Analog of Small Holstein Polaron in Hydrogen-Bonded Amide Systems

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A class of amide-I (C=O stretch) related excitations and their contribution to the spectral function for infrared absorption is determined by use of the Davydov Hamiltonian. The treatment is a fully quantum, finite-temperature one. A consistent picture and a quantitative fit to the absorption data for crystalline acetanilide confirms that the model adequately explains the anomalous behavior cited by Careri *et al.* The localized excitation responsible for this behavior is the vibronic analog of the small Holstein polaron. The possible extension to other modes and biological relevance is examined.

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Recently, there has been reawakened interest in crystalline acetanilide (ACN) with emphasis on an anomalous temperature-dependent ir absorption peak at $\approx 1650\ \mathrm{cm}^{-1}$; see Careri *et al.*[1,2] One of the major points of this work is that the absorption strength is found to vary as $\exp(-\beta T^2)$ at low temperatures, to high accuracy, which follows straightforwardly from the Davydov model used here. The physics is analogous to the zero-phonon line seen in other contexts.[3] A second point is that I have employed a fully quantum mechanical, finite-temperature methodology similar to that used by Yarkony and Silbey[4] in treating excitons and by Holstein[5] for polarons. This can be done because of the similarity of the Davydov Hamiltonian to the Hamiltonians used in these two cases.

The structure of this crystal is similar to α-helical proteins[6] and so it seems plausible that an understanding of ACN could shed light on the behavior of this class of proteins.

The Davydov Hamiltonian[7] can be written $H = H_{\mathrm{ex}} + H_{\mathrm{ph}} + H_{\mathrm{int}}$, with

$$H = \sum_{ni} [E_A B_{ni}^\dagger B_{ni} + J(B_{n+1i}^\dagger B_{ni} + B_{n+1i} B_{ni}^\dagger)] + \sum_{\mathbf{q}s} \hbar\omega_{\mathbf{q}s}(a_{\mathbf{q}s}^\dagger a_{\mathbf{q}s} + \tfrac{1}{2}) + (1/\sqrt{N}) \sum_{ni,\mathbf{q}s} X_{\mathbf{q}s}^{ni} \hbar\omega_{\mathbf{q}s}(a_{\mathbf{q}s} + a_{-\mathbf{q}s}^\dagger) B_{ni}^\dagger B_{ni}, \tag{1}$$

$$X_{\mathbf{q}s}^{ni} = i\chi[1/(2M\hbar\omega_{\mathbf{q}s}^3)]^{1/2} \sin(\mathbf{q}\cdot\mathbf{b})(\hat{\boldsymbol{\epsilon}}_{\mathbf{q}s}\cdot\mathbf{b}/b)\exp(i\mathbf{q}\cdot\mathbf{R}_{ni}), \quad \omega_{\mathbf{q}s} = 2\omega_{0s}\sin(\mathbf{q}\cdot\mathbf{b}/2), \quad E_A = E_0 - D,$$

where (i) $B_{ni}^\dagger, B_{ni}$ are the creation and annihilation operators for the amide-I (C=O stretch) mode at site n on the ith chain, (ii) $a_{\mathbf{q}s}^\dagger, a_{\mathbf{q}s}$ are the operators for the lattice modes $\omega_{\mathbf{q}s}$, with polarization vector $\hat{\boldsymbol{\epsilon}}_{\mathbf{q}s}$, (iii) χ is the coupling constant for the mode-lattice interaction, (iv) E_0 is the vibrational energy of the amide mode when the molecule of mass M is isolated and D is the static shift due to lattice effects, and (v) J is the dipole-dipole interaction energy between adjacent C=O dipoles displaced by $\mathbf{b}$ on the same chain ($J < 0$ here). Built into the Hamiltonian is one-dimensional transport of the excitations via dipole-dipole interaction and coupling to the longitudinal modes of the assumed lattice structure.

Extending the variational method often applied to the polaron and exciton problems,[4,5,8] I write a general form for the trial state of the low-lying energy eigenstates of the system,

$$|k\rangle_t = \sum_{mj} \phi_{mj}(k)\Theta_{mj} B_{mj}^\dagger |0\rangle_E |(n_{\mathrm{ph}})\rangle;$$

$\phi_{mj}(k)$ is the amplitude of the amide-I excitation and Θ_{mj} is a unitary transformation which displaces the mjth lattice site. Note that equivalently one can canonically transform the Hamiltonian to incorporate the lattice displacements, in which case the trial state would be a linear combination of product states for the noninteracting system. Then with $\exp(-U_{mj}) \equiv \Theta_{mj}$, $|k\rangle_t$ becomes

$$|k\rangle_t = \exp(-U) \sum_{mj} \phi_{mj}(k) B_{mj}^\dagger |0\rangle_E |(n_{\mathrm{ph}})\rangle, \tag{2}$$

$$U = -(1/\sqrt{N}) \sum_{ni,\mathbf{q}s} \tilde{X}_{\mathbf{q}s}^{ni} B_{ni}^\dagger B_{ni}(a_{\mathbf{q}s} - a_{-\mathbf{q}s}^\dagger), \quad \tilde{X}_{\mathbf{q}s}^{ni*} = \tilde{X}_{-\mathbf{q}s}^{ni},$$

with $\tilde{X}_{\mathbf{q}s}^{ni}$ a variational parameter. By inspection, the canonical transformation would be $\tilde{H} = e^U H e^{-U}$, where H is given by Eq. (1). Writing down an expression for the average energy of the system (temperature comes in via n_{ph}), one can then vary the energy with respect to $\phi_{mj}(k)$ and $\tilde{X}_{\mathbf{q}s}^{ni}$, imposing the normalization constraint by including a Lagrange multiplier. I summarize the results: (I) For $\tilde{X}^{ni}_{\mathbf{q}s}$ chosen to be site independent, one obtains (a) an extended plane-wave solution, $\phi_{mj}(k)=(1/\sqrt{N})\exp(i\mathbf{k}\cdot\mathbf{R}_{mj})$ for which $\tilde{X}^{ni}_{\mathbf{q}s}\sim\delta_{\mathbf{q},0}$. Correspondingly, $\tilde{H}$ is given by $\tilde{H}=\tilde{H}_0+\tilde{V}$, where in wave-vector representation,

$$\tilde{H}_0=\sum\nolimits_{\mathbf{k}}(E_A-2|J|\cos\mathbf{k}\cdot\mathbf{b})B^{\dagger}_{\mathbf{k}}B_{\mathbf{k}}+H_{\mathrm{ph}} \tag{3}$$

and $\tilde{V}$ contains off-diagonal terms. (b) There is also a localized solution (the Davydov soliton), this solution being valid for $\chi^2/4|J|M\omega_{0s}^2\lesssim1$. However, in the limit of $\chi^2/4|J|M\omega_{0s}^2\gtrsim1$ the excitation becomes localized to the region around a single site and this solution can be used to construct Bloch-type states for the system. In this case (II), $\tilde{X}^{ni}_{\mathbf{q}s}=X^{ni}_{\mathbf{q}s}$ and $\phi_{mj}(k)=(1/\sqrt{N})\exp(i\mathbf{k}\cdot\mathbf{R}_{mj})$. This *severely* localized excitation is analogous to the Holstein polaron.[5,9] Here $\tilde{H}=\tilde{H}_0+\tilde{V}$, for which

$$\tilde{H}_0=\sum\nolimits_{\mathbf{k}}[E_A+\Delta-2|J|\exp(-S)\cos\mathbf{k}\cdot\mathbf{b}]B^{\dagger}_{\mathbf{k}}B_{\mathbf{k}}+H_{\mathrm{ph}} \tag{4}$$

and $\tilde{V}$ contains the off-diagonal terms. Here $\Delta=-(1/N)\sum_{\mathbf{q}s}\hbar\omega_{\mathbf{q}s}|X^{ni}_{\mathbf{q}s}|^2$ is the shift in energy of the localized excitation due to phonon *dressing* (the largest contribution coming from the short-wavelength modes) and $\langle\Theta^{\dagger}_{n+1i}\times\Theta_{ni}\rangle_L=\exp(-S)$, where

$$S=(1/N)\sum\nolimits_{\mathbf{q}s}(2n_{\mathbf{q}s}+1)|X^{ni}_{\mathbf{q}s}|^2(1-\cos\mathbf{q}\cdot\mathbf{b})$$

is a temperature-dependent modulation factor (for the dipole-dipole interaction) which is a measure of the coherence of the excitation.

As pointed out, the Davydov soliton cannot be photoinduced since the time taken for a cooperative distortion of the lattice in the formation of the soliton is much longer than the absorption time of the photon[1,7] (Franck-Condon principle). Therefore, of the excitations discussed above, only (Ia) and (II) are relevant to any treatment of the photoinduced spectral properties of the system. With the spectral function $I(\omega)\equiv|\mu|^2/(2\pi)\int dt I(t)\times\exp(i\omega t)$, where μ is the dipole matrix element and

$$I(t)=\sum_{ni,mj}\langle[B^{\dagger}_{ni}(t)+B_{ni}(t)][B^{\dagger}_{mj}(0)+B_{mj}(0)]\rangle$$

with $\langle\ldots\rangle$ denoting the thermal average, one obtains the following: For the excitation (Ia),

$$I(\omega)\simeq|\mu|^2N\Gamma_{\mathrm{ex}}/\pi[(\omega-E/\hbar)^2+\Gamma_{\mathrm{ex}}^2], \tag{5}$$

where $E=E_0-D-2|J|$ and $\Gamma_{\mathrm{ex}}\equiv1/\tau_{\mathrm{ex}}$ is the radiative decay constant of the free *extended* vibrational excitation. This equation indicates that there will be a temperature-independent absorption peak at $\omega=E/\hbar$ with half-width Γ_{ex}. For the localized excitation, case (II),

$$I(\omega)\simeq|\mu|^2N\Gamma_0\exp(-W)/\pi[(\omega-E_1/\hbar)^2+\Gamma_0^2], \tag{6}$$

where $E_1=E_A+\Delta-2|J|\exp(-S)$ and $\exp(-W)$ is the ubiquitous Debye-Waller factor which measures the probability that the phonon distribution remains unchanged during the absorption process.[10] W is given by

$$W=(1/N)\sum_{\mathbf{q}s}(2n_{\mathbf{q}s}+1)|X^{ni}_{\mathbf{q}s}|^2. \tag{7}$$

Here two assumptions have been made: (1) a very long radiative lifetime, τ, of the excitation ($\tau\sim1/\Gamma_0$, the lifetime of the C=O stretch mode in an isolated molecule) and (2) a temperature of the system less than the Debye temperature. From these equations it should be noted that the absorption peak corresponding to the localized vibronic excitation may be temperature dependent both in strength and in position.

Now, the expressions Δ and W will be evaluated to check for consistency with the absorption data. These expressions all contain the term $|X^{ni}_{\mathbf{q}s}|^2$ given by

$$|X^{ni}_{\mathbf{q}s}|^2=\chi^2[(\hat{\mathbf{q}}\cdot\hat{\mathbf{b}})^2\delta_{s,1}]\sin^2(\mathbf{q}\cdot\mathbf{b})/2M\hbar\omega_{\mathbf{q}s}^3,$$

where $\hat{\boldsymbol{\epsilon}}_{\mathbf{q}s}\cdot\mathbf{b}/b=i\hat{\mathbf{q}}\cdot\hat{\mathbf{b}}$, $s=1$ being the longitudinally polarized phonons. Converting sums to q-space integrals, one obtains

$$\Delta\simeq-\chi^2q_{\mathrm{D}}^3f(q_{\mathrm{D}}b)/Mn(2\pi\omega_{01})^2, \tag{8}$$

where $q_{\mathrm{D}}^3=6n\pi^2$, n is the number density of molecules in the crystal, and f is a function of $q_{\mathrm{D}}b$. The dispersion relation for the crystal is assumed to be of the form $\omega_{\mathbf{q}1}=2\omega_{01}\sin(\mathbf{q}\cdot\mathbf{b}/2)$.[11]

$$W\simeq\begin{cases}\alpha+\beta T^2, & T<<\theta_{\mathrm{D}},\\ \gamma T, & T>>\theta_{\mathrm{D}}.\end{cases} \tag{9}$$

α, β, and γ are positive constants: $\alpha=\chi^2g/8Mn\hbar\pi^2(\omega_{01}b)^3$ and $\beta=\chi^2k_{\mathrm{B}}^2/12Mn\omega_{01}^5(\hbar b)^3$. Here g is also a function of $q_{\mathrm{D}}b$.

The data used to evaluate these expressions are $b=4.9$ Å, $n=5.38\times10^{27}$ m^{-3}, $M=2.25\times10^{-25}$ kg, $\omega_{01}=1.39\times10^{13}$ s^{-1} (reconstructing the dispersion relation[11] used here from the Raman data for the true crystal[12]). The estimated value of J is 1.5–4 cm^{-1}.[2] With use of these data $q_\mathrm{D}b = 3.35$, $f(q_\mathrm{D}b) = 0.044$, $g(q_\mathrm{D}b) = 4.3$, and $\theta_\mathrm{D} = 356$ K.

The value of χ is not known precisely, and therefore I eliminate it by considering the ratio $|\Delta|/\beta$. With use of Eqs. (8) and (9),

$$(|\Delta|/\beta)_\mathrm{cal} \simeq 18n\,(\hbar\omega_{01}b)^3 f/k_\mathrm{B}^2.$$

Hence, $(|\Delta|/\beta)_\mathrm{cal} \simeq 8.3\times10^{-18}\,\mathrm{J\,K}^2$. Now, from Fig. 1, $|\Delta| \simeq 15\ \mathrm{cm}^{-1}$. Performing a least-squares fit of the absorption data, plotted as log(intensity) versus (temperature)^2, one obtains $\beta = 2.75\times10^{-5}\ \mathrm{K}^{-2}$, where β is the inverse of the slope in Fig. 2. Consequently, one obtains $(|\Delta|/\beta)_\mathrm{expt} \simeq 10.8\times10^{-18}\ \mathrm{J\ K}^2$, which differs from the calculated value by approximately 20%.

Now, estimating the coupling constant by using the experimentally determined value of β, one obtains $\chi = 3.88\times10^{-10}$ N, which is within an order of magnitude of the model-independent estimate (6.2×10^{-10} N) used by Careri *et al.*[2]

The separation between the two peaks in Fig. 1 is given by $E - E_1 = |\Delta| - 2|J|[1-\exp(-S)]$. Using the estimated value of χ and evaluating the expression for S, one obtains $S(T=0) \simeq 0.24$. Thus $E - E_1$ should vary from $\sim |\Delta| - 2|J|$ at high temperature to $\sim |\Delta| - 0.42|J|$ at $T = 0$ K. By inspection of Fig. 1, very little variation is observed in the separation of the peaks (to within 1–2 cm^{-1}) which suggests a low value, 1.5 cm^{-1} say, for $|J|$. With this estimate, $\chi^2/4|J|M\omega_{01}^2 \simeq 29$ which is consistent with the assumption that the excitation corresponding to the 1650-cm^{-1} peak is analogous to the Holstein polaron. It should be emphasized that the linear behavior obtained in Fig. 2 for $T \ll \theta_\mathrm{D}$ (356 K) and the departure therefrom for $T \gg \theta_\mathrm{D}$ (not shown) are specific to coupling between the amide-I mode and acoustic lattice modes of the idealized crystal. The model used by Careri *et al.*[2] assumes a low-frequency optical mode, in which case good agreement with experiment *over the experimental temperature range* can only be achieved if this mode has a complicated functional dependence on temperature—which is difficult to justify.[13]

The agreement of the data with the Davydov model, as applied here with all of the lattice modes being considered, occurs because the short-wavelength phonons are responsible for the self-trapping of the vibronic excitation but the temperature modulation is governed by the low-frequency (acoustic) modes at temperatures below θ_D. It should be pointed out that the calculation here can be extended to include the sidebands associated with multiphonon processes and that the model can be extended to modes other than the C=O stretch mode, for example, modes which involve N–H stretch and which are likely to couple to the lattice. Additionally, this Hamiltonian gives one the frame-

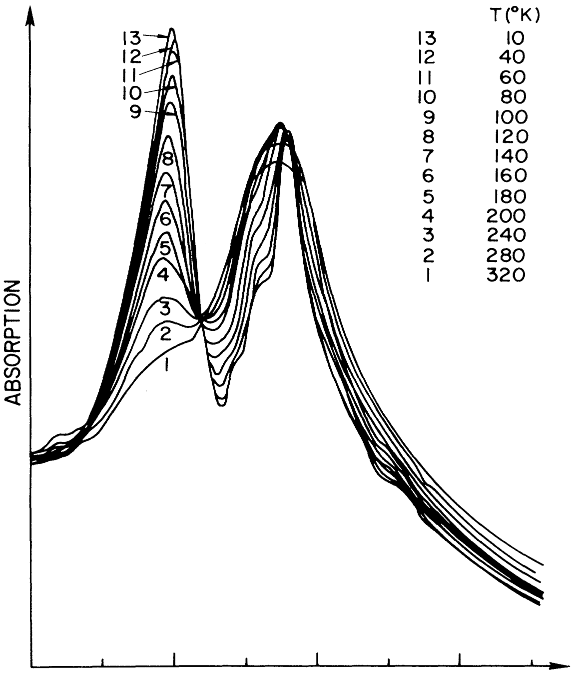

FIG. 1. Infrared absorption spectra of crystalline ACN in the amide-I region (10–320 K), taken from Fig. 5 of Careri *et al.* (Ref. 2).

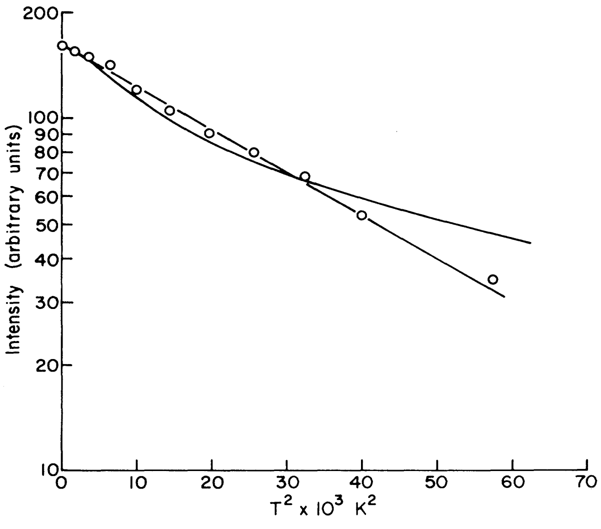

FIG. 2. Intensity of the 1650-cm^{-1} peak vs the square of the temperature. Data points and the least-squares–fitted curves are shown. The straight line is obtained with the Davydov model. The other curve is a plot of the theoretical expression used in Fig. 15 of Careri *et al.* (Ref. 2).

work to tackle the transport properties of the localized excitation observed here.[14]

With regard to the applicability of the Davydov model to biological processes, there has been much speculation in the literature with no concrete confirmation of the existence of the localized excitations predicted by the model. The application of the model to ACN is the first confirmation of the validity of the Davydov model to anything remotely resembling a biological molecule. This gives one some hope that one may see similar behavior in α-helical proteins. A factor which may influence whether such an excitation, if photoexcited, can be observed in an α-helix is the dimensionality of its *lattice*—for a one-dimensional lattice the intensity is temperature independent but depends on the length of the chain being considered. Finally, I wish to point out that in contrast to the Davydov soliton it is clear that the more localized excitation can be photoinduced and is possibly easier to excite chemically. If this is the case then it may well be that this excitation (not the Davydov soliton) is more relevant to biology.

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