Critical anomalies of vibrational line shape at order-disorder phase transitions

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We study the critical behavior of the line-shape parameters for stretching excitations in dipolar molecular solids. A theoretical model based on coupled anharmonic oscillators is used, with the assumption of two discrete orientations of the associated dipole moments. At the phase transition from a disordered into an antiferroelectric or ferroelectric dipolar configuration, the line shape is predicted to exhibit inflection-point anomalies with divergent temperature derivatives and universal ratios of the critical amplitudes.

I. INTRODUCTION

The problem of anomalous thermal broadening of vibrational spectra near an order-disorder phase transition in molecular solids has recently arisen in connection with optical investigations of alkali cyanide crystals.[1-4] Typically, one is looking at the high-frequency stretching vibrations of the CN^- molecular ions which are spread into a narrow vibrational band under the action of intermolecular forces. In the orthorhombic paraelectric phase, the ionic electric dipole moments are randomly oriented either parallel or antiparallel to a crystal axis. At lower temperatures, the dipolar subsystem undergoes an order-disorder continuous phase transition (the transition temperature T_c is 89 K in KCN and 172 K in NaCN) into an antiferroelectric[5] or ferroelectric[6] configuration. Due to the anharmonicity of the vibrational potential, the critical fluctuations of the dipolar electric fields can be expected to perturb the stretching frequency, and may thus affect the line shape of the excitation spectrum.

The purpose of this Brief Report is (a) to present a theoretical model of coupled vibrational excitations based on the physical picture outlined above, and (b) to predict the type of critical anomalies occurring in the vibrational response using the theory of critical phenomena. We will focus on the one-photon–one-vibrational-exciton (ground to nth excited state) processes, ignoring the librational and translational degrees of freedom, which do play an important role in the assignment of mode symmetries in optical spectroscopy, but are irrelevant to the present problem.

II. MODEL SYSTEM

We consider N coupled anharmonic oscillators on a periodic Bravais lattice, $R_i = 1, 2, \ldots, N$. The electric dipole moment of the ith oscillator P_i is allowed two discrete orientations, which are described by a pseudospin $S_i^z \equiv S_i = \pm 1$. Denoting by x_i the stretching coordinates and by p_i the conjugate momenta, we write the vibrational Hamiltonian

$$\mathcal{H}_{\text{vib}} = \frac{1}{2} \sum_i (p_i^2 + \omega_0^2 x_i^2 - 2cx_i^3) + \frac{1}{2} \sum_i \sum_{j\,(\neq i)} \Phi_{ij} x_i x_j \ , \quad (1)$$

where ω_0 is the stretching frequency, c the cubic anharmoni-

city parameter, and Φ_{ij} a short-range interoscillator coupling.

The dipolar interaction energy is given by

$$\mathcal{H}_{\text{dip}} = -\frac{1}{2} \sum_i \sum_{j\,(\neq i)} P_i P_j f(R_{ij}) S_i S_j \ , \quad (2)$$

where $P_i = P(x_i)$ is the magnitude of the ith dipole moment, and $f(R_{ij})$ with $R_{ij} = |R_i - R_j|$ represents the radial dependence of the long-range dipole-dipole coupling. Assuming a linear relation between the dipole moment and x_i, say, $P(x_i) = P_0 + (dP/dx)_0 x_i$, and introducing $J_{ij} \equiv P_0^2(R_{ij})$, Eq. (2) becomes

$$\mathcal{H}_{\text{dip}} = \mathcal{H}_S - \lambda \sum_{i,j} J_{ij} S_i S_j x_i - \frac{1}{2}\lambda^2 \sum_{i,j} J_{ij} S_i S_j x_i x_j \ . \quad (3)$$

Here

$$\mathcal{H}_S = -\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j$$

is a rigid Ising Hamiltonian, and the last two terms represent a vibrational-orientational coupling. The parameter $\lambda = (dP/dx)_0/P_0$ is of the order of inverse equilibrium oscillator length.

Compared with the stretching vibrations, dipolar reorientation is an extremely slow process.[7,8] Therefore the second term in (3) can be viewed as the potential energy in a static force field $F_i = \lambda \sum_j J_{ij} S_i S_j$. Since the frequency of small-amplitude anharmonic oscillations is a linear function of the applied field, cubic anharmonicity provides a mechanism by which dipolar fields affect the vibrational frequency.

Ignoring for the moment the interoscillator coupling, we obtain by using elementary second-order perturbation theory the perturbed energy of the nth oscillator level in a field F_i:

$$E_n(F_i) = (n + \tfrac{1}{2})\hbar\omega_0 - \tfrac{15}{4}(c\hbar/\omega_0^2)^2[(n+\tfrac{1}{2})^2 + \tfrac{7}{60}]$$
$$- 3(n + \tfrac{1}{2})(c\hbar/\omega_0^3)F_i \ . \quad (4)$$

An optical transition involves the energy difference between the perturbed nth and ground level. Defining an optical transition frequency

$$\omega_n(i) \equiv [E_n(F_i) - E_0(F_i)]/\hbar \ ,$$

we find

$$\omega_n(i) = \omega_n - (3\lambda cn/\omega_0^3) \sum_k J_{ij} S_i S_k \ , \quad (5)$$

with

$$\omega_n = n\omega_0 - \tfrac{15}{4}n(n+1)(c^2\hbar/\omega_0^4) \ .$$

The last term in (5) plays the role of a random frequency shift due to dipolar orientations.

Since we focus on optical transitions which involve a single vibrational excitation with energy $\hbar\omega_n(i)$, we can treat them in terms of excitons within the single-phonon approximation.[9] Writing

$$x_i = \sum_n (M_{n0}B_{in}^\dagger + M_{0n}B_{in})$$

and introducing a new interoscillator coupling $\tilde{\Phi}_{ij} \equiv \Phi_{ij} - \lambda^2 J_{ij}S_iS_j$, we obtain a quasiharmonic effective Hamiltonian

$$\mathscr{H}_{\text{eff}} = \sum_{i,n} \hbar\omega_n(i)B_{in}^\dagger B_{in} + |M_{n0}|^2 \sum_{i,j,n} \tilde{\Phi}_{ij}B_{in}^\dagger B_{jn} - \tfrac{1}{2}\sum_{i,j}J_{ij}S_iS_j \ ,$$

(6)

where $M_{n0} = \langle n,i|x_i|0,i\rangle$ is the matrix element for a transition between the perturbed ground and nth excited state of the ith oscillator, and $B_{in}^\dagger$ and B_{in} denote exciton creation and annihilation operators, respectively, which satisfy the usual boson commutation relations. The value of M_{n0} is $M_{10} = (\hbar/2\omega_0)^{1/2} + O(c)$ for $n=1$, and $M_{n0} = O(c)$ for $n>1$. By assumption, the contributions due to nonlocal $i \neq j$ terms are much smaller than the anharmonic part, thus M_{n0} is site independent.

Although the detailed shape of J_{ij} will not be essential, it should be noted that the Fourier transform J_q has a maximum at some point $q_0 = Q/2$, where Q is a reciprocal-lattice vector. The choice $Q=0$ then corresponds to a ferroelectric, and $Q \neq 0$ to an antiferroelectric dipolar arrangement in the ordered phase, respectively. In view of its long-range character, J_q has a strong directional anisotropy near $q=0$.[10] In a ferroelectric, the point $q=0$ coincides with the maximum of J_q, and thus the anisotropy has a strong influence on the critical behavior.

III. VIBRATIONAL RESPONSE AND MOMENTS

A periodic external force $F_j^{\text{ext}}e^{i\omega\tau}$ applied to the jth oscillator induces time-dependent vibrations $x_i(\tau)$ in the system. The vibrational spectral function is defined as

$$\chi(\omega) = (2N\hbar)^{-1}\int_{-\infty}^{+\infty} d\tau\, e^{i\omega\tau}\sum_{i,j}\langle x_i(\tau)x_j(0)\rangle \ , \qquad (7)$$

where $\langle\ \rangle$ means a canonical average with respect to the Hamiltonian (6). The function (7) is simply related to the cross section for first-order Raman scattering.

Using the relation

$$x_i(\tau) = \sum_n [M_{n0}B_{in}^\dagger(\tau) + M_{0n}B_{in}(\tau)]$$

and the equations of motion for the exciton operators, we can rewrite Eq. (7) in the form

$$\chi(\omega) = -\sum_n a_n \operatorname{Im} G_n(z) \ , \qquad (8)$$

where $z = \omega^2 - \omega_n^2 + i\epsilon$ and $a_n = 2\omega_n|M_{n0}|^2/\hbar$, while $G_n(z)$ represents the vibrational response due to the nth harmonic process, i.e., one involving a transition between the ground

and nth excited vibrational states. One has for Stokes scattering ($\hbar\omega_n \gg k_BT$)

$$G_n(z) = N^{-1}\sum_{i,j}\langle[(z\underline{I} - \underline{V} - a_n\tilde{\underline{\Phi}})^{-1}]_{ij}\rangle \ . \qquad (9)$$

We denote by $\tilde{\underline{\Phi}}$ an off-diagonal matrix with elements $\tilde{\Phi}_{ij}$, by $\underline{I}$ the unit matrix, and by $\underline{V}$ the diagonal matrix

$$V_{ij} = -\delta_{ij}(6\lambda cn\omega_n/\omega_0^3)\sum_k J_{ik}S_iS_k \ .$$

Notice that $a_1 = 1 + O(c)$, while $a_{n>1} = O(c^2)$.

The line shape of the vibrational spectrum (8) will be investigated by evaluating the frequency moments of $G_n(z)$. The Mth moment is defined as

$$\mu_M = -\pi^{-1}\int_{-\infty}^{+\infty}dz'\, z'^M \operatorname{Im} G_n(z'+i\epsilon) \ , \qquad (10)$$

where the integration is along the real axis. From (9) follows

$$\mu_M = N^{-1}\sum_{i,j}\langle\{[\underline{V} + a_n(\tilde{\underline{\Phi}} - \lambda^2\underline{SJS})]^M\}_{ij}\rangle \ , \qquad (11)$$

where S is a diagonal matrix $S_{ik} = \delta_{ik}S_i$. Thus we obtain for the vibrational frequency shift $\Delta = \mu_1$

$$\Delta = a_n\Phi_0 - \lambda(\lambda a_n + b_n)N^{-2}\sum_q J_{-q}C_q \ , \qquad (12a)$$

and the vibrational linewidth Γ, defined by $\Gamma^2 \equiv \mu_2 - \mu_1^2$,

$$\Gamma^2 = \lambda^2(\lambda a_n + b_n)^2\left[N^{-2}\sum_q |J_q|^2 C_q - \left(N^{-2}\sum_q J_{-q}C_q\right)^2\right] \ . \qquad (12b)$$

Here $b_n = 6cn\omega_n/\omega_0^3$, and $C_q \equiv \langle S_qS_{-q}\rangle$ represents the pseudospin two-point correlation function. It should be noted that the results (12) have been obtained without the use of approximations, and are formally exact for $\hbar\omega_0 \gg k_BT$. In the same limit, the correlation functions are determined solely by the Ising Hamiltonian $\mathscr{H}_S$.

IV. CRITICAL BEHAVIOR OF Δ AND Γ

Let us consider the quantities

$$\tfrac{1}{2}N^{-2}\sum_q J_{-q}\langle S_qS_{-q}\rangle \equiv -U \ ; \qquad (13a)$$

$$\tfrac{1}{2}N^{-2}\sum_q |J_q|^2\langle S_qS_{-q}\rangle \equiv W \ , \qquad (13b)$$

which appear in Eqs. (12). Obviously, U is equal to the internal energy per dipole, namely,

$$U = -\tfrac{1}{2}N^{-1}\sum_{i,j}J_{ij}\langle S_iS_j\rangle = N^{-1}\langle\mathscr{H}_S\rangle \ , \qquad (14)$$

which is further related to the free energy $\mathscr{F} = -N^{-1}\ln Z$, where Z is the dipolar Ising partition function, via the thermodynamic identity $U = \partial\mathscr{F}/\partial\beta$, with $\beta \equiv 1/k_BT$. Thus

$$U_{\text{crit}} \cong -\beta^{-1}\partial\mathscr{F}/\partial t \ , \qquad (15)$$

where $t = (T-T_c)/T_c$ is the reduced temperature. This relation applies in the critical region, i.e., for $|t| \ll 1$.

To derive a similar relation between W and $\mathscr{F}$, we perform a Hubbard-Stratonovich transformation[11] of the dipolar par-

tition function in terms of continuous spin variables ϕ_i:

$$Z = (2\pi)^{-N/2} D^{-1/2} \left[\prod_j \int_{-\infty}^{+\infty} d\phi_j \right] \exp(-\mathscr{H}[\phi]) \quad ;$$

$$\mathscr{H}[\phi] = \tfrac{1}{2} \sum_{i,j} (\underline{J}^{-1})_{ij} \phi_i \phi_j - \sum_j \ln(2\cosh\phi_j) \quad . \tag{16}$$

Here D is the determinant and $\underline{J}^{-1}$ the inverse of the $N \times N$ matrix $\tilde{J}_{ij} = \beta J_{ij}$. One can easily prove that the spin-correlation functions transform according to the rule $S_i \rightarrow \sum_k (\underline{J}^{-1})_{ik} \phi_k$. Thus Eq. (13b) becomes

$$W = \beta^{-2} \tfrac{1}{2} \sum_q \langle \phi_q \phi_{-q} \rangle = \beta^{-2} \tfrac{1}{2} \langle \phi_i^2 \rangle \quad , \tag{17}$$

where the last average is, of course, i independent. Thus W is related to the composite-operator average $\langle \phi_i^2 \rangle$ of field theory,[12] and its critical part is proportional to first derivative of the free energy,[13] i.e.,

$$W_{\text{crit}} \propto \partial \mathscr{F} / \partial t \quad . \tag{18}$$

Therefore, according to (15) and (18), U and W should exhibit the same critical behavior.

For Ising systems with short-range interactions and spatial dimensionality $d < d^*$, where d^* is the marginal dimensionality ($d^* = 4$ for short-range coupled systems), renormalization-group (RG) approaches suggest that the singular part of the free energy can be written in the scaling form[12,14]

$$\mathscr{F}_{\text{sing}}(t) = |t|^{2-\alpha} F_{\pm}(h/|t|^{\Delta_h}) \quad , \tag{19}$$

where α is the critical exponent for the specific heat, Δ_h is the crossover exponent for the external field h, and $F_{\pm}(x)$ represents the scaling function with $\pm$ referring to $t \gtrless 0$. Adding the regular part of $\mathscr{F}$, one obtains in zero field

$$\mathscr{F} = \tilde{A}_1 t + \tilde{A}_2 t^2 - \tilde{A}_{\pm} |t|^{2-\alpha} \quad . \tag{20}$$

It is essential to include the first of these terms, $\tilde{A}_1 t$, since it contributes a finite amount to $\partial \mathscr{F} / \partial t$ as $t \rightarrow 0$. The second term, which is due to the regular part of the specific heat, can be ignored in our case. The nonuniversal constants $\tilde{A}_1$, $\tilde{A}_2$, and $\tilde{A}_{\pm}$ depend on parameters of the model, and can be, in principle, calculated by the RG approach.[14] It should be mentioned that $\tilde{A}_+/\tilde{A}_- = 0.55$ at $d = 3$, which is a universal ratio.[12]

It has been argued[15,16] that antiferroelectric dipolar systems should exhibit the same critical behavior as short-range coupled systems of the same dimensionality. The reason is that the fluctuations which become critical have q vectors near $q_0 \neq 0$, and hence the dipolar anisotropy at $q = 0$ becomes ineffective. Therefore the critical behavior of the vibrational frequency shift Δ and linewidth Γ for the case of an *antiferroelectric* structure can simply be deduced

from (12), (13), (15), (18), and (20). We find

$$\Delta(t) = \Delta(0) + A_{\pm} t |t|^{-\alpha} \quad , \tag{21a}$$

$$\Gamma(t) = \Gamma(0) - B_{\pm} t |t|^{-\alpha} \quad , \tag{21b}$$

where the indices $+$ and $-$ again refer to $t \rightarrow \pm 0$. The amplitudes have a universal ratio: $A_+/A_- = B_+/B_- = 0.55$.

According to Eqs. (21) the vibrational line-shape parameters exhibit an inflection-point anomaly as $T \rightarrow T_c$. Notice that both Δ and Γ remain finite at T_c, however, their derivatives diverge, e.g., $d\Delta/dT \propto |T - T_c|^{-\alpha}$. Since the specific-heat exponent is usually rather small ($\alpha \cong 0.12$ at $d = 3$), the predicted singularities are rather weak.

A different situation arises when the ordered structure is ferroelectric. It is well known that for $|t| \ll 1$, uniaxial dipolar ferroelectrics and ferromagnets exhibit a quasi-four-dimensional asymptotic critical behavior,[17] i.e., the same as short-range systems at $d = d^* = 4$. RG theories then predict a modified Landau-type form for the free energy with mean-field exponents (e.g., $\alpha = 0$) and logarithmic correction factors:[12,16,17]

$$\mathscr{F} = \bar{A}_1 t + \bar{A}_2 t^2 - \bar{A}_{\pm} t^2 |\ln|t||^{1/3} + O(\ln|\ln|t||) \quad , \tag{22}$$

with a mean-field ratio $\bar{A}_+/\bar{A}_- = 0.25$.

Thus the predicted critical behavior of the vibrational line-shape parameters for *ferroelectric* systems is,[18]

$$\Delta(t) = \Delta(0) + A'_{\pm} t |\ln|t||^{1/3} \quad , \tag{23a}$$

$$\Gamma(t) = \Gamma(0) - B'_{\pm} t |\ln|t||^{1/3} \quad . \tag{23b}$$

The universal amplitude ratios are now $A'_+/A'_- = B'_+/B'_- = 0.25$.

The same type of critical anomalies can be obtained for the infrared-absorption linewidths and frequency shifts.

For $T > T_c$, Eqs. (21) and (23) agree with similar expressions derived by Meissner and Binder[15] and Binder, Meissner, and Mais[16] for the critical behavior of the Debye-Waller factor near structural phase transitions. Below T_c, however, their results differ in view of an extra contribution due to the order parameter, which is absent in the present case.

In conclusion, it should be stated that the results (21) and (23) apply to any transition between the ground and nth excited vibrational state. In particular, the critical exponents are n independent, whereas the amplitudes $A_{\pm}$, etc., and the limiting values $\Delta(0)$ and $\Gamma(0)$, as well as the spectral intensities a_n [cf. Eqs. (8) and (12)], are generally n dependent. A novel feature is the predicted amplitude ratios, which are always universal, i.e., n independent.

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