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SPECTROSCOPY OF THE AMIDE-I MODES OF ACETANILIDE

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INTRODUCTION

In 1973, Careri published evidence of an "unconventional" amide-I (CO stretching) band at 1650 cm^{-1} in crystalline acetanilide ($CH_3CONHC_6H_5$), abbreviated ACN.[1] Following the "soliton" theory of Davydov,[2] this band has been assigned to a "self-trapped state" in which CO vibrational energy is localized near a single ACN molecule through interactions with lattice phonons.[3,4] A complementary "polaron" picture[5] of this self-trapped state has been presented recently by Alexander and Krumhansl.[6,7]

In this contribution best available data are presented of the integrated intensity of the 1650 cm^{-1} band as a function of temperature. The experimental procedures and data reduction were highly rigorous and are believed to be to most reliable data available. A concise theory of polaron states is presented and used to interpret the data.

SPECTROSCOPIC MEASUREMENTS

In our early experimental work we performed both infrared absorption spectroscopy and Raman spectroscopy. We soon focused on Raman spectroscopy, however, for several reasons. For one, it was easier to control sample temperature since ACN is essentially transparent at the wavelength of the illumination source. Also, the method itself afforded us an additional technique for determining the sample temperature in the illuminated volume, by the Stokes/anti-Stokes ratio technique described below. Moreover, when Raman spectra are taken with oriented single crystals and with polarized illumination and detection, more detailed information about the crystal structure and symmetry of vibrational centers is provided.

The Raman measurements reported here were made on single crystals of acetanilide prepared as follows. Primary standard grade ACN (N-phenylacetamide), 99.995% pure by assay, was purified using a multiple-pass zone refiner. The zone refined material was placed in a glass tube and the vessel was sealed under vacuum. Single crystals were grown from the melt as the vessel was lowered through a modified Bridgeman-Stockbarger furnace at a rate of 2 cm/day; the temperature gradient at the tip of the furnace was approximately 110 K/cm. The crystal of ACN is [100] tabular; thus cleavage was nearly perfect parallel to the [100] face and fairly good cleavage was obtained along the [001] face. The crystals used were, on average, 10 mm along the y, 4 mm on the z, and 1 mm along the x axis. Single crystals were cleaved and their orientations were determined using x-ray precession methods and a cross-polarizing microscope. The crystals were mounted in an oxygen-free copper cold cell, which enclosed the crystal in an inert atmosphere (He) to protect it from water vapor and pump oil. The temperature of the Raman cell was measured using an Au-cromel thermocouple.

In addition to the thermocouple measurements, the crystal temperature was determined directly by measuring the Stokes to anti-Stokes ratio of the intensities for a particular low-frequency mode by scanning over the -200 cm^{-1} to +200 cm^{-1} region in a single scan with an incident power of the laser below 50 mW. This allowed assessment of the amount of heating within the focal volume of the laser. Under these conditions local heating of the crystal was observed to be less than 10 K.

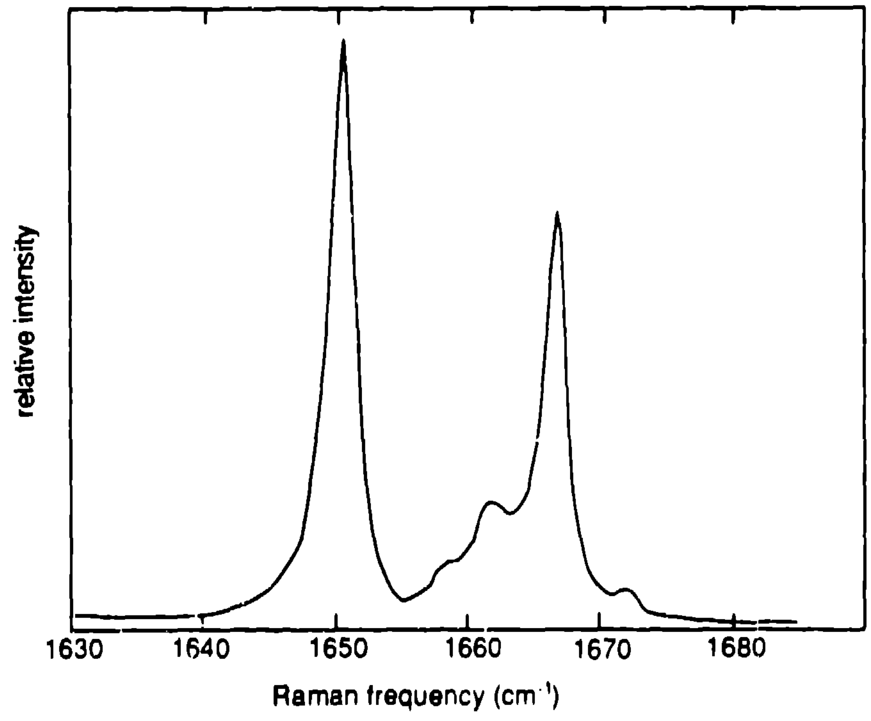

Fig. 1 Raman spectrum of the amide-I region of ACN at 21 K. Both the illumination polarization and the selected observation polarization were parallel to the crystal x axis.

Raman spectra were obtained on a 3/4-meter double monochromator (Spex model 1403) interfaced to a Nicolet 1180E computer. The 514.5 nm line of an argon-ion laser (Spectra Physics Model 171) was used as the exciting line. An interference filter was used to suppress plasma frequencies and a quartz crystal wedge was used at the entrance slit of the monochromator as a polarization scrambler. The accuracy of the frequency measurements was checked periodically by scanning over the attenuated laser line using a reduced slit width on the monochromator. Although all data was recorded digitally, for illustrative purposes a typical low-temperature spectrum is shown in Fig. 1.

In Table 1 are listed the actual numerical values for measurements of the intensity (i.e. integrated area) of the Raman line at 1650 cm^1 for a range of temperatures. These results are in general agreement with infrared absorption measurements over the same temperature range.[8] The reader should notice, however, that these data differ somewhat from those in Table III of Ref. 3, which were discussed in detail in Ref. 6. The difference is that *peak* intensities were recorded in Ref. 3 while *integrated* intensities are listed here. This distinction is important since integrated intensities are what the theories calculate. The integrated intensities result from fitting Lorentzian lineshapes to the spectra. Any apparent asymmetry of the lineshape (see Fig. 1) is actually dealt with properly by accounting for the real contributions of weaker amide-I features at 1659 cm^{-1} and 1662 cm^{-1}, as well as the tail of the 1665-cm^{-1} "normal" amide-I feature itself.

Table 1. Normalized integrated Raman intensity values of the 1650-cm^{-1} band. Temperature uncertainties are due primarily the the method for estimating the degree of heating caused by absorption in the focal volume of the laser beam.

Temp	σ	Relative Intensity	σ
21	4	1.00	.016
21	4	.996	.016
53	4	.892	.019
53	4	.895	.019
100	10	.710	.022
100	10	.726	.022
149	6	.496	.025
149	6	.507	.025
227	12	.356	.028
227	12	.346	.028
305	8	.170	.032
305	8	.169	.032

THEORY

The theory presented in this section is taken almost literally from Ref. 9.

As a theoretical model we use a linear coupling (or Fröhlich[10]) Hamiltonian operator of the form

$$\hat{H} = \hat{H}_0 + J\hat{V} \quad , \tag{1}$$

where

$$\hat{H}_0 = \sum_{q=1}^{R} \left\{ \Omega_0 \hat{B}_q^\dagger \hat{B}_q + \sum_{j=1}^{M} \left[\omega_j \hat{b}_{qj}^\dagger \hat{b}_{qj} + \chi_j \left(\hat{b}_{qj} + \hat{b}_{qj}^\dagger \right) \hat{B}_q^\dagger \hat{B}_q \right] \right\} \tag{2}$$

$$\hat{V} = \sum_{q=1}^{R} \left(\hat{B}_q^\dagger \hat{B}_{q+1} + \hat{B}_q^\dagger \hat{B}_{q-1} \right) \tag{3}$$

The parameters in Eqs. (1) - (3) are defined as follows:

J	is the nearest neighbor, electromagnetic coupling energy which was calculated as 4 cm^{-1} in Ref. 4,
Ω_0	is the undressed amide-I vibrational energy,
R	is the number of ACN molecules in a linear chain,
M	is the number of phonon modes coupled to each ACN molecule,
$\{\omega_j\}$	with j = 1, 2, ...M is the set of phonon energies, and
$\{\chi_j\}$	is the corresponding set of coupling energies.

To begin our analysis, we assume CO vibrational energy to be localized at a single ACN molecule. We do this for two reasons: i) this assumption is approximately true, and ii) it provides the basis for a perturbation expansion (in small J) which includes the effects of $\hat{V}$ to which we shall return later. Thus we are led to consider the operator

$$\hat{h} = \Omega_0 \hat{B}^\dagger \hat{B} + \sum_{j=1}^{M} \left[\omega_j \hat{b}_j^\dagger \hat{b}_j + \chi_j \left(\hat{b}_j + \hat{b}_j^\dagger \right) \hat{B}^\dagger \hat{B} \right] \tag{4}$$

where the subscripts, q, have been temporarily dropped for typographical convenience.

The eigenvalue equation

$$\hat{h} | \psi \rangle = E | \psi \rangle \tag{5}$$

is satisfied exactly by the eigenvalue-eigenstate pair

$$E = N\,\Omega_0 + \sum_{j=1}^{M}\left[n_j\,\omega_j - N^2\frac{\chi_j^2}{\omega_j}\right] \qquad (6)$$

$$|\,\psi\,\rangle = |\,N\,\rangle \prod_{j=1}^{M} |\phi_j\,\rangle \qquad (7)$$

where

$$|\phi_j\,\rangle = \sqrt{n_j\,!}\,\exp\!\left(-\,\frac{1}{2}N^2\frac{\chi_j^2}{\omega_j^2}\right)\sum_{m_j=0}^{\infty}\left[\frac{\left(-N\,\frac{\chi_j}{\omega_j}\right)^{m_j-n_j}}{\sqrt{m_j\,!}}\;L_{n_j}^{m_j-n_j}\left(N^2\frac{\chi_m^2}{\omega_j^2}\right)|\,m_j\,\rangle\right]$$

and where $\hat{B}^{\dagger}\,\hat{B}\,|N\rangle = N\,|\,N\,\rangle$ and $\hat{b}_j^{\dagger}\,\hat{b}_j\,|\,m_j\,\rangle = m_j\,|\,m_j\,\rangle$.

At this point, three comments are appropriate:

i) $L_n^m(\bullet)$ is an associated Laguerre polynomial using the normalization in Gradshteyn and Ryzhik[11] and not (for example) that in Morse and Feshbach.[12]

ii) The expression for $|\phi_j\rangle$ in Eq. (8) is not new knowledge. It is the number representation of the displaced Hermite polynomial eigenstate (more commonly seen in the position representation) that has been employed in the theory of color centers.[13-18]

iii) Equation (6) predicts an overtone spectrum that has been observed in ACN.[19] Thus, it is an experimental fact that

$$\sum_{j=1}^{M}\frac{\chi_j^2}{\omega_j} = 24.7\ \mathrm{cm}^{-1} \qquad (9)$$

As has been pointed out by Alexander and Krumhansl,[6,7] a correct calculation of the temperature dependent intensity of the 1650 band in ACN follows that for a "zero phonon" band of a color center. This point is made with particular clarity by Krumhansl in reference.[7] Thus one seeks the sum of all transitions from the ground states $|\,m_j\rangle$ to first excited states with $m_j = n_j$. Since the ground states are thermally populated with probabilities

$$P_j = \left[1 - \exp\left(-\frac{\hbar\omega_j}{kT}\right)\right]\exp\left(-\,m_j\,\frac{\hbar\omega_j}{kT}\right) \qquad (10)$$

the desired temperature dependence is

$$W(T) = \prod_{j=1}^{M} W_j\,(T)\,. \qquad (11)$$

where

$$W_j(T) = \sum_{m_j=0}^{\infty} P_j\,|\langle m_j|\phi_j\rangle|^2 \tag{12}$$

and $|\phi_j\rangle$ is calculated from Eq. (8) with $n_j = m_j$. Using the identity number 8.976 from Gradshteyn and Ryzhik,[11] the sum in Eq. (12) is readily computed to be

$$W_j(T) = \exp\left[-\frac{\chi_j^2}{\omega_j^2}\coth\left(\frac{\hbar\omega_j}{2kT}\right)\right] I_0\left[\frac{\chi_j^2}{\omega_j^2}\operatorname{csch}\left(\frac{\hbar\omega_j}{2kT}\right)\right] \tag{13}$$

where $I_0[\bullet]$ is the modified Bessel function of the first kind, of order zero.

Returning to our original Hamiltonian, we perform a first order perturbation calculation as follows. A zero order estimate of an eigenstate that exhibits the translational symmetry of the model is

$$|\psi^{(0)}\rangle = \frac{1}{\sqrt{R}}\sum_{q=1}^{R} \exp(ikq)|\tilde{\psi}_q\rangle \tag{14}$$

where

$$k = \frac{2\pi}{R}\nu \tag{15}$$

and $\nu = 0, \pm 1, \ldots, \frac{R}{2}\left(\pm\frac{R-1}{2}\right)$ for R even(odd). In Eq. (14), $|\tilde{\psi}_q\rangle$ is calculated from Eq. (7) and Eq. (8) with $N = 1$. Then to first order in J the energy is

$$E(k) \doteq \Omega_0 - \sum_{j=1}^{M}\chi_j^2/\omega_j + 2J\prod_{j=1}^{M}\exp\left(-\chi_j^2/\omega_j^2\right)\cos k \tag{16}$$

A localized solution can be constructed as a wave packet of the eigenstates approximated in Eq. (14). Thus the linewidth, ΔE, of such a wave packet must satisfy the inequality

$$\Delta E < 4J\prod_{j=1}^{M}\exp\left(\frac{-\chi_j^2}{\omega_j^2}\right) \tag{17}$$

Finally we note from Eq. (11) and Eq. (13) that

$$W(0) = \prod_{j=1}^{M}\exp\left(-\chi_j^2/\omega_j^2\right) \tag{18}$$

Thus the same (Franck-Condon) factor that reduces the low-temperature intensity of the 1650-cm^{-1} band also reduces its linewidth, thereby increasing the lifetime of a localized state.

COMPARISON OF THEORY WITH DATA

In Fig. 2 Raman spectra in the range 20 – 200 cm^{-1} are presented. We have observed a total of 30 distinct features in the (xx), (yy), and (xy) Raman spectra between 20 and 200 cm^{1} at 21 K. This is in qualitative agreement with the data of Gerasimov[20] where 27 bands were observed at 113 K. A more complete analysis of these data will be presented by one of us (CTJ) in a forthcoming publication. In the present discussion we consider whether coupling to these phonon modes can account for the temperature dependence of the 1650-cm^{-1} band. Ideally we would like to assign an ω_j and χ_j in Eq. (2) to each phonon mode that contributes to self-trapping of the 1650-cm^{-1} band. Since this is impractical, we assume that each ACN molecule couples to M phonon modes, all having the identical frequency ω_1 and coupling strength χ_1. In other words we view ω_1 and χ_1 as the average frequency and coupling strength of the M phonon modes that contribute to the self-trapping.

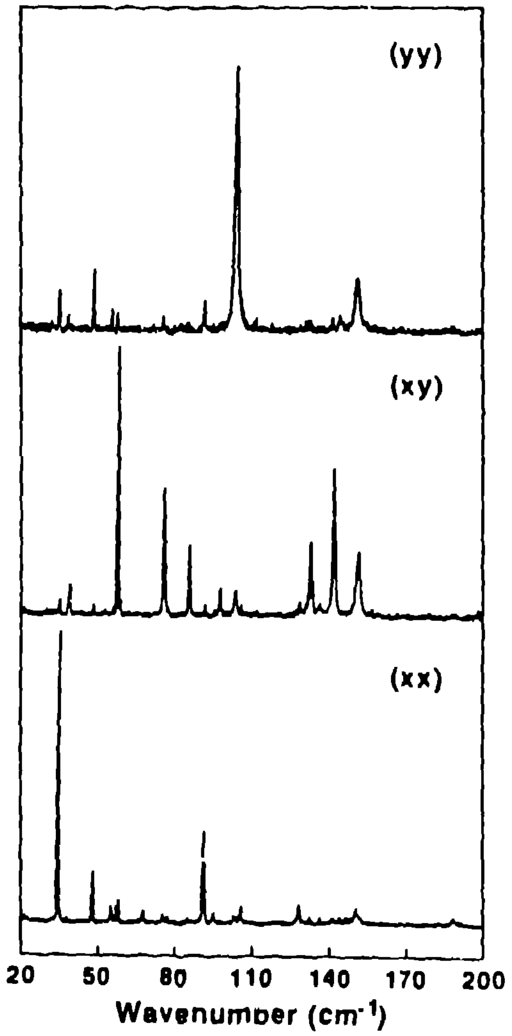

Fig. 2. Raman spectra of crystalline acetanilide in the optical phonon region (20 – 200 cm^{-1}) at 21K in the (a) xx, (b) yy, and (c) xy orientations.

Then, from Eq. (9),

$$\frac{\chi_1^2}{\omega_1} = \frac{24.7}{M}\ \mathrm{cm}^{-1} \tag{19}$$

and from Eqs. (11) and (13), and expressing ω_1 in wave numbers,

$$\frac{W(T)}{W(0)} = \left\{\frac{\exp\left[-\frac{24.7}{M\omega_1}\coth\left(0.7174\,\frac{\omega_1}{T}\right)\right] I_0\left[\frac{24.7}{M\omega_1}\ \mathrm{csch}\left(0.7174\,\frac{\omega_1}{T}\right)\right]}{\exp\left[-\frac{24.7}{M\omega_1}\right]}\right\}^M \tag{20}$$

The solid curve in Fig.3 is plotted from Eq. (20) with M and ω_1 adjusted to give the least squares fit to the data. These optimum values are found to be

M = any value ≥ 12

$\omega_1 = 71\ \mathrm{cm}^{-1}$.

The effect of varying the parameter M, the number of coupled modes, is illustrated by Fig. 4 in which Eq. (20) is plotted for a range of M values while keeping ω_1 constant at 71 cm^{-1}. The curves quickly converge after M ≈ 8.

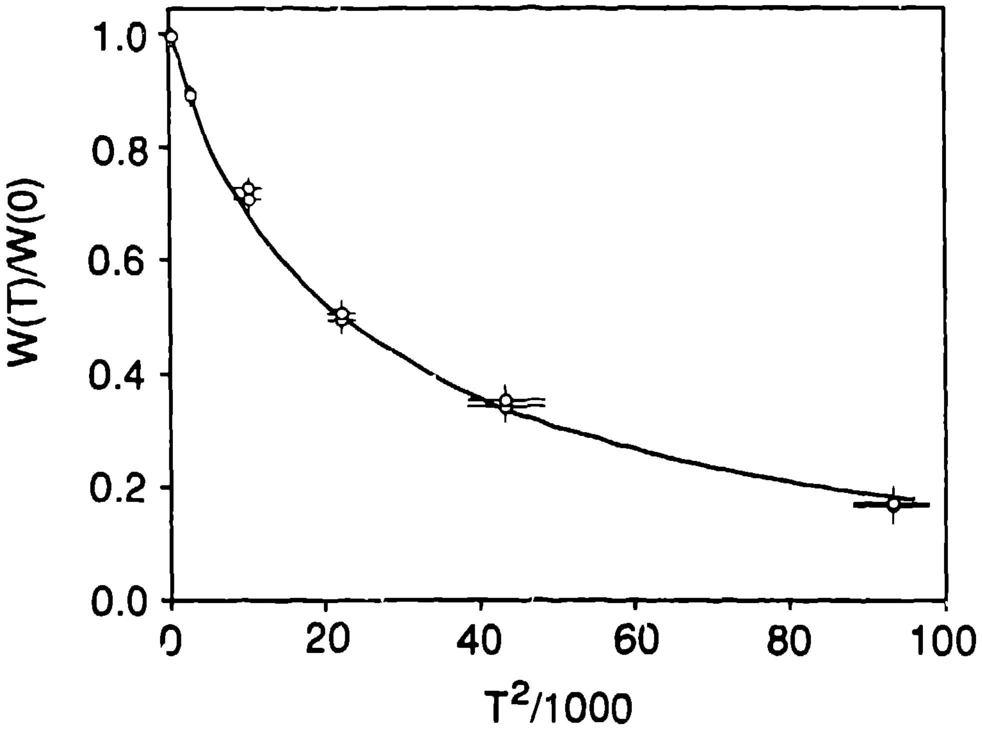

Fig. 3. Data points "o" indicate measurements of relative integrated intensity of the 1650 cm^{-1} line in crystalline acetanilide. The solid curve is calculated from Eq. (20) with M = 20 and ω_1 = 71 cm^{-1}.

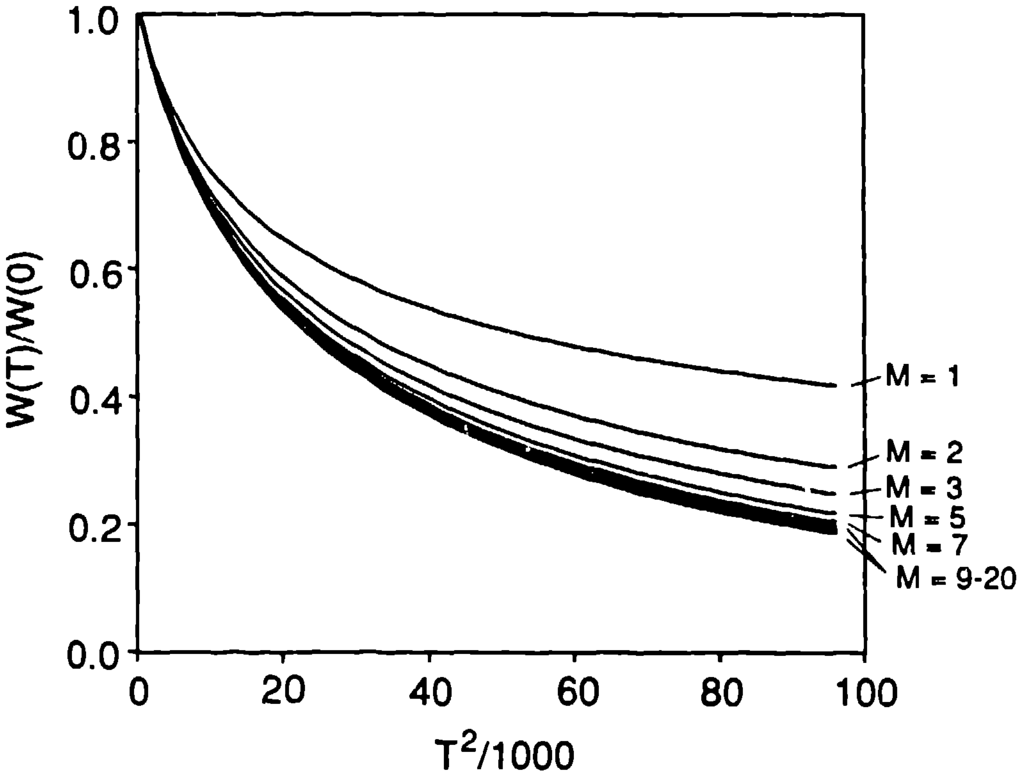

Fig. 4. Plots of Eq. (20) with different values of M, and for $\omega_1 = 71$ cm^{-1}.

CONCLUDING COMMENTS

1. We have presented a concise theory of polaron states in crystalline acetanilide (ACN). Being in the number representation, this theory complements that developed for color centers,[13-18] and it is in agreement with the point of view expressed recently by Krumhansl and Alexander.[6,7]

2. We display here (Fig. 1) our best Raman-spectroscopic measurements of the relative intensity of the 1650-cm^{-1} polaron state in ACN as a function of absolute temperature.

3. We show (Fig. 2) a spectrum of the Raman-active optical phonon modes in the range between 20 and 200 cm^{-1}. These measurements were made on carefully prepared single crystals of ACN.

4. We conclude that the data in Fig. 1 are consistent with the assumption of polaron formation through interactions with a band of 10-20 optical phonon modes clustered near 72 cm^{-1}. We note that this conclusion is at variance with Alexander and Krumhansl who suggest[6] the data require acoustic phonon modes in addition to the optical mode near 70 cm^{-1} in order to explain both the temperature dependence and the energy shift of the 1650-cm^{-1} band. We emphasize that we cannot exclude the possibility that acoustic phonons participate in the self-trapping, but we assert that they are not necessary to explain the data.

5. From Eq. (17) our theory predicts a polaron linewidth that is less than 11.5 cm^{-1}. This is consistent with our experimental observations as well as those of Ref. 3.

6. We note from Eq. (17) that the polaron linewidth is proportional to the Franck-Condon factor (FCF) as defined in Eq. (18). Thus, as has previously been suggested,[21] one might consider the following scenario: i) An optical photon excites a polaron, which is self-trapped by optical-mode phonons. Since the FCF is relatively large, this localized polaron is unstable. ii) The unstable polaron relaxes into a wave packet that is self-trapped by acoustic-mode phonons. From Eq. (18) this would have a much smaller FCF and from Eq. (17) a much smaller linewidth and, therefore, greater stability. The final state, in this scenario, would correspond to the "soliton" proposed by Davydov.[22]

REFERENCES

1. G. Careri, in *Cooperative Phenomena*, edited by H. Haken and M. Wagner (Springer, Berlin, 1973) p. 391.
2. A.S. Davydov, Sov. Phys. Usp. **25**, p.898 (1982; Usp. Fiz. Nauk **138**, p.603 (1982).
3. G. Careri, U. Buontempo, F. Galluzzi, A. C. Scott, E. Gratton, and E. Shyamsunder, Phys. Rev. B **30**, 4689 (1984).
4. J. C. Eilbeck, P. S. Lomdahl, and A. C. Scott, Phys. Rev. B **30**, 4703 (1984).
5. T. Holstein, Ann. Phys. (N.Y.) **8**, p.325 (1959).
6. D. M. Alexander and J. A. Krumhansl, Phys. Rev. B **33**, 7172 (1986).
7. J. A. Krumhansl, in *Energy Transfer Dynamics*, edited by T. W. Barrett and H. A. Pohl (Springer, Berlin, 1987) p. 174.
8. G. Careri, E. Gratton and E. Shyamsunder, Phys. Rev. B **37**, p.4048 (1988).
9. Alwyn C. Scott, Irving J. Bigio and Clifford T. Johnston, Phys. Rev. B 39, p. 12883 (1989).
10. H. Fröhlich, Adv. Phys. **3**, 325 (1954).
11. I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals Series and Products* (Academic, New York 1965).
12. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953) p. 784.
13. K. Huang and A. Rhys, Proc. Roy. Soc. (London) **204A**, 406 (1950).
14. M. Lax, J. Chem. Phys. **20**, 1752 (1952).
15. R. C. O'Rourke, Phys. Rev. **91**, 265 (1953).
16. J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959).
17. T. H. Keil, Phys. Rev. **A601**, 140 (1965).
18. D. B. Fitchen, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968) p. 293.
19. A. C. Scott, E. Gratton, E. Shyamsunder, and G. Careri, Phys. Rev. B **32**, 5551 (1985).
20. V. P. Gerasimov, Opt. Spektrosk. **43**, 705 (1977) [Opt. Spectros. (USSR) **43**, 417 (1978)].
21. A. C. Scott, in *Synergetics of the Brain*, edited by E. Bazar, F. Flohr, H. Haken, and A. J. Mandell (Springer, Berlin, 1983) p. 345.
22. A. S. Davydov, *Biology and Quantum Mechanics* (Pergamon, New York, 1982).