Red-shifted infrared spectra at low temperatures of amide I (C=O stretching) vibrations of crystalline acetanilide measured by Careri et al. are shown to be due to vibron solitons, which are nonlinearity-induced localized modes of vibrons arising from their nonlinear interactions with optic-type phonons. A nonlinear eigenvalue equation giving the eigenfrequency of stationary solitons is solved approximately by introducing lattice Green's functions, and the obtained result is in good agreement with the experimental result. Inclusion of interactions with acoustic phonons yields the Debye-Waller factor in the zero-phonon line spectrum of vibron solitons, in a manner analogous to the case of impurity-induced localized harmonic phonon modes in alkali halides.

§ 1. Introduction

Recently, a new amide I band (essentially C=O stretching) observed in infrared and Raman spectra of crystalline acetanilide (CH₃CONHC₆H₅)ₓ or ACN with a red shift of about 15 cm⁻¹ from a main absorption peak at about 1665 cm⁻¹ has been assigned to Davydov-like solitons.¹ The soliton here is a dynamical self-sustaining entity arising from a self-trapping of amide I vibrons interacting with low frequency phonons and obeying a discrete-version of the one-dimensional (1d) nonlinear Schrödinger equation.² Several of implications of such a finding to soliton physics are listed below: (1) This probably adds one more example to solitons on microscopic level in solid state physics, such as those in polyacetylene, quasi 1d magnetic systems and CDW systems.³ In contrast to conventional solitons observed in almost all cases on macroscopic level in hydrodynamics and plasma physics, here much discussion and debates have been given on the existence and assignment of solitons. (2) This shows that Davydov-like solitons may exist in an organic solid of ACN in which chains of hydrogen bonded peptide groups run through the crystal in a manner similar to the three spines of hydrogen bonded peptide groups in alpha helix. (3) There is a good reason to believe that Davydov-like solitons are likely to exist in α helical proteins, and an implication of this to biophysics and biochemistry is a fascinating problem.

In a previous paper,⁴ hereafter referred to as (I), the present author developed a theory of vibron solitons to show that Davydov's idea⁵ can be formulated in a more physically reasonable and quantitatively correct form by employing a nonlinearly coupled 1d model oscillator-lattice system and by formulating the problem in the framework of lattice dynamics. This is to treat vibron solitons as dynamical localized vibron modes which appear below the bottom of the vibron frequency band due to a negative effective on-site potential of fourth order anharmonicity induced by vibron-phonon interactions. Here vibron solitons are governed by a discrete version of the 1d nonlinear Klein-Gordon equation, stationary ones of which have the properties similar to localized modes in lattice dynamics due to an impurity or a lattice defect.
It is the purpose of this paper to show that the spectroscopic properties of Davydov-like solitons obtained by Careri et al.\textsuperscript{1,2)} can be well accounted for by a slightly modified version of the vibron soliton theory developed in (1). This is done by allowing each amide I oscillator in ACN to interact nonlinearly with optic type lattice vibrations rather than with acoustic phonons. Although the employed model itself is somewhat similar to that used by Careri et al.,\textsuperscript{2)} the present theory is different from theirs in the following respects: (1) Vibron solitons are nonlinearity-induced localized modes in lattice dynamics, whereas, conceptually Davydov solitons are the corresponding exciton modes with exciton transfer by exchange-type interactions.\textsuperscript{5)} (2) Nonlinear differential-difference equations are treated by introducing lattice Green's functions to get an approximate solution of a nonlinear eigenvalue problem without introducing a continuum nor a strongly localized mode approximation. (3) Inclusion of interactions with acoustic phonons yields the Debye-Waller factor in the zero-phonon line of soliton-induced infrared spectra, in a manner analogous to the case of impurity-induced infrared absorption in alkali halide crystals,\textsuperscript{6)} but somewhat different from the method used by Alexander.\textsuperscript{7)}

This paper is organized as follows. In the next section the model Hamiltonian is introduced for the oscillator and lattice systems, and equations of motion for these systems are studied. In § 3 lattice Green's functions are introduced to solve nonlinear eigenvalue equations. The temperature-dependence of the absorption coefficient is studied in § 4. The last section is devoted to concluding remarks.

\section{Model Hamiltonian and equations of motion}

Acetanilide is an organic solid in which two close chains of hydrogen-bonded amide groups run through the crystal, where the nearly-planar amide groups display bond distances which are close to those found in polypeptides. To understand the essential features of the absorption band at 1650 cm\textsuperscript{-1} as being due to vibron solitons, we pay attention to a single hydrogen-bonded chain running in the \( b \) (or hydrogen-bonded) direction of the ACN crystal (Peptide geometry in ACN is shown in Ref. 2). We simulate the amide I vibration system and the optic-type low frequency phonon system in ACN by an oscillator system and a lattice system governed by the model Hamiltonian:

\begin{equation}
H_{\text{osc}} = \sum_n \left[ \frac{\mu q_n^2}{2} \right] + \left( \mu_0 q_n \right) q_n - \sum_{n,m} L(n,m) q_n q_m, \quad L(n,m) = L(|m-n|)
\end{equation}

and

\begin{equation}
H_{\text{latt}} = \sum_n \left[ \frac{Mu_n^2}{2} + \frac{Ku_n^2}{2} \right],
\end{equation}

respectively. Here indices \( n \) and \( m \) count molecules along the hydrogen-bonded chain. In the oscillator Hamiltonian \( H_{\text{osc}} \), \( \omega_0 \) is the eigenfrequency of the amide I vibration of a peptide group. The quantities \( q_n, \mu \) and \( L(n,m) \) are the normal coordinate of the amide I vibration of the \( n \)th peptide group (\( n \)th amide I oscillator), its effective mass and a dipole-dipole interaction force constant between the \( n \)th and \( m \)th amide I oscillators, respectively. The quantities \( u_n, M \) and \( K \) in the Hamiltonian \( H_{\text{latt}} \) for the lattice system are the displacement of the \( n \)th low frequency vibration probably involving the hydrogen-bonding proton, its effective mass and a force constant, respectively. The oscillator-lattice interaction is assumed to be described by the following model Hamiltonian:
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\[ H_{\text{int}} = \sum_n (A/2) q_n^2 u_n, \]  

(2·3)

where \( A \) is an interaction constant. In Eqs. (2·2) and (2·3) a single relevant local phonon mode per site is taken to contribute to the oscillator-lattice interaction by modulating the on-site vibrational energy of the oscillator system. Modulations of dipole-dipole interactions of amide I oscillators by their coupling with other degree of phonon modes are assumed to be negligible as compared with those of the on-site potential energy.

Equations of motion obeyed by the oscillator and lattice systems are written as

\[ \mu \ddot{q}_n + \mu \omega_0^2 q_n - 2 \sum_m L(n, m) q_m + A q_n u_n = 0, \]  

(2·4)

\[ M \ddot{u}_n + K u_n + (A/2) q_n^2 = 0. \]  

(2·5)

Equations (2·4) and (2·5) constitute coupled nonlinear differential-difference equations, exact analytical solutions to which are unobtainable. These equations, however, can be treated analytically by limiting our discussion to the case in which characteristic frequencies associated with the time-variation of \( u_n \) and \( Q_n Q_n^* \) are much smaller than the frequency \((K/M)^{1/2}(\approx 10^{15} \text{ sec}^{-1})\) of the optical mode involving proton motion in the lattice system. Here \( Q_n \) and \( Q_n^* \) are the negative and positive frequency parts of \( q_n \), the main time-dependence of the former and the latter being given by \( \exp(-i\omega_0 t) \) and \( \exp(i\omega_0 t) \), respectively. We can then neglect the first term on the left-hand side of Eq. (2·5) to obtain

\[ u_n = -(A/2K) q_n^2. \]  

(2·6)

Inserting this back into Eq. (2·4), we get

\[ \ddot{q}_n + \omega_0^2 q_n - (2/\mu) \sum_m L(n, m) q_m - (A^2/2K\mu) q_n^3 = 0. \]  

(2·7)

We observe that Eq. (2·7) is also derivable from the following effective oscillator Hamiltonian:

\[ H_{\text{osc}} = \sum_n [(\mu \dot{q}_n^2/2) + U(q_n)] - \sum_{nm} L(n, m) q_n q_m, \]  

(2·8)

where

\[ U(q) = (\mu \omega_0^2/2) q^2 - (A^2/8K) q^4. \]  

(2·9)

It is understood that we are concerned here exclusively with the region

\[ |q| < (2K\mu)^{1/2} \omega_0 / A \equiv q_0, \]  

(2·10)

where \( \pm q_0 \) are the maximum points of \( U(q) \): For \( |q| > q_0 \), which is entirely out of concern here, inclusion to \( v(q) \) of a higher order positive anharmonic term of the form \( D q^6 (D > 0) \) is generally required. Condition (2·10) will be examined numerically at later stage. It is seen that the oscillator-lattice interaction so treated amounts to inducing a negative on-site potential of fourth order anharmonicity.

Equation (2·7) is an equation of motion for vibrons with the dispersion relation characterized by wave vector \( k \):

\[ \omega^{(0)}(k) = [\omega_0^2 - (2/\mu) \sum_m L(n, m) \exp[ik(m-n)a]]^{1/2} \]  

(2·11)
under the influence of the induced attractive potential, where \( a \) is the lattice constant of the oscillator system. We pay particular attention to a localized vibron mode the eigenfrequency of which appears below the bottom

\[
\omega^{(0)}(0) = \left[ \omega_0^2 - (2/\mu) \sum_n L(n, m) \right]^{1/2} = \omega_1 \tag{2·12}
\]

of the vibron frequency band \( \omega^{(0)}(k) \), a situation quite analogous to localized phonon modes due to an impurity or a defect in lattice dynamics, the latter being due to a static, spatially localized harmonic perturbation potential.

Before closing this section, a remark is given on the conventional continuum approximation to reduce Eq. (2·7) to the nonlinear Klein-Gordon equation

\[
(\partial^2 q/\partial x^2) - (1/c_1^2)(\partial^2 q/\partial t^2) - m^2 c_1^2 q + mgq^3 = 0 . \tag{2·13}
\]

Here

\[
c_1 = [(2/\mu) \sum L(1) l^2 \alpha]^1/2, \quad m = \omega_1/c_1^2 \quad \text{and} \quad g = A^2 / 2K\mu\omega_1 \tag{2·14}
\]

are the velocity of long-wavelength vibrons, the mass of the vibrons and a coupling constant, respectively. In the above equations, we have taken the 1d oscillator system in the direction of the \( x \)-axis. As is well known, Eq. (2·13) admits envelope-soliton solutions having the properties similar to those governed by the 1d nonlinear Schrödinger equation. Such a continuum approximation, however, can only be used when a spatial extent of localized modes governed by Eq. (2·7) is much larger than the lattice constant \( a \). This point will be examined in the next section.

§ 3. Vibron solitons

To treat Eq. (2·7) with attention paid to nonlinearity-induced localized modes appearing below the bottom \( \omega_1 \) of the vibron frequency band \( \omega^{(0)}(k) \), we divide \( q_n \) into negative and positive frequency parts:

\[
q_n = Q_n + \bar{Q}_n^* = \tilde{Q}_n \exp(-i\omega_1 t) + \tilde{Q}_n^* \exp(i\omega_1 t) . \tag{3·1}
\]

We insert this into Eq. (2·7) and employ a rotating-wave approximation to retain only terms with their principal time-dependence given by \( \exp(-i\omega_1 t) \) and its complex conjugate, since we are concerned here solely with the absorption spectra of ACN around the frequency range \( \omega \sim 1650 \text{ cm}^{-1} \). For ACN and most of polypeptide systems, such an approximation procedure can be used, since the inequality

\[
\omega_0^2 \gg (2/\mu) \sum L(n, m) \tag{3·2}
\]

holds for these systems \( (h\omega_0 = 1665 \text{ cm}^{-1}, (2/\mu) \sum L(n, m) \approx 3 \sim 4 \text{ cm}^{-1}, \text{ cf., Eq. (3·19)}) \). An equation obeyed by the \( Q_n \)'s is then written as

\[
\dot{Q}_n + \omega_0^2 Q_n - (2/\mu) \sum L(n, m) Q_n - (3A^2 / 2K\mu)|Q_n|^2 Q_n = 0 . \tag{3·3}
\]

We seek solutions to this equation in the form

\[
Q_n = \phi_n \exp[-i(\omega t - kna)] . \tag{3·4}
\]
Here \( \omega \) and \( k \) are real constants identified as the eigenfrequency and momentum of vibron solitons under consideration, while \( \phi_n \) is a real envelope function depending on site index \( n \) and time variable \( t \). Putting Eq. (3.4) into Eq. (3.3), we get a pair of equations

\[
\dot{\phi}_n + \left[ \omega_0(k)^2 - \omega^2 \right] \phi_n - \frac{2}{\mu} \sum_{l=1}^{\infty} L(l) \cos(kl\alpha) \left( \phi_{n+1} + \phi_{n-1} - 2\phi_n \right) - \frac{3A^2}{2K_\mu} \phi_n^3 = 0, \quad (3.5)
\]

\[
2\omega \phi_n + (2/\mu) \sum_{l=1}^{\infty} L(l) \sin(kl\alpha) \left( \phi_{n+1} - \phi_{n-1} \right) = 0, \quad (3.6)
\]

the former and the latter being considered as determining the frequency eigenvalue and the envelope function and the soliton momentum, respectively. Except in the case of a continuum limit, where solutions to Eqs. (3.5) and (3.6) take the form

\[
\phi(x, t) = a \text{sech}[a(3A^2/4K\mu c_1^2)]^{1/2} \gamma(x - vt), \quad \gamma = [1 - (v^2/c_1^2)]^{-1/2},
\]

\[
\omega = \left[ \omega_0^2 + c_1^2 k^2 - (3A^2/4K\mu) c_1^2 \right]^{1/2} = \omega(k),
\]

\[
k = \gamma m^* v, \quad m^* = \omega(0)/c_1^2,
\]

these differential-difference equations cannot be solved analytically. In the above equations \( a \) and \( v \) are constants identified as the soliton amplitude and the soliton velocity, respectively. This implies that in such a general situation the soliton momentum is not well defined.

Let us pay particular attention to stationary localized modes or stationary vibron solitons for which \( k = 0 \) and \( \phi_n \) is time-independent. A red-shifted absorption band at about 1650 cm\(^{-1}\) in ACN can be considered as being due to such solitons. Equation (3.5) then reduces to

\[
\omega v^2 \phi_n - (2/\mu) \sum_m L(n, m) \phi_m - (3A^2/2K\mu) \phi_n^3 = \omega^2 \phi_n, \quad (3.10)
\]

while Eq. (3.6) is automatically satisfied. Equation (3.10) is a nonlinear eigenvalue equation determining the eigenvalue \( \omega \) and the eigenfunction \( \phi_n \). The situation here is somewhat similar to localized modes due to an impurity or a defect in a harmonic lattice in lattice dynamics, where a term linear with respect to the \( \phi_n \)’s and non-vanishing only at the impurity site replaces the last term on the left-hand side. Here we define the vibron soliton amplitude \( a \) by the relation

\[
\phi_n = a \xi_n \quad \text{with} \quad \max|\xi_n| = 1.
\]

In terms of 1d lattice Green’s function

\[
G(n, m; \omega) = \frac{1}{N} \sum_k \frac{\exp[ik(m-n)a]}{\omega_0(k)^2 - \omega^2} = G_{m-n}(\omega), \quad \omega < \omega_1,
\]

an equation obeyed by the \( \xi_n \)’s is then rewritten as

\[
\xi_n = \lambda a^2 \sum_m G(n, m; \omega) \xi_m^3 \quad \text{with} \quad \lambda = 3A^2/2K_\mu.
\]

In Eq. (3.12) \( N \) is the total number of amide I oscillators in the system. An explicit expression for \( G(n, m; \omega) \) can be obtained by taking the limit \( N \rightarrow \infty \) and by assuming the \( L(n, m) \)’s to be nonvanishing only for nearest neighbour pairs:
\[ G(n, m; \omega) = \frac{1}{[(\omega_0^2 - \omega^2)^2 - (4L/\mu)^2]^{1/2}} \left[ \frac{4L/\mu}{((\omega_0^2 - \omega^2)^2 + ((\omega_0^2 - \omega^2)^2 - (4L/\mu)^2)^{1/2})^{m-n}} \right]^{(m-n)}, \]

where \( L \) is the nearest-neighbour force constant. Incidentally, Eq. (3.14) in the continuum limit with \( x = na \) reduces to

\[ G(n, m; \omega) = G(x, x'; \omega) = \frac{1}{2c_1} \exp\left[\frac{-((\omega_1^2 - \omega^2)^{1/2}/c_1)|x - x'|}{(\omega_1^2 - \omega^2)^{1/2}}\right]. \]

for which Eq. (3.13) reduces to a nonlinear integral equation with solutions given by Eqs. (3.7) and (3.8) with \( k = v = 0 \). The continuum approximation can only be used for the \( \phi_n \)'s varying fairly smoothly with respect to the site index \( n \), otherwise we should treat the original equation (3.10) or (3.13). In this paper we limit our discussion to studying Eq. (3.13). The merit of the use of the Green's-function method here is that it provides us with a more straightforward procedure in solving the nonlinear eigenvalue problem and that it can be applied to any type of lattice, including two- or three-dimensional one. It is noted here that the use of continuum approximation in higher-dimensional cases often gives a misleading result. This point will be discussed elsewhere.

In studying Eq. (3.13), we pay attention to a spatially symmetric or s-like mode \( \xi_n = \xi_{-n} \) localized at \( n = 0 \). In terms of

\[ g_p(\omega) = \lambda c^2 \psi_p(\omega), \]

the eigenvalue equation giving the frequency eigenvalue \( \omega \) and the eigenfunctions \( \xi_n \) is written as

\[ 1 - g_0(\omega) = 2 \sum_{p=1}^{\infty} g_p(\omega) \xi_p^2. \]

This is to be treated simultaneously with

\[ \xi_n - g_0(\omega) \xi_n^3 = \sum_{p=1}^{\infty} g_p(\omega) (\xi_{n+p}^3 + \xi_{n-p}^3). \]

Equations (3.17) and (3.18) can be treated by using a successive approximation. Before doing this, the assessment of the localization of the localized mode and the frequency eigenvalue is required by estimating numerical values of \( L(n, m), \mu, A \) and \( K \) in addition to \( \omega_n \approx 1665 \text{ cm}^{-1} \). We do this by using the nearest-neighbour approximation for the \( L(n, m)'s \) and by making one-to-one correspondence of the present theory with that of Careri et al. \(^2\) developed along the line with the Davydov formalism, \(^3\) since numerical values of pertinent physical quantities were estimated by these workers. A result of such a procedure is written as

\[ J = \hbar L/\mu \omega_0 \approx 3 \sim 4 \text{ cm}^{-1}, \quad \chi = \hbar A/2 \mu \omega_0 \approx 6 \times 10^{-11} \text{ N}, \]

\[ K \approx 1.3 \times 10 \text{ N/m}, \quad E_1 = \hbar \omega_0 - 2J = E_0 - 2J \approx \hbar \omega_1 \approx 1665 \text{ cm}^{-1}. \]

In terms of dimensionless quantities

\[ \epsilon = (E_1 - E)/2J \quad \text{and} \quad \gamma = (\mu \omega_0/\hbar) \alpha^2, \]

an approximate expression for \( g_p(\omega) = g_p(\epsilon) \) is given by
\( g_p(\epsilon) = \Gamma y [1 + \epsilon^2 - 1]^{-1/2} [1 + \epsilon + [(1 + \epsilon^2 - 1)^{1/2}]^{-p}, \quad p > 0 \) (3.21)

with

\[
\Gamma = (3/2) \left( \chi^2 / KJ \right) = \begin{cases} 7.50 & \text{for } J \approx 3 \text{ cm}^{-1}, \\ 5.63 & \text{for } J \approx 4 \text{ cm}^{-1}. \end{cases}
\] (3.22)

The quantity \( y \) related to the soliton amplitude has remained undetermined. Since the temperature at which the soliton absorption line is observed (10 K \( \leq T \leq 240 \) K) is much lower than \( \hbar \omega_0 / k_B = 2.3 \times 10^3 \) K (\( k_B \): Boltzmann constant), it is reasonable to assume that the principal contribution to \( \alpha^2 \) comes from the mean square displacement associated with the zero-point motion of the amide I oscillator. This amounts to taking

\( y = 1/2. \) (3.23)

With these numerical estimations, we use the successive approximation by first assuming that the localized mode under consideration is localized predominantly at the site \( n = 0 \). Equation (3.17) then reduces to

\[ 1 - g_0(\omega) = 0 \text{ or } \epsilon = (\Gamma^2 y^2 + 1)^{1/2} - 1. \] (3.24)

Insertion of Eqs. (3.22) and (3.23) into Eq. (3.24) gives

\[ \epsilon = \begin{cases} 2.88 & \text{for } J \approx 3 \text{ cm}^{-1}, \\ 1.99 & \text{for } J \approx 4 \text{ cm}^{-1}. \end{cases} \] (3.25)

The binding energy \( E_B = E_1 - E \) of the stationary solitons, which can be considered as the origin of the red-shift of the main amide I absorption line in ACN, is therefore given by

\[ E_B = \begin{cases} 17.3 \text{ cm}^{-1} & \text{for } J \approx 3 \text{ cm}^{-1}, \\ 15.9 \text{ cm}^{-1} & \text{for } J \approx 4 \text{ cm}^{-1}. \end{cases} \] (3.26)

From Eq. (3.25), the numerical value of the quantity

\[ \delta = \{1 + \epsilon + [(1 + \epsilon^2 - 1)^{1/2}]^{-1}, \] (3.27)

which gives a measure of the localization of the vibron soliton, is given by

\[ \delta = \begin{cases} 0.13 & \text{for } J \approx 3 \text{ cm}^{-1}, \\ 0.17 & \text{for } J \approx 4 \text{ cm}^{-1}. \end{cases} \] (3.28)

Our assumption of the localized mode being strongly localized at a single oscillator site is thus justified, and in effect we do not need to proceed any more in our successive approximation procedure. The result (3.26) is therefore a good approximate solution to the nonlinear eigenvalue problem. It is seen that the result so obtained, which contains no adjustable parameter, is in fairly good agreement with the experimental data.\(^2\)

The consistency of the present theory based on the use of the effective potential \( U(q) \) with minimum and maximum points at \( q = 0 \) and \( \pm q_0 \), respectively, is checked here by estimating numerically the quantities \( q_0, a/q_0 \), and \( U(\pm q_0) / \hbar \omega_0 \). By the use of Eqs. (3.19), (3.20) and (3.22), these quantities are rewritten as
Inserting the numerical values of $\omega_0, J$ and $\Gamma$ obtainable from Eqs. (3·19) and (3·22) and taking $\mu$ to be the reduced mass of C=O unit, we get

$$q_0 = 3 \times 10^{-9} \text{ cm}, \quad a/q_0 = 1.34 \times 10^{-1} y^{1/2}, \quad U(\pm q_0)/\hbar \omega_0 = 3 \hbar \omega_0/16 J\Gamma.$$  \(3\cdot30\)

From the second of the above equations, it is seen that the condition (2·10) is well satisfied for vibron solitons under consideration. The numerical value of $q_0$ so obtained is shown to be about one third of the bond length of C=O unit in peptide (1·24 Å). This and the third of Eqs. (3·30) also give further proof of the consistency of the present theory.

§ 4. Absorption coefficient

We have so far limited our discussion to the case of coupling of amide I oscillators with optical phonons which involve hydrogen bonding protons. Here we take into account their interactions with acoustic phonons as well to account for the temperature dependence of the absorption spectra associated with vibron solitons in ACN. As noted by Alexander,\(^7\) the absorption strength of the red-shifted line is shown to vary as $\exp(-\beta T^2)$ at low temperatures, where $\beta$ is a constant. Our observation is to understand this as a zero-phonon line spectrum resulting from random thermal modulations of the amide I vibron solitons by the acoustic phonons in a manner quite analogous to the case of low-temperature infrared spectra of localized or resonant phonon modes due to impurities or defects in alkali halides.\(^6\)

The Hamiltonian to be considered takes the form

$$H = H_{\text{osc}}^{\text{eff}} + H_{\text{ph}} + H'. \quad (4·1)$$

In the above equations, $H_{\text{osc}}^{\text{eff}}$ is a quantal-version of the Hamiltonian of the effective amide I oscillator (A-oscillator) system given by Eq. (2·8), satisfying the eigenvalue equation

$$H_{\text{osc}}^{\text{eff}}|v\rangle = \hbar \omega(v)|v\rangle. \quad (4·2)$$

Here, in terms of a quantum number $v$ the eigenstate and the energy eigenvalue are collectively denoted by $|v\rangle$ and $\hbar \omega(v)$, respectively. The quantity $H_{\text{ph}}$ is the Hamiltonian for the acoustic-phonon system taken to be a set of harmonic oscillators,

$$H_{\text{ph}} = \sum_j h_j(Q_j) = \sum_j \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial Q_j^2} + \frac{\hbar^2 \omega_j^2}{2} \right] Q_j^2 \quad (4·3)$$

with

$$h_j(Q_j) \phi_{n_j}(Q_j) = \hbar \omega_j \left( n_j + \frac{1}{2} \right) \phi_{n_j}(Q_j) \equiv \hbar \omega_j(n_j) \phi_{n_j}(Q_j),$$

$$n_j = 0, 1, 2, \cdots, \omega(N) = \sum \omega_j(n_j). \quad (4·4)$$

Here $h_j$, $Q_j$ and $\omega_j$ are the Hamiltonian, the normal coordinate and the eigenfrequency of the $j$th harmonic oscillator, respectively, in which $m$ is an effective mass, and $\phi_{n_j}(Q_j)$ is an eigenfunction of $h_j$ characterized by integer $n_j$. The index $j$ will be specified later on. The quantity $H'$ describes interactions between the A-oscillator system and the acoustic-phonon system, which we take to be linear in the $Q_j$'s:
Explicit expressions for $V(q)$ and the index $j$ are given in the Appendix. In studying the total system governed by Eq. (4.1), we employ an adiabatic approximation to assume that the phonon state depends adiabatically on the X-oscillators state. This may be justified on the ground that the characteristic frequency of about 1650 cm$^{-1}$ of the X-oscillator system is much larger than the maximum frequency of about 200 cm$^{-1}$ of the phonon system. In obtaining the adiabatic potential $U_{\nu}$ associated with the state $|\nu\rangle$ of the X-oscillator system, we neglect a change in wave function of the X-oscillator system caused by the perturbation $H'$. The effective Hamiltonian $H_{\text{eff}}^{\nu}(\nu)$ for the state $|\nu\rangle$ is then written in terms of a set of the Hamiltonian of the displaced harmonic oscillators of the phonon system:

$$H_{\text{eff}}^{\nu}(\nu) = \hbar \omega(\nu) + \sum_j \left( m \omega_j^2 Q_j^2 / 2 \right) + \sum_j \chi_j(\nu) Q_j - \sum_j (\hbar^2 / 2m) (\partial^2 / \partial Q_j^2)$$

$$= U_{\nu} - \sum_j (\hbar^2 / 2m) (\partial^2 / \partial Q_j^2) = \sum_j h_j [Q_j - Q_{0j}(\nu)] + \text{const}$$

with

$$\chi_j(\nu) = \langle \nu | V_j(q) | \nu \rangle, \quad Q_{0j}(\nu) = - \chi_j(\nu) / m \omega_j^2.$$  

Within the framework of the first order Born approximation, the absorption coefficient per unit volume of the X-oscillator system $A(\omega)$ is given by

$$A(\omega) = \frac{4 \pi \omega}{nc \hbar V_0} \int_{-\infty}^{\infty} \frac{d \nu}{\nu} \exp(-i\omega t) \left\langle \sum_{\nu_f} \left| \mu(\nu) \nu_f \right\rangle \left| \mu(\nu) \nu_f \right\rangle \prod_{j} S(n_j, n_j'; \nu_i, \nu_f) e^{i(\omega(n_f) - \omega(n_i)) t} \right\rangle T,$$

where

$$\mu(t) = \exp(iH_{\text{osc}}^{\text{eff}} t / \hbar) \mu \exp(-iH_{\text{osc}}^{\text{eff}} t / \hbar),$$

$$S(n_j, n_j'; \nu_i, \nu_f) = \int_{-\infty}^{\infty} d n_j \phi_{n_j}[\eta_j - \eta_{0j}(\nu_i)] \phi_{n_j}[\eta_j - \eta_{0j}(\nu_f)],$$

in which

$$\eta_j = Q_j(m \omega_j / \hbar)^{1/2}, \quad \eta_{0j}(\nu) = Q_{0j}(\nu)(m \omega_j / \hbar)^{1/2} = - \chi_j(\nu)(\hbar / m \omega_j)^{1/2} / \hbar \omega \ll 1.$$  

In the above equations $\nu_i(n_j)$ and $\nu_f(n_j')$ with $\omega(N_j) = \sum_j \omega_j(n_j)$ and $\omega(N_f) = \sum_j \omega_j(n_j')$ are the quantum numbers denoting initial and final states of the X-oscillator system (the $j$th harmonic oscillator), respectively. The quantities $c$, $\mu$ and $n$ are the light velocity, an effective dipole moment of the X-oscillator system and the refractive index, respectively. The quantity $V_0$ is the volume of the total system, and the angular bracket with subscript $T$ denotes an average over all initial states being in canonical equilibrium. A straightforward calculation gives
\[
S(n_j, n_j'; v_i, v_f) = \begin{cases} 
0 & \text{for } n_j' \neq n_j, n_j \pm 1, \\
1 - (1/2)[n_j + (1/2)]\eta_{0j}(v_i, v_f)^2 & \text{for } n_j' = n_j, \\
[(n_j+1)/2]^{1/2}\eta_{0j}(v_i, v_f) & \text{for } n_j' = n_j + 1, \\
-(n_j/2)^{1/2}\eta_{0j}(v_i, v_f) & \text{for } n_j' = n_j - 1, 
\end{cases}
\quad (4\cdot12)
\]

and therefore
\[
\prod \sum_{i, n_j} S(n_j, n_j'; v_i, v_f) e^{i\omega_{ij}(v_i, v_f)t} \sim \prod \sum_{j}[1 + f_j(t; v_i, v_f)],
\quad (4\cdot13)
\]

where
\[
f_j(t; v_i, v_f) = \frac{\eta_{0j}(v_i, v_f)^2}{2}[(n_j+1)e^{i\omega_{ij}t} + n_j e^{-i\omega_{ij}t} - (2n_j+1)],
\quad (4\cdot14)
\]
in which
\[
\eta_{0j}(v_i, v_f) = \eta_{0j}(v_i) - \eta_{0j}(v_f) \ll 1.
\quad (4\cdot15)
\]

Within the framework of the present approximation procedure, the thermal average in the integrand of Eq. (4·8) can be done separately for the phonon state and the A-oscillator state. The average over the former and the latter is denoted by the angular bracket with subscript \(jT\) and \(vT\), respectively. Taking first the average over the phonon state gives
\[
\langle \prod \sum_{j} [1 + f_j(t; v_i, v_f)] \rangle_{jT} = \langle \exp[\sum_{j} f_j(t; v_i, v_f)] \rangle_{jT} = \exp\langle \exp[\sum_{j} f_j(t; v_i, v_f)] - 1 \rangle_{jT} = \exp\langle \sum_{j} f_j(t; v_i, v_f) \rangle_{jT}.
\quad (4\cdot16)
\]

Here the symbol \(\exp[\sum_{j} f_j]\) is a leveraged exponential function which levels off a product of the \(f_j\)’s by erasing out those terms in which any of the \(f_j\)’s appears with a power higher than unity, and the superscript \((c)\) attached to the bracket symbol denotes a cumulant average. By virtue of Eq. (4·16), Eq. (4·8) reduces to
\[
A(\omega) = \frac{4\pi\omega}{n c h V_0} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \sum_{j} e^{-F_0(T; v_i, v_f)} e^{-F(t; t; v_i, v_f)} \langle v_i | \mu(t) | v_f \rangle \langle v_f | \mu | v_i \rangle \rangle_{vT},
\quad (4\cdot17)
\]

where
\[
F_0(T; v_i, v_f) = \sum_{j} \langle \eta_{0j}(v_i, v_f)^2[n_j + (1/2)] \rangle_{jT},
\quad (4\cdot18)
\]
\[
F(t; t; v_i, v_f) = (1/2) \sum_{j} \langle \eta_{0j}(v_i, v_f)^2[(n_j+1)e^{i\omega_{ij}t} + n_j e^{-i\omega_{ij}t}] \rangle_{jT}.
\quad (4\cdot19)
\]

In the expansion of the factor \(\exp[F_1(T; t; v_i, v_f)]\),
\[
\exp[F_1(T; t; v_i, v_f)] = 1 + F_1(T; t; v_i, v_f) + [F_1(T; t; v_i, v_f)^2/2!] + \cdots,
\quad (4\cdot20)
\]
the first, the second and the third on the right-hand side are contributions to zero-, one- and two-phonon processes. Generally speaking, one-and multi-phonon processes yield weak side-band effects. Paying attention exclusively to the zero-phonon process and therefore the main absorption line, we get
The result so obtained is characterized by the Debye-Waller factor $\exp[-F_0(T; v_i, v_f)]$.

Up to now, no specification has been made of the quantum number $v$. It may be divided into two parts, one being associated with bound states or vibron-soliton states and the other with continuum or scattering states of vibrons. The former and the latter are denoted by $v_s$ and $v_c$, respectively. Corresponding to this, the absorption coefficient is divided into two parts:

$$A(\omega) = A_s(\omega) + A_c(\omega), \quad (4.22)$$

the first and the second on the right-hand side being considered as corresponding to the soliton absorption line and the vibron absorption line appearing at about 1650 cm$^{-1}$ and 1665 cm$^{-1}$, respectively, in ACN as observed by Careri et al.$^{1,2)}$ Using Eqs. (A.10) $\sim$ (A.12), we obtain

$$\eta_0(v_s; v_s, v_{sf}) \cong \eta_0(v_c; v_c, v_{cf}) \text{ or } F_0(T; v_s, v_{sf}) \gg F_0(T; v_c, v_{cf}), \quad (4.23)$$

since the following relation holds:

$$N^{-1/2}\sum_n \langle v_s | Q_n Q_n^* + Q_n^* Q_n | v_s \rangle \cong N^{-1/2}\langle v_c | Q_n Q_n^* + Q_n^* Q_n | v_c \rangle, \quad (4.24)$$

in view of the fact that the mean square displacement of the A-oscillator system associated with the state $|v_c\rangle$ as defined above is a sum of a large number of oscillatory functions with respect to space variable $n$. It is therefore seen that the temperature-dependence of $A_c(\omega)$ is very weak as compared with that of $A_s(\omega)$. For the evaluation of $F_0(T; v_s, v_{sf})$, we assume the soliton density is so small that their mutual interactions are negligible. Confining ourselves to such a case, we need only to consider a single excited state corresponding to the first excited state of single-soliton states. Collecting together the above-mentioned reasonings, we get approximate expressions for $A_s(\omega)$ and $A_c(\omega)$:

$$A_s(\omega) = \frac{4\pi N_s \omega}{n c h V_0} \int_{-\infty}^{\infty} d\tau e^{-i\omega \tau} \langle \mu_1(t) \mu_1 \rangle_{v_s T} \equiv e^{-F_0(T)} A_s^{(0)}(\omega), \quad (4.25)$$

$$A_c(\omega) = \frac{-4\pi \omega}{n c h V_0} \int_{-\infty}^{\infty} d\tau e^{-i\omega \tau} \langle \mu(t) \mu \rangle_{v_c T}, \quad (4.26)$$

where

$$F_0(T) = \eta^{(s)}_s \sum_j \langle B_j^2 \rangle_{|n_j + (1/2)|} / \omega_j \cong \eta^{(s)}_s B^2 \sum_j \langle \delta_{n_j} \rangle_{|n_j + (1/2)|} / \omega_j = \beta_0 + \beta T^2 \quad \text{for } T \ll \Theta. \quad (4.27)$$

In Eq. (4.25), $N_s$ and $\mu_1$ are the soliton number and an effective dipole moment associated with a single soliton state, respectively. In Eq. (4.27), $\eta^{(s)}_s$ is an abbreviation of $\eta^{(s)}_s(v_s, v_{sf})$ defined by Eq. (A.12). In proceeding from the first to the second of the right-hand side of Eq. (4.27), we have neglected the $j$-dependence of $B_j$, and rewritten it as $B$, since the $j$-dependence of $\epsilon_0(j)$ and $c_j$ in Eq. (A.11) comes principally from $\omega_j$. In arriving at the last equality in Eq. (4.27), we have used the Debye approximation for the frequency spectrum of acoustic phonons, where $\beta_0$ and $\beta$, explicit expressions of which are omitted here, are constants, and $\Theta$ is the Debye temperature of ACN crystal. It is seen
that the soliton absorption line spectrum $A_s(\omega)$ is written as a product of the acoustic-phonon-free soliton absorption line spectrum $A_s^{(0)}(\omega)$ and the Debye-Waller factor. The quantity $A_s^{(0)}(\omega)$ may be taken to be of Lorentzian type:

$$A_s^{(0)}(\omega) = \frac{C \mu_i^2}{\pi} \frac{\gamma_s \omega}{(\omega^2 - \omega_s^2)^2 + \gamma_s^2 \omega^2},$$

(4·28)

where $\omega_s$ is the eigenfrequency of the vibron soliton given as a solution to Eqs. (3·17) and (3·18). The quantities $\gamma_s$ and $C$ are a natural width of the single-soliton absorption line and an unimportant constant factor, respectively. Since the vibron soliton energy is much higher than those of acoustic phonons, no temperature dependence actually exists for $A_s^{(0)}(\omega)$ within the framework of the approximation procedure employed above. It is also seen that the temperature-dependence of the vibron absorption line, if any, is very different from that of the vibron soliton absorption line due to the absence of the Debye-Waller factor for $A_s(\omega)$ as seen from Eq. (4·26). If we identify $A_s(\omega)$ and $A_c(\omega)$ given by Eqs. (4·25) with Eqs. (4·27) and (4·26), respectively, as the absorption spectra at about 1650 cm$^{-1}$ and at about 1665 cm$^{-1}$, respectively, of crystalline ACN observed by Careri et al.,2) the result obtained here seems to account for the experimental results of these workers at least in a semi-quantitative manner.

We close this section by giving the remark that the temperature dependence of the vibron absorption line at about 1650 cm$^{-1}$ is similar to the case of localized or resonant harmonic phonon modes due to impurities in alkali halide crystals,6) where the impurity-induced infrared absorption spectra have a characteristic temperature-dependence of the form $\exp(-\beta T^2/\beta = \text{const})$ at low temperatures. Although the mechanism of the appearance of localized modes is different in these two cases, the Debye-Waller factor arises from one and the same origin that the localized modes undergo random thermal modulations by low-frequency acoustic phonons.

§ 5. Concluding remarks

A red-shifted absorption band at about 1650 cm$^{-1}$ from the main amide I absorption band at about 1665 cm$^{-1}$ in ACN appears to be another example of the existence on microscopic level of solitons in solid state physics as shown by Careri et al.1),2) These workers also studied, both analytically and numerically, model dynamical systems to understand the soliton-associated vibrational properties of ACN. Alexander exploited a small-polaron analog of solitons to understand the temperature-dependence of soliton-induced absorption spectrum.7) In all these works the Davydov Hamiltonian originally employed to study solitons in $\alpha$ helical proteins6) was employed. In this paper, a vibron soliton theory developed in (I) is applied to account for the experimental results by Careri et al.4) as a test of the theory. In short, a vibron soliton is a nonlinearity-induced localized mode of optical phonons or vibrons, while the Davydov soliton is the corresponding exciton mode with transfer by exchange interactions. Except the notional difference of the vibron soliton from the Davydov soliton, which was discussed in some detail in (I),4) the result obtained here is different from those of Careri et al.1),2) and of Alexander7) in the following important respects: (1) By the use of a lattice Green's function method to treat a nonlinear eigenvalue problem, we have shown analytically that a vibron soliton in ACN is localized predominantly at a single amide-I-oscillator site. (2) The obtained result for
the binding energy of a stationary soliton, which contains no adjustable parameter, is in good agreement with the experimental data. (3) Random thermal modulations of the vibron soliton by its interactions with acoustic phonons yield the Debye-Waller factor in the zero-phonon soliton line spectrum which can account for the temperature-dependence of the absorption coefficient. The properties of the eigenfrequencies and the absorption coefficient of vibron solitons in ACN have several things in common with those of localized phonon modes due to impurities in, for example, alkali halides, though the origin of the occurrence of localized modes are different.

Another point worth mentioning before closing this section is that the experimental finding by Careri et al. shows that one should make a more serious search for solitons in α helical proteins and related biopolymers. Solitons of metabolic importance, if any, would be high-temperature solitons sustained by some sort of coherence in highly nonlinear systems. Davyrov-like or vibron solitons in ACN, which are a kind of non-topological solitons, do not appear robust enough to preserve their integrity at room temperature.

Appendix

— Interactions of the A-Oscillator System with Acoustic Phonons —

Let \( v_{na} \) be the \( \alpha \)-component of the displacement vector \( v_n \) from the equilibrium position \( R_n \) of an \( n \)th molecule participating in acoustic-type lattice vibrations in interaction with the A-oscillator system in ACN. Since we are primarily concerned with low frequency phonons, we assume without loss of generality that a set of such molecules constitute a Bravais lattice composed of \( N \) lattice points. We take the interaction Hamiltonian \( H' \) to be of a three-dimensional version of vibron-acoustic phonon interactions discussed in (I) (see also Ref. 4)):

\[
H' = \sum_{n} \sum_{l} \sum_{a} (A_{la} / 2) q_n^2 (v_{n+l,a} - v_{n-l,a}) ,
\]

(A·1)

where \( A_{la} \) is an interaction constant, in which the index \( l \) stands for the range of the oscillator-phonon interactions. In terms of normal coordinates \( Q_{k\eta} \) defined by

\[
v_{na} = N^{-1/2} \sum_{k\eta} e_a(k\eta) Q_{k\eta} \exp(i k \cdot R_n) ,
\]

\[
Q_{k\eta}^* = Q_{-k\eta} ,
\]

\[
e^* (k, \eta) = e(-k, \eta) = e(k, \eta) ,
\]

(A·2)

Eq. (A·1) is rewritten as

\[
H' = i N^{-1/2} \sum_{k\eta} \sum_{n} \sum_{a} A_{la} q_n^2 e_a(k, \eta) \exp(i k \cdot R_n) \sin(k \cdot R_l) Q_{k\eta} ,
\]

(A·3)

where \( e_a(k\eta) \) is the \( \alpha \) component of the polarization vector \( e(k, \eta) \) associated with wave vector \( k \) and branch \( \eta \) (\( \eta = 1, 2, 3 \); two transverse and one longitudinal). In accordance with the use of the rotating-wave approximation, we replace the factor \( q_n^2 \) in Eq. (A·3) by \( Q_n Q_n^* + Q_{-n}^* Q_{-n} \), where \( Q_n \) and \( Q_{-n}^* \) are defined by Eq. (3·1). We also introduce real normal coordinates \( Q_{1k\eta} \) and \( Q_{2k\eta} \) by the relation

\[
Q_{k\eta} = 2^{-1/2} (Q_{1k\eta} + i Q_{2k\eta}) ,
\]

\[
Q_{1,-k\eta} = Q_{1k\eta} ,
\]

\[
Q_{2,-k\eta} = - Q_{2k\eta} .
\]

(A·4)

The index \( j \) in Eqs. (4·1) and (4·2) is therefore composed of three indices:
\[ j = (r, k, \eta), \quad r = 1, 2; \quad k \geq 0; \quad \eta = 1, 2, 3. \]  
\hspace{1cm} (A \cdot 5)

Inserting Eq. (A \cdot 4) into Eq. (A \cdot 3) and taking the matrix element of \( H' \) with respect to \( | v \rangle \), we get

\[ \chi_j(v) = -2^{1/2} \sum_l \sum_a A_{la} e_a(j) \lambda_j(v) \sin(k \cdot R_l) \]  
\hspace{1cm} (A \cdot 6)

with

\[ \lambda_{1 \eta \phi}(v) \equiv \lambda_j(v) = N^{-1/2} \sum_n \sin(k \cdot R_n) \langle v | Q_n Q_n^* + Q_n^* Q_n | v \rangle, \]  
\hspace{1cm} (A \cdot 7)

\[ \lambda_{2 \eta \phi}(v) \equiv \lambda_j(v) = N^{-1/2} \sum_n \cos(k \cdot R_n) \langle v | Q_n Q_n^* + Q_n^* Q_n | v \rangle. \]  
\hspace{1cm} (A \cdot 8)

An explicit expression for \( \eta_0(v_i, v_f) \) defined by Eq. (4 \cdot 15) is therefore written as

\[ \eta_0(v_i, v_f) = 2^{1/2} \sum_l A_{la} e_a(j) \sin(k \cdot R_l)[(\hbar/m \omega_j)^{1/2} / \hbar \omega_j][\lambda_j(v_i) - \lambda_j(v_f)]. \]  
\hspace{1cm} (A \cdot 9)

For long wavelength phonons, this is separated into two factors

\[ \eta_0(v_i, v_f) \simeq \eta^{(1)}_0(v_i, v_f) \eta^{(2)}_0(v_i, v_f) \]  
\hspace{1cm} (A \cdot 10)

with

\[ \eta^{(1)}_0(v_i, v_f) \simeq 2^{1/2} \sum_l A_{la} e_a(j) (R_l / c_j)(\hbar m)^{-1/2} \omega_j^{-1/2} \equiv B_j \omega_j^{-1/2}, \]  
\hspace{1cm} (A \cdot 11)

\[ \eta^{(2)}_0(v_i, v_f) \simeq N^{-1/2} \sum_n \{ \langle v_i | Q_n Q_n^* + Q_n^* Q_n | v_i \rangle - \langle v_f | Q_n Q_n^* + Q_n^* Q_n | v_f \rangle \}, \]  
\hspace{1cm} (A \cdot 12)

the former and the latter being associated entirely with the phonon system and the A-oscillator system, respectively. In obtaining the above result, we have put

\[ \omega_j = c_j k, \]  
\hspace{1cm} (A \cdot 13)

where \( c_j \) is the velocity of the \( j \)th phonon mode, and neglected terms containing \( k^3 \) and higher order terms.

References


4) For a review of solitons in solid state physics, see, for example, K. Maki, Solitons in One Dimensional Systems, in Electronic Properties of Inorganic Quasi-One Dimensional Compounds, ed. P. Monceau, Physics and Chemistry of Materials with Low Dimensional Structures, Series B; Quasi-One Dimensional Structure (D. Reidel Publishing Company, 1985), and also references cited therein.


6) A. S. Davydov, Biology and Quantum Mechanics (Pergamon Press, New York, 1982), chap. VII.

