \pi t_0 \partial P(\Delta_s, \Delta_b)/\partial \Delta_b \ . \qquad (2)$$

Note that when inversion symmetry is present $(T > T_c)$ $B = 0$ and $P_s = 0$. Also, if the transition is of second order the curvature of $-F_e + \Delta_b^2/4\lambda_b$ vanishes at $\Delta_b = 0$ when $T = T_c$, i.e., $A_b(T = T_c) = 1$.

The effective Lagrangian for small oscillations $\delta_n^s(t)$ and $\delta_n^b(t)$ around the ground-state values of Δ_n^s and Δ_n^b,

respectively, is then

$$\pi t_0 \mathcal{L} = \sum_n \frac{1}{4\lambda_n^s} \left[-(\dot{\delta}_n^s)^2 + \left(\frac{\dot{\delta}_n^s}{\omega^{s0}} \right)^2 \right]$$

$$+ \sum_n \frac{1}{4\lambda_n^b} \left[-(\dot{\delta}_n^b)^2 + \left(\frac{\dot{\delta}_n^2}{\omega_n^{b0}} \right)^2 \right]$$

$$+ \frac{A_s}{4\lambda_s} \delta_s^2 + \frac{A_b}{4\lambda_b} \delta_b^2 + B \delta_s \delta_b - P_s E \delta_s - P_b E \delta_b \ . \qquad (3)$$

Here $\omega_n^{s0}, \omega_n^{b0}$ are bare phonon frequencies in the absence of electron-phonon interaction, and $\delta_s = \sum_n \delta_n^s$, $\delta_b = \sum_n \delta_n^b$. For $T > T_c$, when $B = P_s = 0$, the s and b modes are uncoupled, and the electric field couples only to the antisymmetric b modes. When $T < T_c$, E couples to the s modes in two ways: first, through the coupling B between the s and b modes and, second, directly via P_s. The treatment of Ref. 6 retained P_s but ignored the B term. In general, however, B is present and, in fact, it dominates the intensity transfer syndrome as shown below.

The frequency dependent conductivity is given in linear response by $\sigma(\omega) = -i\omega P(\omega)/E(\omega)$, where $E = E(\omega) \times \exp(i\omega t)$. The equation of motion of Eq. (3) yields for this ratio

$$\sigma(\omega) = \frac{-i\omega}{\pi t_0} \frac{[D_s^{-1}(\omega) + A_s]2\lambda_b P_b^2 + [D_b^{-1}(\omega) + A_b]2\lambda_s P_s^2 - 8\lambda_s \lambda_b B P_s P_b}{[D_s^{-1}(\omega) + A_s][D_b^{-1}(\omega) + A_b] - 4\lambda_s \lambda_b B^2} \ , \qquad (4)$$

where

$$D_s(\omega) = \sum_n \lambda_n^s [(\omega/\omega_n^{s0})^2 - 1]^{-1}/\lambda_s$$

and similarly for $D_b(\omega)$ by $s \to b$.

The poles of Eq. (4) determine the absorption frequencies. Clearly, the term B mixes the s and b modes and induces new absorptions near the s-mode frequencies. We consider in particular the case where two frequencies ω_n^{s0} and ω_n^{b0} happen to be nearby, for some n. $D_s(\omega)$ and $D_b(\omega)$ are then dominated by a single term and the poles of Eq. (4) are at $\omega_\pm$,

$$\omega_\pm^2 = \frac{1}{2} \{\omega_s^2 + \omega_b^2 \pm [(\omega_b^2 - \omega_s^2)^2 + \beta]^{1/2}\} \ , \qquad (5)$$

where

$$\beta = \lambda_n^s \lambda_n^b (4\omega_n^{s0} \omega_n^{b0})^2 B^2 \ ,$$

$$\omega_s^2 = [1 - \lambda_n^s A_s/\lambda_s](\omega_n^{s0})^2 \ ; \qquad (6)$$

$$\omega_b^2 = [1 - \lambda_n^b A_b/\lambda_b](\omega_n^{b0})^2$$

are the normal mode frequencies if $B = 0$. If we neglect P_s, which is valid at least near T_c, the intensity ratio of the $\omega_\pm$ modes is (for $\omega_b > \omega_s$)

$$\frac{I(\omega_-)}{I(\omega_+)} = \frac{[(\omega_s^2 - \omega_b^2)^2 + \beta]^{1/2} - (\omega_b^2 - \omega_s^2)}{[(\omega_s^2 - \omega_b^2)^2 + \beta]^{1/2} + (\omega_b^2 - \omega_s^2)} \ . \qquad (7)$$

Thus the new mode at ω_- gains intensity as β grows below T_c until the ratio (7) reaches 1 at $\beta \gg (\omega_s^2 - \omega_b^2)^2$. In addition, the frequencies $\omega_\pm$ are pushed apart. Far below the transition P_s may become more important than P_b and

then the right-hand side of (7) is inverted and the ratio can be larger than 1.

The total absorption from Eq. (4) satisfies a sum rule which depends on temperature only through P_b and P_s. Near T_c, when P_s is neglected, the sum rule depends weakly on temperature. Hence, as $I(\omega_-)$ grows $I(\omega_+)$ must weaken, and the scenario for intensity transfer is manifest. If ω_s is very near ω_b a strong intensity transfer results even if β is small; the present mechanism is therefore the most sensitive probe of dimerization.

We proceed now to describe experimental results on TMPD-CA and then confront them with the above theoretical ideas. TMPD-CA was prepared using the following procedure. TMPD·HCl was obtained from general purposes reagent by recrystallizing it from methanol and dissolving it in hot water. The solution was then neutralized with Na_2CO_2 and then free amine was extracted with methylene chloride. Chloranil by Fluka was recrystallized twice from benzene solution. The TMPD-CA crystals were prepared by adding one portion of saturated TMPD solution to three portions of chloranil-saturated solution. After about one day small black crystals were obtained, washed twice with benzene, and dried. As these crystals are sensitive to air, they were stored in nitrogen atmosphere at $-20\,^\circ\mathrm{C}$. Pellets for ir absorption measurements were obtained by pressing the crystals with KBr for 10 min at 10 atm. The samples were stable during the measurements inside evacuated Dewar. However, after four hours in open air the crystals changed color and ir absorption spectra. Temperature-dependent absorption spectra were obtained on nicolet fast Fourier transform ir computerized
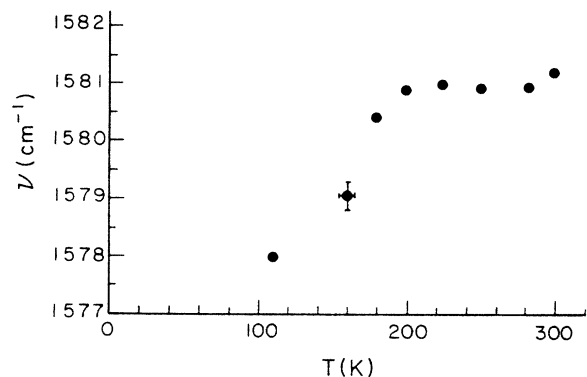
FIG. 1. Frequency of the $C\!=\!O$ mode as function of temperature.

FIG. 3. Absorption spectra in the 1200-cm^{-1} range at various temperatures. The inset shows relative (fraction of total) intensities for the three modes.

instrument. The spectrometer was carefully and thoroughly purged using dry nitrogen flow. A number of samples were used for the measurements and showed similar spectra. The 300 K spectrum is in good general agreement with a previously known one.[10]

Figure 1 shows the temperature dependence of the $C\!=\!O$ mode frequency, which is sensitive to the amount of charge transfer.[7] This mode shows a weak temperature dependence which is somewhat steeper below ~250 K. From the extrapolation between the neutral and fully charged CA (Ref. 7) we estimate a charge transfer of $\rho \simeq 0.63$ at 300 K, increasing continuously to $\rho \simeq 0.65$ at 110 K.

Figures 2 and 3 show remarkable and clear intensity transfer cases. New modes at 1220 and 764 cm^{-1} appear below 250 K, and their intensities grow at the expense of nearby modes. This observation suggests that the phase transition near 250 K (Ref. 9) is of the "neutral-ionic"-type with the onset of dimerization.
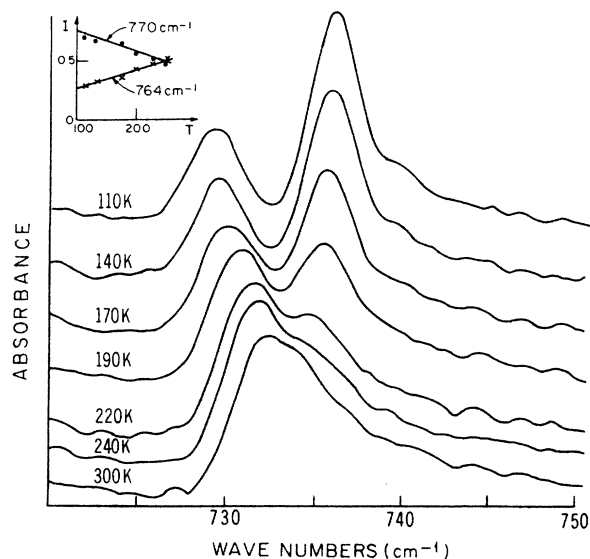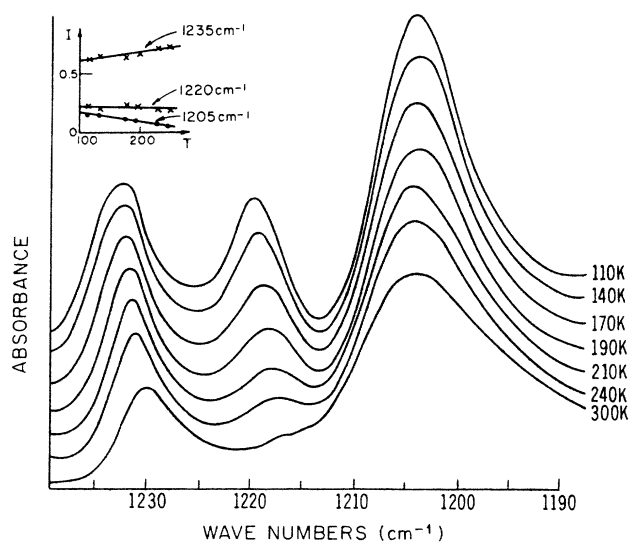
Figure 2 shows an intensity transfer where the "new" s mode at 764 cm^{-1} becomes stronger than the "old" b mode at 770 cm^{-1}. Note also that the frequencies are indeed pushed apart as temperature is lowered. The combined intensities are fairly constant down to 110 K (at lower temperatures the direct coupling P_s may appear and increase the overall absorption).

Figure 3 shows an interesting case where a "new" mode appears between two "old" ones. The new mode at 1220 cm^{-1} shifts to higher frequencies upon cooling; thus it is pushed away from the mode at 1205 cm^{-1}, which is its companion in the two-mode scheme of Eq. (7). Indeed the relative weight of the 1205-cm^{-1} mode decreases as shown in the inset of Fig. 3. The combined intensities here decrease by ~40% with temperature. Since the intensity separation near 300 K is not clear, the transition temperature where the 1220- and 764-cm^{-1} modes disappear can only be estimated as $T_c \simeq 250$–300 K.

Intensity transfer may also appear in inhomogeneous systems as in TTF-CA films[3] or doped TTF-CA.[11] In this case the *same* mode appears at two frequencies as determined by the distribution of charge trasnfer. The intensity transfer which we observe in TMPD-CA is, however, not due to inhomogeneity since (1) the charge transfer ρ depends very weakly on temperature (Fig. 1). Thus an inhomogeneous mixture of the low and high ρ phases cannot yield lines separated by 6–15 cm^{-1} as in Figs. 2 and 3. (2) Inhomogeneity may be expected in a first-order transition. Here, however, the transition is continuous as seen from Fig. 1 and the ESR data.[9]

In conclusion, we have shown that a coupling between symmetric site modes and antisymmetric bond modes yields an unusual spectroscopic feature of "neutral-ionic" dimerization transitions. The consequent intensity transfer syndrome was demonstrated in TMPD-CA and should be a sensitive tool for observing this transition in other systems as well.

FIG. 2. Absorption spectra in the 700-cm^{-1} range at various temperatures. The inset shows the relative intensity of each mode.

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