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# NONLINEARLY VIBRATIONAL ENERGY-SPECTRA OF MOLECULAR CRYSTALS*

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The nonlinear quantum vibrational energy spectra of amide-I in the molecular crystals acetanilide are calculated by using the discrete nonlinear Schrödinger equation appropriate to this kind of crystals. The numerical results obtained by this method are in good agreement with the experimental values. Meanwhile, the energy levels at high excited states have also been obtained for the acetanilide, which is helpful in researching the Raman scattering and infrared absorption properties of the this kind of crystals.

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Recently, scientists have always been interested in the nonlinear properties of the organic molecular crystals, for example, acetanilide $(CH_3COHNC_6H_5)_x$, or ACN.[1−13] In ACN two close chains of hydrogen-bonded amide-I groups run through the crystal. The space group is $D_{2h}^{15}$ (Pbca) and the unit cell or factor group is $D_{2h}$ for this kind of crystals. There are eight molecules in a unit cell and at the amide-I frequency each of them has one degree of freedom. Thus there are three infrared-active modes ($B_{1u}$, $B_{2u}$, and $B_{3u}$), four Raman-active modes ($A_g$, $B_{1g}$, $B_{2g}$, and $B_{3g}$), and one inactive mode ($A_u$). However, at low frequencies ($<200\,\mathrm{cm}^{-1}$), each molecule exhibits six degrees of freedom (three of translation and three of rotation), thus there are a total of 48 low-frequency modes [24 Raman active modes ($6A_g + 6B_{1g} + 6B_{2g} + 6B_{3g}$), 18 infrared-active modes ($6B_{1u} + 6B_{2u} + 6B_{3u}$) and six ($A_u$) modes] corresponding to the acoustic modes of translation and rotation. All of these active modes are seen in infrared absorption and Raman scattering experiments.[1−5] The ACN is an interesting system because the nearly-planar amide-I group displays bond distances which are close to those found in polypeptides. Since the physical properties of such a hydrogen-bonded amide-I system are very sensitive to bond distances, therefore the study of ACN exhibits some new phenomena,[1−5] for example, in the experiments of infrared absorption and Raman scattering, when the crystalline acetanilide is cooled down below room temperature from 320 to 10 K, a new amide-I band occurs with a red shift from the main peak, $1666\,\mathrm{cm}^{-1}$, by about $16\,\mathrm{cm}^{-1}$. The intensity of this new band steadily increases from room temperature to 70 K. The band at $1650\,\mathrm{cm}^{-1}$ is not present in the amorphous materials or ACN methylated at the position where the hydrogen-bonded distances occur, but after annealing it is fully recovered. In Raman spectra of the ACN we can also observe some similar phenomena as the above.[1−3,7,8]

As is well known, the characteristic feature of the amide-I group CONH in polypeptides is the amide-I mode, mainly involving C═O stretching. This mode is observed as an infrared absorption peak at about $1666\,\mathrm{cm}^{-1}$ in the ACN and near that value in a wide variety of materials including the amide-I groups. The corresponding spectroscopic evidence of the new band presented and the detailed measurements of the crystal structure and specific heat as a function of temperature[1−3] preclude an assignment of the new band to: 1) a conventional amide-I mode, 2) crystal defect states, 3) Fermi resonance, and 4) frozen kinetics between two different subsystems. A correct idea is to assign to a self-trapping of amide-I vibrational energy[1−5] on the basis of the following experimental facts: 1) $^{15}N$ substitution which induces a small shift on the amide-I at $1666\,\mathrm{cm}^{-1}$ also shifts the new band by the same amount. 2) Deuterium substitution at the NH position strongly affects both the amide-I and the new band in a complicated way. 3) Upon cooling a parallel decrease of the normal amide-I integrated

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absorption and increase of the 1650 $cm^{-1}$ band integrated absorption is observed. 4) The 1650 $cm^{-1}$ band and the amide-I band show the same dichroism over the temperature range integrated. 5) The measurements of specific heat, the dielectric constant and the volume expansion as functions of temperature rule out the occurrence of rotational isomerism or of a polymorphic transition which would affect some other infrared and Raman absorption bands, but not affect the new band. The self-trapping mechanism of amide-I vibrational energy proposed by Scott et al.[1−5] comes from the Davydov model of vibration energy transport in alpha-helix protein.[7,8] They have given a good account of the properties of the first excited states in this model. Scott et al.[4] and Alexander et al.[6] and Pang[12] have also obtained the exponential dependence of the absorption intensity on the temperature, $\exp(-\beta T^2)$, and explained the changes of intensity of the new band with decreasing temperature observed in the experiments[1−6] in terms of the above model.

Inspection of the acelanilide structure reveals two channels of hydrogen-bonded peptide groups approximately in the longitudinal direction with the sequence: ···H—N—C═O···H—N—C═O···H—N—C═O···. The dotted lines indicated the hydrogen-bond. For a detailed analysis it is necessary to consider the two chains and their interaction. First of all, we here will only consider one of them, since it suffices to convey the basic idea. The Hamiltonian of the systems proposed by Scott et al. used to describe the situation is[7,8]

$$H = H_{\rm v} + H_{\rm p} + H_{\rm int} = \sum_n [\varepsilon_0 \hat{B}_n^+ \hat{B}_n + J(\hat{B}_{n+1}^+ \hat{B}_n + \hat{B}_n^+ \hat{B}_{n+1})] + \sum_n \left[\frac{P_n^2}{2M} + \frac{1}{2}\beta(u_{n+1} - u_n)^2\right] + \chi \sum_n (u_{n+1} - u_{n-1}) \hat{B}_n^+ \hat{B}_n, \quad (1)$$

where $\hat{B}_n^+(\hat{B}_n)$ is the boson creation (annihilation) operator of quantum of intramolecular vibrations with energy $\varepsilon_0 = 1666\,{\rm cm}^{-1}$ at site $n$ (C═O stretch mode or amide-I), $u_n$ and $P_n$ are the molecular displacement and momentum operators for the peptide at site $n$, $M$ and $\beta$ are molecular mass and force constant of molecular chains respectively; $J = 4.0\,{\rm cm}^{-1}$ is the intersite transfer energy produced by dipole-dipole interactions. The nonlinear coupling constant $\chi = \dfrac{{\rm d}\varepsilon_0}{{\rm d}l}$ arises from the modulation of on-site energy by the molecular displacement. The vibrational part $H_{\rm v}$ and the phonon part $H_{\rm p}$ and the interaction part $H_{\rm int}$ are defined as the individual terms in Eq.(1). From then on, much work has been done on the Davydov model and related models.[2,4] A new Hamiltonian was also proposed to improve the above models[9−13] and better results were gained which are consistent with the experimental data.[1−4]

The Hamiltonian (1) is, by construction, quantum-mechanical; Davydov analysis is based on the coherent state ansatz and is therefore as "classical" as a quantum-mechanical treatment can be. An alternative approach would be started from purely classical equations, and subsequently do semi-classical or Bohr-Sommerfeld quantization. This has been done by Scott et al.[14−18] and the present authors.[19,20] The advantage of this method is that it allows for an arbitrary number of amide-I quanta.

The starting point is to define the classically normal amide-I displacement and momentum coordinates $Q_n$ and $P_n$, for which the Hamiltonian is $\sum_n (P_n^2 + Q_n^2)$. The motion can then be described in terms of the complex mode amplitude $A_n \equiv \omega_0^{1/2}(P_n - {\rm i}Q_n)$. In terms of $A_n$ the classical analogue of $H_{\rm v}$ in Eq.(1) becomes

$$H_{\rm v\text{-}clas} = \sum_n [\omega_0 |A_n|^2 - J(A_{n+1}^* A_n + A_n^* A_{n+1})], \quad (2)$$

where $\omega_0$ is the amide-I harmonic vibrational frequency. It is then assumed that the amide-I mode interacts with some (unspecified) low-frequency mode $q_n$, with adiabatic energy $H_{\rm p\text{-}clas} = \dfrac{1}{2}\beta_{\rm clas} \sum_n q_n^2$. The interaction energy is taken to be $H_{\rm int\text{-}clas} = \chi_{\rm clas} \sum_n q_n |A_n|^2$. The total classical Hamiltonian is then given by

$$H_{\rm clas} = H_{\rm v\text{-}clas} + H_{\rm p\text{-}clas} + H_{\rm int\text{-}clas}. \quad (3)$$

Minimising Eq.(3) with respect to $q_n$ yields $q_n = -\dfrac{\chi_{\rm clas}}{\beta_{\rm clas}} |A_n|^2$. Thus Eq.(3) reduces to

$$H_{\rm clas} = \sum_n \left[\omega_0 |A_n|^2 - J(A_{n+1}^* A_n + A_n^* A_{n+1}) - \frac{1}{2}\gamma |A_n|^4\right], \quad (4)$$

where $\gamma = \chi^2_{\rm clas}/\beta_{\rm clas}$ is a nonlinear interaction constant. The equation of motion corresponding to Eq.(4) is

$$\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - \omega_0\right)A_n + J(A_{n+1} + A_{n-1}) + \gamma|A_n|^2 = 0. \quad (5)$$

In addition to the energy $H_{\rm clas}$, Eq.(5) has another constant of motion, i.e., the number

$$N = \sum_n |A_n|^2. \quad (6)$$

Eguation (5) is just the discrete nonlinear Schrödinger or self-trapping dynamic (DSTD) equation for one-chain molecule. Thus vibrations of the acetanilide are a nonlinear problem from the above result.

Upon quantization,[5−8] the complex mode amplitudes are replaced by harmonic oscillator creation (annihilation) operator $\hat{B}^+_n(\hat{B}_n)$ with the properties: $\hat{B}^+_n|n\rangle = \sqrt{(n+1)}|n+1\rangle$, $\hat{B}_n|n\rangle = \sqrt{n}|n-1\rangle$, and commutator $[\hat{B}_n, \hat{B}^+_m] = \delta_{nm}$. The number expressed by Eq.(6) and the energy by Eq.(4) then become operators

$$\hat{N} = \sum_n \left(\hat{B}^+_n\hat{B}_n + \frac{1}{2}\right), \quad (7)$$

$$\hat{H} = \left(\omega_0 - \frac{1}{2}\gamma\right)\hat{N} - J\sum_n(\hat{B}^+_{n+1}\hat{B}_n + \hat{B}^+_n\hat{B}_{n+1}) - \frac{1}{2}\gamma\sum_n \hat{B}^+_n\hat{B}_n\hat{B}^+_n\hat{B}_n. \quad (8)$$

Practically $J \ll \gamma$ and $J \ll \omega_0$, thus, the dispersion effect with $J$ in one-chain in Eq.(4) is approximately replaced by zero dispersion. If we again have in mind that the acetanilide is composed of two chains, then, the DSTD equation of the acetanilide becomes

$$\sum_{\alpha=1}^{2}\left[\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - \omega_0\right)A_{\alpha,n} + \gamma|A_{\alpha,n}|^2A_{\alpha,n} - \varepsilon(A_{\alpha+1,n} + A_{\alpha-1,n})\right] = 0. \quad (9)$$

The general form of the DSTD equation is

$$\left(\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t} - \omega_0\right)A + MA + \gamma D(|A|^2)A = 0, \quad (10)$$

where $A = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$ is a complex 2-vector, $D(|A|^2) = \begin{bmatrix} |A_1|^2 & 0 \\ 0 & |A_2|^2 \end{bmatrix}$ denotes the diagonal matrix, and $M = \begin{bmatrix} 0 & \varepsilon \\ \varepsilon & 0 \end{bmatrix}$ is a real symmetric matrix with interchain interaction $\varepsilon$. Thus Eqs.(7) and (8) becomes

$$\hat{N} = \hat{B}^+_1\hat{B}_1 + \hat{B}^+_2\hat{B}_2 + 1, \quad (11)$$

$$\hat{H} = \left(\omega_0 - \frac{1}{2}\gamma\right)\hat{N} - \frac{1}{2}\gamma\sum_{\alpha=1}^{2}\hat{B}^+_\alpha\hat{B}_\alpha\hat{B}^+_\alpha\hat{B}_\alpha - \varepsilon\sum_{\alpha\neq\beta}^{2}\hat{B}^+_\alpha\hat{B}_\beta, \quad (12)$$

where we take $\hbar = 1$ and assume that both frequencies and energies are measured in the same unit ($\mathrm{cm}^{-1}$).

Choosing now basic function set, $|n,k\rangle = |n_1\rangle|n_2\rangle$, where $n(= n_1 + n_2)$ is the total quantum number, $k = 1, 2, \cdots, d(n)$, and $d(n) = n + 1$ is equal to the number of ways that $n$ particles are distributed in two states. Consider the common eigenfunction, $|\psi_n\rangle$, of both operators. If we take

$$|\psi_n\rangle = C_1|n,1\rangle + C_2|n,2\rangle + \cdots + C_{d(n)}|n,d(n)\rangle, \quad (13)$$

then Hamiltonian equation $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ can reduce to an algebra equation with column vector $\overline{C}_n = \mathrm{col}(C_1, C_2, \cdots, C_{d(n)})$

$$H_n\overline{C}_n = E_n\overline{C}_n, \quad (14)$$

where $H_n$ is a $d(n) \times d(n)$, real, symmetrical matrix with the diagonal elements $E_{\rm rr} = \langle n,r|\hat{H}|n,r\rangle$ and the off-diagonal elements $H_{\rm rs} = \langle n,r|\hat{H}|n,s\rangle$, where $1 \le r \le d(n)$, $1 \le s \le d(n)$, and $r \neq s$.

Employing the above formulae, we can easily calculate numerically the quantum vibrational energy levels of acetanilide using the generally accepted experimental data of the physical parameters, which are $\beta = (9.6-26)\mathrm{N/m}$, $M = (3.52-4.50)\times10^{-25}\,\mathrm{kg}$, $\chi = (56-62)\mathrm{PN}$, $J = (3.5-4)\mathrm{cm}^{-1}$, $r_0 = (0.2-0.5)\mathrm{nm}$, $\varepsilon_0$=1666 $\mathrm{cm}^{-1}$, $\varepsilon$=11.70 $\mathrm{cm}^{-1}$, for two-channel model of acetanilide. The parameter values needed in our calculations are $\omega^1_0 = 1669.8$, $\varepsilon^1 = 11.7\,\mathrm{cm}^{-1}$, $\gamma^1 = 31.5\,\mathrm{cm}^{-1}$, and $\omega^2_0 = 1673.1\,\mathrm{cm}^{-1}$, $\varepsilon^2 = 11.7\,\mathrm{cm}^{-1}$, $\gamma^2 = 34.8\,\mathrm{cm}^{-1}$, which are obtained from the above formulae and the experimental data. Our calculated results of quantum vibrational energy levels together with the experimental data[1−10] are listed in Table 1.

It is a major advantage of the above method that it allows for treatment of more than one amide-I quantum; the validity (in the zero dispersion limit) is directly testable through Eq.(14). It is clear from this table that our calculated values are in good agreement with the experimental data. This shows that

the model introduced here is suitable for the study of the vibrational spectra of the acetanilide with fewer parameters and simpler computational program.

From Table 1, we can easily find that the distributions of vibrational energy spectra of the acetanilide have the following features: 1) The vibrational energy spectra consist of a series of manifolds (i.e., energy levels with a common total vibrational quantum number $n$). As $n$ increases, the distances between energy levels decrease significantly. 2) The vibrational spectra have strong local-mode pattern since $\gamma$ is much greater than $\varepsilon$. 3) The local-mode degeneracies of energy levels appear at higher-lying vibrational states, beginning to occur at $n = 6$.

These results are useful for us not only to understand the properties of distribution of energy levels and of infrared absorption and Raman scattering of acetanilide molecules, but also for studying the quantum chaotic effect of higher energy state in acetanilide molecular system. This work is going to do in the near future.

**Table 1.** quantum vibrational energy levels (in $cm^{-1}$) of the acetanilide.

| $n$ | Exp.[a] | Cal.(1)[b] | Cal.(2)[c] | $n$ | Exp.[a] | Cal.(1)[b] | Cal.(2)[c] |
|---|---|---|---|---|---|---|---|
| 1 | — | 1626.6 | 1626.6 | 7 | | 10801.5 | 10732.7 |
| | 1650 | 1650.0 | 1650.0 | | | 10801.5 | 10732.7 |
| 2 | — | 3232.6 | 3230.6 | | | 10987.3 | 10938.7 |
| | 3251.0 | 3245.1 | 3241.8 | | | 10987.8 | 10939.0 |
| | 3282.0 | 3289.1 | 3288.4 | | | 11093.1 | 11058.7 |
| 3 | 4808.0 | 4811.9 | 4802.9 | | | 11117.4 | 11080.8 |
| | — | 4815.9 | 4806.3 | | | 11179.7 | 11146.7 |
| | 4866.0 | 4868.5 | 4864.3 | | | 11248.5 | 11217.9 |
| | — | 4911.3 | 4907.7 | 8 | | 12219.4 | 12127.5 |
| 4 | 6308 | 6358.0 | 6338.8 | | | 12219.4 | 12127.5 |
| | — | 6358.7 | 6339.4 | | | 12437.6 | 12369.0 |
| | 6410 | 6436.0 | 6426.4 | | | 12437.6 | 12369.1 |
| | — | 6464.2 | 6453.8 | | | 12583.8 | 12533.2 |
| | — | 6519.1 | 6511.3 | | | 12592.2 | 12539.9 |
| 5 | | 7871.0 | 7838.5 | | | 12662.3 | 12617.8 |
| | | 7871.1 | 7838.6 | | | 12719.3 | 12674.8 |
| | | 7984.8 | 7966.6 | | | 12793.8 | 12752.5 |
| | | 7997.5 | 7977.8 | 9 | | 13605.8 | 13487.5 |
| | | 8053.6 | 8038.2 | | | 13605.8 | 13487.5 |
| | | 8111.0 | 8097.2 | | | 13856.0 | 13764.2 |
| 6 | | 9352.1 | 9303.1 | | | 13856.0 | 13764.2 |
| | | 9352.1 | 9303.1 | | | 14039.8 | 13968.2 |
| | | 9503.7 | 9472.0 | | | 14041.0 | 13969.3 |
| | | 9506.9 | 9474.5 | | | 14138.7 | 14080.9 |
| | | 9578.9 | 9555.5 | | | 14175.7 | 14115.4 |
| | | 9622.4 | 9598.2 | | | 14245.2 | 14188.2 |
| | | 9687.6 | 9666.3 | | | 14323.5 | 14269.7 |

(a) From the compilation of Refs.[1,8–11]. (b) Results obtained from $\omega_0^1$, $\varepsilon$ and $\gamma^1$. (c) Results obtained from $\omega_0^2$, $\varepsilon$ and $\gamma^2$.

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