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Low-frequency light scattering from disordered hydrogen-bonded solids

V. Mazzacurati* and V. Merlo†
Dipartimento di Fisica, Università di Roma "La Sapienza", piazzale Aldo Moro 2, Roma, I-00185, Italy

G. Ruocco
Dipartimento di Fisica, Università di L'Aquila, via Vetoio, Coppito, L'Aquila, I-67100, Italy

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We present an analysis of the disorder-induced light-scattering spectrum observed in Raman-scattering experiments from various kinds of disordered solids. In particular, the shape of the Raman spectra in the $\omega \rightarrow 0$ limit is discussed. In this limit hydrogen-bonded solids show an anomalous behavior; the Raman spectra do not show the ω^2 frequency dependence expected in this kind of system. In this paper we propose a model to describe low-frequency light-scattering spectra in disordered hydrogen-bonded solids. The model is developed for a system composed of incoherent scatterers whose induced polarizability is a very strongly varying function of the instantaneous relative distance between scatterers. As a consequence, the usual one-phonon expansion of the induced polarizability is no longer meaningful, and a full multiphonon treatment is carried out. The results of the model are found to explain qualitatively the observed low-frequency behavior of the Raman scattering in these systems. Moreover, a conjecture is made for the possible physical origin of the proposed induction mechanism in ice I_h.

I. INTRODUCTION

It is well known that all disordered solids exhibit a wide Raman band, with a frequency range extending continuously from zero to a few hundred wavenumbers, thus roughly covering the entire energy region of the density of dynamical states.[1-4] The physical origin of this spectral component has been identified to be the disorder in the effective atomic and/or molecular polarizability induced by structural or by "electrical" disorder.[5] If Λ is the correlation length of the "disordered" variable, then all the phonons with wavevector $|\mathbf{k}| = k < 2\pi/\Lambda$ are, in principle, allowed to appear in the already mentioned band with k-dependent coefficients, giving rise to the disorder-induced light scattering (DILS).

A rigorous evaluation of shape, intensity, and polarization rules of DILS spectra is, generally speaking, a very difficult task; indeed it implies the identification of the microscopic mechanism, which modulates the effective polarizability together with some knowledge of both the structural disorder and the atomic dynamics. Simple models have thus been developed in order to predict, at least qualitatively, some general features of this spectral component,[6,7] and a detailed review can be found in Ref. 8. It has been shown that the spectral shape $I(\omega)$ of the DILS component in the low-frequency region (where the atomic motion is well described by quasiharmonic Debye-like excitations) is[9]

$$I(\omega)=\rho(\omega)C(\omega,\Lambda)[n(\omega,T)+1]/\omega \tag{1.1}$$

(for the Stokes side), where $\rho(\omega)$ is the density of states, $n(\omega,T)$ is the Bose factor, and $1/\omega$ accounts for the usual normalization of the harmonic phonon propagator. The function $C(\omega,\Lambda)$ represents the coupling coefficient of the ω mode with the radiation field and may depend on the correlation length Λ. Since $\rho(\omega) \propto \omega^2$ [and $n(\omega,T) \approx K_B T/\hbar\omega$] for $\omega \rightarrow 0$, the low-frequency shape of the spectrum is completely determined by $C(\omega,\Lambda)$.

A qualitative analysis of the function $C(\omega,\Lambda)$ can be then conveniently carried out dividing the disordered systems into two broad classes: (a) those solids having a high degree of dynamical correlation between all atomic or molecular components (for example amorphous solids, strong glasses, etc.) and (b) those systems in which, on the contrary, the components responsible for the reciprocal polarizability modulation are at least partially (dynamically) uncorrelated (for example solid electrolytes).

In the first class mentioned the low-frequency behavior of $C(\omega,\Lambda)$ may be predicted to be ω^2-like assuming that[7,10,11] the modulation of the effective polarizability induced on each molecule by the surrounding ones can be expanded in series of relative displacements and retaining only the linear term (one-phonon approximation). A general expression for $C(\omega,\Lambda)$ has been derived by Martin and Brenig[7]

$$C(\omega,\Lambda)=\omega^2[A_1\exp(-\omega^2\Lambda^2/8\pi^2c_1^2) + A_t\exp(-\omega^2\Lambda^2/8\pi^2c_t^2)] , \tag{1.2}$$

where c_1 and c_t are the longitudinal and transverse sound velocity, and A_1 and A_t are mode-dependent intensity coefficients. This behavior has been found experimentally by Nemanich in the Raman spectra of As_2S_3 at low temperature.[8]

Something different happens in the class-b systems, whose prototype is the silver iodide crystal in its α phase (α-AgI). In this system the iodine lattice is ordered and the dynamics of the iodine ions can be well described by quasiharmonic phonons, while silver ions are topological-

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ly disordered and free to diffuse from site to site.[12] Hence their dynamics is almost totally uncorrelated from that of the iodine ions. The main contribution to the disorder-induced polarizability of the iodine ions is given by the presence of the disordered silver sublattice; therefore the light-scattering spectrum will reflect both the vibrational dynamics of the iodine lattice and the diffusive motion of the silver system. Since the Ag^+ ions dynamics contributes to the light scattering well below the typical instrumental resolution[13,14] the entire observed spectrum can be attributed to iodine lattice modes. Therefore in this system $C(\omega,\Lambda)$ contains the correlation function of the relative displacement of dynamically uncorrelated atoms, so that it turns out to be ω independent in the frequency range $\omega \ll 2\pi c_t/\Lambda$. However, since the correlation length Λ of the polarizability disorder is nonvanishing, then the coupling coefficients for longitudinal and transverse modes becomes decreasing functions of ω; in this case the expression for the function $C(\omega,\Lambda)$ becomes[14]

$$C(\omega,\Lambda)=[A_l\exp(-\omega^2\Lambda^2/8\pi^2c_l^2)+A_t\exp(-\omega^2\Lambda^2/8\pi^2c_t^2)]\ . \quad (1.3)$$

Many disordered solids that have been investigated show a DILS low-frequency spectral behavior that cannot be explained by either theory. Among them an interesting class is represented by hydrogen-bonded solids with some degree of disorder. Two typical examples are ice I_h and KH_2PO_4 (KDP) in its paraelectric phase.

In the case of ice I_h single crystals[15,16] it can be observed that the behavior of DILS for $\omega \to 0$ deviates from ω^2, despite the high harmonicity of the acoustic modes describing the low-frequency dynamics of this crystal. Also the KDP spectrum taken in the $x[zx]y$ configuration shows a very similar shape[17,18] in the low-frequency region.

Other examples may be quoted, where the DILS deviation from the ω^2 behavior cannot be explained thus posing the question: May DILS spectra of Debye-like harmonic excitations be predicted to deviate from the ω^2 scaling even in homogeneous dynamically correlated disordered solids?

The predicted line shapes we mentioned earlier [Eqs. (1.2) and (1.3)] can be derived from a microscopic point of view, provided that the mechanism of induced polarizability is well described by regular and smooth functions of the distance between different molecules and/or of the molecular reciprocal orientations; this will certainly be the case in atomic, ionic, and molecular systems where the action of the intermolecular forces does not cause a severe rearrangement of the electronic states.[5,10] The renormalized effective atomic or molecular polarizability may in such a case be expanded in terms of displacements from the equilibrium positions of each molecule or atom (hereafter called "scattering units") giving rise (for Debye-like excitations) to the already-mentioned first-order leading term, while multiphonon processes deriving from higher-order terms may be shown to be negligible in comparison.

In this paper an additional mechanism for the polarizability modulation is proposed. We suppose that, due to a rearrangement of the electronic states, the effective polarizability of a given scattering unit is drastically changed even for a very small displacement of the atoms from their equilibrium positions, where the polarizability itself attains its maximum (or minimum) value. This mechanism is thought to be relevant for systems like hydrogen-bonded or strongly covalent solids. In the next section, general relations for the light-scattering intensity are briefly reported in order to introduce the quantities of interest in further calculations. Then, in Sec. IV, the scattering equations are specialized to the proposed model for the polarizability modulation. In the last section the assumption underlying the model will be justified on physical grounds in the case of ice I_h.

II. BASIC LIGHT-SCATTERING THEORY

The light-scattering spectral density $I(\mathbf{q},\omega)$ can be written in terms of the correlation function of the spatial Fourier transform of the macroscopic polarizability density tensor $P_{\alpha\beta}(\mathbf{r},t)$,

$$\tilde{P}_{\alpha\beta}(\mathbf{q},t)=\int d\mathbf{r}\, e^{-i\mathbf{q}\cdot\mathbf{r}}P_{\alpha\beta}(\mathbf{r},t) \quad (2.1)$$

and reads[19]

$$I(\mathbf{q},\omega)\propto\sum_{\alpha,\beta,\gamma,\delta}\hat{\mathbf{m}}_\alpha\hat{\mathbf{n}}_\beta\hat{\mathbf{m}}_\gamma\hat{\mathbf{n}}_\delta I_{\alpha\beta\gamma\delta}(\mathbf{q},\omega)\ , \quad (2.2)$$

where

$$I_{\alpha\beta\gamma\delta}(\mathbf{q},\omega)=\frac{1}{2\pi N}\int dt\, e^{i\omega t}\langle\tilde{P}_{\alpha\beta}(\mathbf{q},t)\tilde{P}^{*}_{\gamma\delta}(\mathbf{q},0)\rangle\ . \quad (2.3)$$

In these equations $\omega=\omega_i-\omega_s$, $\mathbf{q}=\mathbf{k}_i-\mathbf{k}_s$, $\hat{\mathbf{m}}$ ($\hat{\mathbf{n}}$) is the polarization unit vector of the scattered (incoming) radiation, whose frequency and wave vector are ω_s (ω_i) and $\mathbf{k}_s$ ($\mathbf{k}_i$), respectively, and the star indicates complex conjugation.

In atomic and/or molecular systems the microscopic description of the polarizability density tensor $P_{\alpha\beta}(\mathbf{r},t)$ can be carried out in a general way through the effective microscopic polarizability tensor $\pi^i_{\alpha\beta}(t)$ associated to each unit. Indeed $P_{\alpha\beta}(\mathbf{r},t)$ can be thought of as the sum of individual atomic (molecular) polarizability contributions $\pi^i_{\alpha\beta}(t)$ as

$$P_{\alpha\beta}(\mathbf{r},t)=\sum_i\pi^i_{\alpha\beta}(t)\delta(\mathbf{r}-\mathbf{R}_i(t))\ , \quad (2.4)$$

where $\mathbf{R}^i(t)=\mathbf{x}^i+\mathbf{u}^i(t)$ is the instantaneous position of the ith unit whose equilibrium position is $\mathbf{x}^i$. So that, from Eq. (2.1),

$$\tilde{P}_{\alpha\beta}(\mathbf{q},t)=\sum_i\pi^i_{\alpha\beta}(t)e^{-i\mathbf{q}\cdot\mathbf{R}^i(t)}\ . \quad (2.5)$$

The effective atomic polarizability tensor $\pi^i_{\alpha\beta}(t)$ will be, in general, a quite complicated function of all the microscopic variables of the system and will depend on the kind of atoms, ions, or molecules the system is composed of, as well as on the mutual interactions that perturb their electronic states. These effects will depend on the density of the system itself so that it is possible to define, for a given unit, an ideal "bare" polarizability $p^i_{\alpha\beta}(t)$ as its polarizability *in vacuo.* Using a perturbative procedure, the effective polarizability can be then written[20] as the sum of the polarizability $p^i_{\alpha\beta}(t)$ plus the "incremental" (or "induced") term $\Delta p^i_{\alpha\beta}(t)$

$$\pi^i_{\alpha\beta}(t)=p^i_{\alpha\beta}(t)+\Delta p^i_{\alpha\beta}(\{\mathbf{R}^j(t)\}_{j=1,\ldots,N}) \ . \tag{2.6}$$

Here the induced polarizability of the ith unit, $\Delta p^i_{\alpha\beta}(\{\mathbf{R}^j(t)\}_{j=1,\ldots,N})$, can be expressed in terms of the ground-state electrical properties of the units themselves, and is a function of all the degrees of freedom of the system.

Depending on the system under study, the relevant contributions to the induced polarizability may be given by different physical effects, namely the dipole–induced-dipole (DID) effect, the electronic overlap, the effect of dispersion forces, and so on.

For example, the effective polarizability coming from the DID effect can be written as[21]

$$\Delta p^i_{\alpha\beta}(t)=\sum_j\sum_{\gamma,\delta}p^i_{\alpha\gamma}(t)\frac{\hat{\mathbf{T}}^{(2)}_{\gamma\delta}(\hat{\mathbf{R}}^{ij}(t))}{|\mathbf{R}^{ij}(t)|^3}p^j_{\delta\beta}(t) \ . \tag{2.7}$$

A further example of a widely used model for the induced polarizability is the bond polarizability model where[22]

$$\Delta p^i_{\alpha\beta}=\sum_{j\in \mathrm{NN}(i)}\{\hat{\mathbf{T}}^{(2)}_{\alpha\beta}(\hat{\mathbf{R}}^{ij}(t))f(|\mathbf{R}^{ij}(t)|)+g(|\mathbf{R}^{ij}(t)|)\delta_{\alpha\beta}\} \ . \tag{2.8}$$

In the previous equations $\mathbf{R}^{ij}(t)=\mathbf{R}^j(t)-\mathbf{R}^j(t)$, the hat stands for unit vector, $\hat{\mathbf{T}}^{(2)}_{\alpha\beta}(\hat{\mathbf{x}})=3\hat{\mathbf{x}}_\alpha\hat{\mathbf{x}}_\beta-\delta_{\alpha\beta}$, NN($i$) indicate the set of nearest neighbors of unit i, and $f(x)$ and $g(x)$ are appropriate smooth functions that can be deduced by *ab initio* calculation or by fitting experimental data.

A generally employed hypothesis on the dependence of the term $\Delta p^i_{\alpha\beta}(t)$ from the degrees of freedom of the system is the pairwise additivity. One says that $\Delta p^i_{\alpha\beta}(t)$ is written as a sum of terms each dependent on the relative distance between the unit i and another unit j, ($j=1\ldots N$),

$$\Delta p^i_{\alpha\beta}(\{\mathbf{R}^j(t)\}_{j=1,\ldots,N})=\sum_j\Pi_{\alpha\beta}(\mathbf{R}^{ij}(t)) \ . \tag{2.9}$$

In Eq. (2.9), $\Pi_{\alpha\beta}(\mathbf{r})$ is the function that specifies the dependence of the effective polarizability on the distance between units. The explicit expression for $\Pi_{\alpha\beta}(\mathbf{r})$ in the particular case of DID and BP (bond polarizability) mechanisms can be easily deduced from Eqs. (2.7) and (2.8).

With this choice for $\Delta p^i_{\alpha\beta}(t)$, from Eqs. (2.5) and (2.6), and in the limit of vanishing exchanged wave vector, Eq. (2.3) can be written as

$$I_{\alpha\beta\gamma\delta}(\mathbf{0},\omega)=\frac{1}{2\pi N}\int dt\, e^{i\omega t}\sum_{i,j}\sum_{i',j'}\langle\Pi_{\alpha\beta}(\mathbf{R}^{ij}(t))\Pi_{\gamma\delta}(\mathbf{R}^{i'j'}(0))\rangle \ . \tag{2.10}$$

In Eq. (20) we have not considered the contribution from the bare polarizability $p^i_{\alpha\beta}(t)$, which cannot give rise to the DILS spectrum.

Usually in solid systems because of the existence of equilibrium positions, the quantities $\Pi_{\alpha\beta}(\mathbf{R}^{ij}(t))$ are expanded in series of relative atomic displacements of the units i and j and only the first-order terms are taken into account (one-phonon approximation). This approximation is a good one provided that the mean-squared relative displacements of the atoms from their equilibrium positions are much less than the square of the typical length scale of the function $\Pi_{\alpha\beta}(\mathbf{r})$. This ensures that higher-order terms in the expansion are negligible, or in other words that $\Pi_{\alpha\beta}(\mathbf{R}^{ij}(t))$ is a smooth function of $\mathbf{r}$ around the equilibrium configuration, where it attains the nonzero value $[\Pi_{\alpha\beta}(\mathbf{R}^{ij})]_{\mathrm{eq}}=\Pi_{\alpha\beta}(\mathbf{x}^{ij})$.

III. FORMULATION OF THE MODEL

In this paper we want to explore the kind of spectral shape arising if one is forced to deal with all the terms in the series expansion of $\Pi_{\alpha\beta}(\mathbf{R}^{ij})$ (multiphonon terms), i.e., when the induction polarizability function is a rapidly varying function of $\mathbf{R}^{ij}$. In order to treat the problem analytically we adopt a Gaussian model for this "anomalous" induction mechanism. This choice has also the advantage that the length scale of the proposed mechanism is naturally related to the standard deviation of the Gaussian, which will be used as an adjustable parameter.

The hypothesis underlying our model are therefore summarized as follows: The system is mechanically ordered, i.e., the motion of the units can be described by the phonon formalism. The system is electrically disordered. As discussed in the introduction this is a prerequisite for the appearance of the DILS spectra in mechanically ordered systems. The system is composed of fully incoherent scatterers, i.e., the configurational average in Eq. (2.10) is nonvanishing only if the pair of units (ij) is the same as $(i'j')$. The contribution to the effective polarizability coming from this anomalous term (in contrast with all the other "normal" contributions for which the one-phonon approximation holds) can be written as

$$\begin{aligned}\Pi_{\alpha\beta}(\mathbf{R}^{ij}(t))&=\Pi_{\alpha\beta}(\mathbf{x}^{ij})\mathcal{A}_{ij}(t)\\&=\Delta\Pi^{ij}_{\alpha\beta}\mathcal{A}_{ij}(t)\end{aligned} \tag{3.1}$$

with

$$\mathcal{A}_{ij}(t)=\exp\{-[\mathbf{u}^{ij}(t)\cdot\hat{\mathbf{R}}^0]^2/2\sigma^2\} \ , \tag{3.2}$$

where $\mathbf{u}^{ij}(t)=\mathbf{u}^i(t)-\mathbf{u}^j(t)$ is the instantaneous relative displacement and $\mathbf{R}^0=\mathbf{x}^i-\mathbf{x}^j$ is the relative distance between the equilibrium positions of the units. σ represents the length scale of the variation of the induced polarizability; the lower σ, the more abrupt the variation. Under the mentioned hypothesis Eq. (2.10) reduces to

$$I_{\alpha\beta\gamma\delta}(\mathbf{0},\omega)=\frac{1}{2\pi N}\sum_{i,j}\Delta\Pi^{ij}_{\alpha\beta}\Delta\Pi^{ij}_{\gamma\delta}\int dt\, e^{i\omega t}\langle\mathcal{A}_{ij}(t)\mathcal{A}_{ij}(0)\rangle\ . \tag{3.3}$$

We will now calculate the spectral shape arising from this contribution; its (possible) physical origin will be discussed in the last section. Assuming that the dynamics can be described within the framework of the harmonic approximation for a mechanically ordered solid and making use of the normal-mode expansion, we can write

$$\mathbf{u}^{ij}(t)=\left[\frac{1}{2NM}\right]^{1/2}\sum_{\mathbf{k},\chi}\frac{\hat{\mathbf{e}}(\mathbf{k}\chi)}{[\omega_\chi(\mathbf{k})]^{1/2}}(e^{i\mathbf{k}\cdot\mathbf{x}_i}-e^{i\mathbf{k}\cdot\mathbf{x}_j})[a_{\mathbf{k}\chi}e^{i\omega_\chi(\mathbf{k})t}+a^*_{-\mathbf{k}\chi}e^{i\omega_\chi(\mathbf{k})t}]\ , \tag{3.4}$$

where $\omega_\chi(\mathbf{k})$, $\hat{\mathbf{e}}(\mathbf{k}\chi)$, and $a_{\mathbf{k}\chi}$ are the eigenfrequency, the polarization vector and the normal coordinate, respectively, of the phonon of the branch χ and wave vector $\mathbf{k}$. Let us define

$$\Gamma_{\mathbf{k}\chi}=\frac{1}{[4NM\sigma^2\omega_\chi(\mathbf{k})]^{1/2}}[\hat{\mathbf{R}}^0\cdot\hat{\mathbf{e}}(\mathbf{k}\chi)]e^{i\mathbf{k}\cdot x_i}(1-e^{-i\mathbf{k}\cdot\mathbf{R}^0})\ . \tag{3.5}$$

Then we have

$$\begin{aligned}\frac{\mathbf{u}^{ij}(t)\cdot\hat{\mathbf{R}}^0}{\sqrt{2}\sigma}&=\sum_{\mathbf{k}\chi}\Gamma_{\mathbf{k}\chi}[a_{\mathbf{k}\chi}e^{-i\omega_\chi(\mathbf{k})t}+a^*_{-\mathbf{k}\chi}e^{i\omega_\chi(\mathbf{k})t}]\\&=\sum_{\mathbf{k}\chi}[A_{\mathbf{k}\chi}(\Gamma_{\mathbf{k}\chi}e^{-i\omega_\chi(\mathbf{k})t}+\Gamma^*_{k\chi}e^{i\omega_\chi(\mathbf{k})t}+iB_{\mathbf{k}\chi}(\Gamma_{\mathbf{k}\chi}e^{-i\omega_\chi(\mathbf{k})t}-\Gamma^*_{k\chi}e^{i\omega_\chi(\mathbf{k})t})]\ ,\end{aligned} \tag{3.6}$$

which implicitly defines $A_{\mathbf{k}\chi}$ and $B_{\mathbf{k}\chi}$ as the real and imaginary part, respectively, of $a_{\mathbf{k}\chi}$. In order to use a more compact notation let us define further the quantities $\gamma^{(\epsilon)}_{\mathbf{k}\chi}(t)$ and $C^{(\epsilon)}_{\mathbf{k}\chi}$ (with $\epsilon=-,+$) as

$$\gamma^{(+)}_{\mathbf{k}\chi}(t)=(\Gamma_{\mathbf{k}\chi}e^{i\omega_\chi(\mathbf{k})t}+\Gamma^*_{\mathbf{k}\chi}e^{i\omega_\chi(\mathbf{k})t})\ ,\quad \gamma^{(-)}_{\mathbf{k}\chi}(t)=i(\Gamma_{\mathbf{k}\chi}e^{-i\omega_\chi(\mathbf{k})t}-\Gamma^*_{\mathbf{k}\chi}e^{i\omega_\chi(\mathbf{k})t}\ , \tag{3.7}$$

and

$$C^{(+)}_{\mathbf{k}\chi}=A_{\mathbf{k}\chi}\ ,\quad C^{(-)}_{\mathbf{k}\chi}=B_{\mathbf{k}\chi}\ , \tag{3.8}$$

so that Eq. (3.1) can be cast in the form

$$\mathcal{A}(t)=\exp[\sum_{\mathbf{k},\chi,\epsilon}\sum_{\mathbf{k}',\chi',\epsilon'}\gamma^{(\epsilon)}_{\mathbf{k}\chi}(t)\gamma^{(\epsilon')}_{\mathbf{k}'x'}(t)C^{(\epsilon)}_{\mathbf{k}\chi}C^{(\epsilon')}_{\mathbf{k}'\chi'}]\ . \tag{3.9}$$

The quantity of interest is the spectrum of the autocorrelation function of the quantity $\mathcal{A}(t)$, i.e.,

$$\mathcal{I}(\omega)=\int dt\, e^{i\omega t}\langle\mathcal{A}(t)\mathcal{A}(0)\rangle=\int e^{i\omega t}c(t)dt \tag{3.10}$$

with

$$c(t)=\left\langle\exp\left[\sum_{\mathbf{k},\chi,\epsilon}\sum_{\mathbf{k}',\chi'\epsilon'}[\gamma^{(\epsilon)}_{\mathbf{k}\chi}(t)\gamma^{(\epsilon')}_{\mathbf{k}'\chi'}(t)+\gamma^{(\epsilon)}_{\mathbf{k}\chi}(0)\gamma^{(\epsilon')}_{\mathbf{k}'\chi'}(0)]C^{(\epsilon)}_{\mathbf{k}\chi}C^{(\epsilon')}_{\mathbf{k}'\chi'}\right]\right\rangle\ . \tag{3.11}$$

The calculation of $c(t)$, given in detail in the Appendix, yields the simple result

$$c(t)=\frac{1}{\sqrt{[1+f(0)]^2-[f(t)]^2)}} \tag{3.12}$$

with

$$f(t)=4k_BT\sum_{\mathbf{k}\chi}\frac{|\Gamma_{\mathbf{k}\chi}|^2}{\omega_\chi(\mathbf{k})}\cos[\omega_\chi(\mathbf{k})t]\ . \tag{3.13}$$

Provided one knows the dynamics of the system (i.e., the eigenvalues and the eigenvectors), Eq. (3.12) together with Eqs. (3.13), (3.5), and (3.10) completely solves the problem of the calculation of the light-scattering spectra with the chosen model polarizability.

In order to show the main features of the resulting spectra we will now explicitly calculate the correlation function $c(t)$ using a Debye model for the dynamics and considering only the longitudinal acoustic phonons in the long wavelength limit. In this limit ($\mathbf{k}\cdot\mathbf{R}^0\rightarrow0$) the expression (3.5) for $\Gamma_{\mathbf{k}\chi}$ becomes

$$|\Gamma_{\mathbf{k}\chi}|^2=\frac{k^2|\mathbf{R}_0|^2}{4MN\sigma^2\omega_\chi(\mathbf{k})}[\hat{\mathbf{R}}_0\cdot\hat{\mathbf{e}}(\hat{\mathbf{k}}\chi)]^2[\hat{\mathbf{R}}_0\cdot\hat{\mathbf{k}}]^2\ , \tag{3.14}$$

and the expression for $f(t)$ follows:

$$f(t)=\frac{4\pi k_BT|\mathbf{R}_0|^2}{5MN\rho\sigma^2}\int_0^{k_D}dk\frac{k^4}{\omega_\chi(\mathbf{k})^2}\cos[\omega_\chi(\mathbf{k})t]\ . \tag{3.15}$$

Assuming a linear dispersion relation, i.e., $\omega_\chi(\mathbf{k})=c_\chi|\mathbf{k}|$, and $k_D^3=3N\rho/4\pi$ the final relation for $f(t)$ then is

$$f(t)=\frac{1}{5}\frac{k_BT}{Mc_L^2}\frac{|\mathbf{R}^0|^2}{\sigma^2}S_L(t) \tag{3.16}$$

with

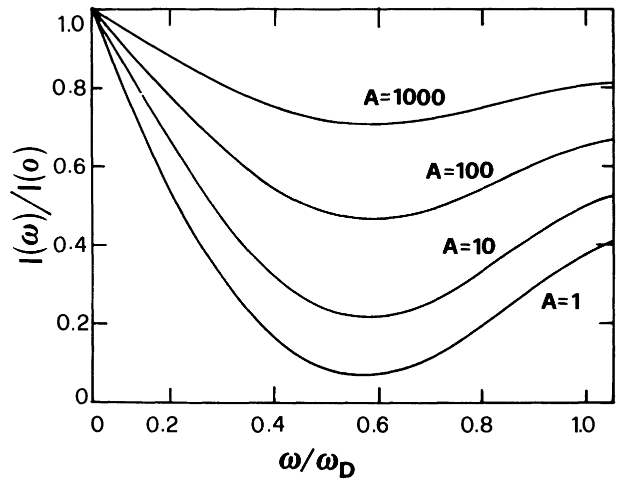

FIG. 1. Low-frequency part of the spectrum of the scattered light calculated according to our model. The different curves refer to different values of the parameters A (see text). All the spectra have been purified from the $\delta(\omega)$ contribution and have been normalized to $I(0)$.

$$S_L(t)=(\omega_D t)^{-3}\int_0^{\omega_D t} x^2\cos x\,dx$$
$$=3(\omega_D t)^{-3}\{2\omega_D t\cos(\omega_D t)+[(\omega_D t)^2-2]\sin(\omega_D t)\}\ . \quad (3.17)$$

The above relationship (3.16) together with Eqs. (3.10), (3.12), and (3.17) allows one to calculate the spectrum of scattered light. It is evident that the parameters determining the shape of the spectrum are $k_B T/Mc_L^2$ (the square of the ratio of the thermal velocity to the sound velocity of the system) and R^0/σ (i.e., the ratio of the nearest-neighbor distance to the length scale of the induced polarizability function). The low-frequency region of the spectra are reported in Fig. 1 as a function of ω/ω_D for some values of the parameters

$$A=(k_B T/5Mc_L^2)(|\mathbf{R}^0|/\sigma^2\ .$$

These spectra have been calculated from the Fourier transform of Eq. (3.12). It is apparent from Fig. 1 that $\mathcal{I}(\omega)=\text{const}$ in the limit $\omega\rightarrow 0$. This behavior is due to the relevance of the multiphonon terms enhanced by the particular form chosen for the polarizability induction mechanism.

IV. DISCUSSION AND CONCLUSIONS

Having calculated the spectrum of the scattered light starting from the polarizability induction mechanisms of Eqs. (3.1) and (3.2), we will now inquire as to the possible physical phenomena that gives rise to this mechanism. In particular we will focus our attention on a particular system, i.e., ice I_h.

The structure of ice in its hexagonal phase (I_h), as far as the oxygen sublattice is concerned, is shown in Fig. 2. Each oxygen atom is surrounded by four equivalent oxygens giving rise to a tetrahedral nearest-neighbors coordination. In the structure one can recognize the existence of distorted hexagons with the oxygen atoms at the vertices. The projection of distorted hexagons can be easily seen both on the (aa′) as well as on the (ca) or (ca′) planes.[23]

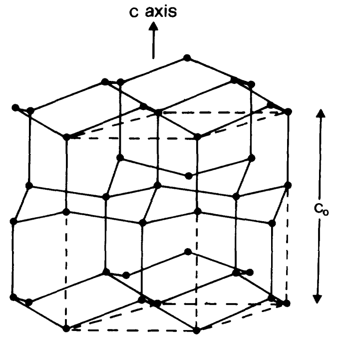

FIG. 2. Arrangement of the oxygen atoms in ice I_h.

Opposite to the oxygen sublattice the hydrogen atoms do not have an ordered arrangement. It is well established[24] that one hydrogen atom is placed along each O—O bond, but the equilibrium position of a proton is not at the center of the bond; in fact $L_{\text{O—O}}=2.765$ Å, while the minimum of the two $L_{\text{O—H}}$ values is $L_{\text{O—H}}=1.015$ Å. In such a way the H_2O molecule is preserved as the basic crystal unit (because of the high energy required to create $H_3{}^+O$ and OH^- defects). Following the statistical model of Pauling[25] there are many possibilities of arranging the protons around a given oxygen atom, even with the constraint of existence of the H_2O molecule, and this gives rise to an orientationally disordered solid.[26]

As far as the diffusive dynamics of protons is concerned, in order to preserve the integrity of all the water molecules and if the assumptions of the Pauling model are accepted, no possibility exists of displacing any single proton along the bond from one equilibrium position to the other without getting other protons involved in the motion. The diffusive dynamics of the protons can only take place with the cooperative motion of a large number of protons. For some peculiar situations, which may statistically occur, the motion can be performed by six protons. Indeed, if the proton distribution in some of the distorted hexagons were those reported in Fig. 3, then the

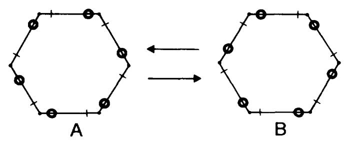

FIG. 3. The two possible arrangements of hydrogen atoms in a "hexagon", which give rise to delocalization of the proton wave function. The oxygen atoms are at the corners of the (nonplanar) hexagons, while the hydrogen atoms (●) occupy one of the two equivalent position (+). Going from situation A to B, all the protons shift counterclockwise.

cooperative motion of the six protons along the bonds should become possible. It can be easily seen that the rearrangement of the six protons shown in the same figure will be independent from the positions of all the other protons of the system. In a very rough approximation (completely uncorrelated hexagons) the probability of occurrence of such a situation is about 0.03, and all these hexagons will be hereafter referred to as "activated rings."

The ground state of activated rings may be thought of as resonating between the two equivalent configurations shown in Fig. 3; this implies that all the protons are delocalized along their bonds, their total eigenfunctions being either symmetric or antisymmetric with respect to the center of the bond. Due to the proton delocalization, we may reasonably assume that the electronic polarizability of the activated rings is higher than that of nonactivated rings.

Even small distortions of the hexagonal structure break the symmetry of the proton Hamiltonian on the activated rings, projecting protons (at least partially) in localized states (A and B in Fig. 3); in such a way the polarizability of the whole ring is drastically lowered, as required by our polarizability model.

The mechanism we have introduced has the effect of enhancing multiphonon processes [only even terms because of the symmetry of $\underline{\Pi}(t)$], giving its maximum contribution in the low-frequency part of the spectrum. In the particular class of systems mentioned earlier, the spectrum may be thought of as the superposition of a normal one-phonon contribution coming from "regular" induction mechanisms (as the DID effect, bond polarizability modulation, electronic overlap, etc.) plus the spectrum coming from the proposed polarizability modulation model. This contribution will be most relevant in the low-frequency region of the spectrum where the regular one-phonon term vanishes like ω^2.

We want to stress that there are certainly multiphonon terms coming from regular mechanisms but these may be predicted to be negligibly small with respect to the one-phonon term in all the frequency ranges examined, and cannot be at the origin of the deviation observed in low-frequency spectra.

Our model, as it stands, allows only a qualitative comparison with the experimental data; its value stays in the fact that it affords a relatively simple picture of the mechanism leading to $\mathcal{J}(\omega)\approx$const for low ω in these compounds. No attempt is made to put our results on a quantitative basis; this would call for a detailed treatment of the scattering rings, which is, at best, mathematically complicated and beyond the aim of the present work.

Moreover, we think that the model can be of some relevance in interpreting also the experimental results from covalent disordered solids even if in these systems the phenomena at the origin of a rapidly varying $\underline{\Pi}(\mathbf{r})$ are not easily identified. For instance, our model accounts qualitatively for the results of Nemanich on As_2S_3 (Ref. 8), which observes in the low-frequency part of his spectra a temperature behavior typical of a two-phonon contribution, while the high-frequency part behaves like a one-phonon contribution.

APPENDIX

In this appendix we will evaluate the correlation function in Eq. (3.11). The thermal average of the physical quantity Q, indicated by $\langle Q \rangle$, can be written as

$$\langle Q \rangle = Z^{-1} \int \left[\prod_{\mathbf{k},\chi,\epsilon} dC_{\mathbf{k}\chi}^{(\epsilon)} \right] Q \exp(-\beta H) , \tag{A1}$$

where H is the Hamiltonian of the system, which in our case turns out to be

$$H = \sum_{\mathbf{k},\chi,\epsilon} \omega_\chi(\mathbf{k}) [C_{\mathbf{k}\chi}^{(\epsilon)}]^2 , \tag{A2}$$

$\beta = 1/k_B T$ and Z is the partition function,

$$\begin{aligned} Z &= \int \left[\prod_{\mathbf{k},\chi,\epsilon} dC_{\mathbf{k}\chi}^{(\epsilon)} \right] \exp(-\beta H) \\ &= \pi^{3N} \exp \left[-\tfrac{1}{2} \sum_{\mathbf{k},\chi} \ln[\beta\omega_\chi(\mathbf{k})] \right] . \end{aligned} \tag{A3}$$

The calculation of the autocorrelation function in Eq. (3.11) thus reduces to the evaluation of the integral

$$c(t) = \pi^{-3N} \exp \left[\tfrac{1}{2} \sum_{\mathbf{k},\chi} \ln[\beta\omega_\chi(\mathbf{k})] \right] \int \left[\prod_{\mathbf{k},\chi,\epsilon} dC_{\mathbf{k}\chi}^{(\epsilon)} \exp \left[- \sum_{\mathbf{k},\chi\epsilon} \sum_{\mathbf{k}',\chi',\epsilon'} C_{\mathbf{k}\chi}^{(\epsilon)} C_{\mathbf{k}'\chi'}^{(\epsilon')} W_{\mathbf{k}\mathbf{k}'\chi\chi'}^{(\epsilon\epsilon')} \right] \right. \tag{A4}$$

with

$$W_{\mathbf{k}\mathbf{k}'\chi\chi'}^{(\epsilon\epsilon')} = \delta_{\mathbf{k}\mathbf{k}'} \delta_{\chi\chi'} \delta_{\epsilon\epsilon'} \beta\omega_\chi(\mathbf{k}) + [\gamma_{\mathbf{k}\chi}^{(\epsilon)}(t) \gamma_{\mathbf{k}'\chi'}^{(\epsilon')}(t) + \gamma_{\mathbf{k}\chi}^{(\epsilon)}(0) \gamma_{\mathbf{k}'\chi'}^{(\epsilon')}(0)] . \tag{A5}$$

In order to simplify the notation in the following we will use the index s to indicate the set of indexes $(\mathbf{k},\chi,\epsilon)$. The matrix $\underline{W}$ is then written as

$$[\underline{W}]_{ss'} = \beta\omega_s \delta_{ss'} + \gamma_s(t)\gamma_{s'}(t) + \gamma_s(0)\gamma_{s'}(0) . \tag{A6}$$

If $\underline{W}$ is a nonsingular and positive-definite matrix, the following relation holds:

$$[\underline{GWG}^{-1}]_{ss'} = \delta_{ss'} \lambda_s , \tag{A7}$$

where λ_s are the eigenvalues of $\underline{W}$ and $\underline{G}$ is $6N \times 6N$ unitary matrix. The argument of the exponential in Eq. (A4) thus becomes

$$-\sum_{ss'} W_{ss'} C_s C_{s'} = - \sum_s (C'_s)^2 \lambda_s \tag{A8}$$

with

$$C'_s=\sum_{s'} G_{ss'}C_{s'}\ ; \tag{A9}$$

moreover,

$$\prod_s dC_s=\prod_s \frac{dC'_s}{|\det \underline{G}|}=\prod_s dC'_s\ . \tag{A10}$$

We then have for $c(t)$

$$\begin{aligned} c(t)&=\pi^{-3N}\exp\left[\tfrac{1}{2}\sum_s \ln(\beta\omega_s)\right]\int\left[\prod dC'_s\right]\exp\left[-\sum_s (C'_s)^2\lambda_s\right]\\ &=\pi^{-3N}\exp\left[\tfrac{1}{2}\sum_s \ln(\beta\omega_s)\right]\prod_s\left[\frac{\pi}{\lambda_s}\right]^{1/2}=\exp\left[\tfrac{1}{2}\sum_s \ln(\beta\omega_s)\right]\exp\left[-\tfrac{1}{2}\mathrm{Tr}\ln(\underline{W})\right]\ . \end{aligned} \tag{A11}$$

In order to proceed further let us define the $6N\times 6N$ diagonal matrix Ω,

$$\Omega_{ss'}=\delta_{ss'}\sqrt{\beta\omega_s}\ . \tag{A12}$$

So doing we can rewrite Eq. (A11) in the form

$$\begin{aligned} c(t)&=\exp\{-\tfrac{1}{2}[-2\,\mathrm{Tr}\ln(\underline{\Omega})+\mathrm{Tr}\ln(\underline{W})]\}\\ &=\exp[\mathrm{Tr}\ln(\underline{\Omega}^{-1}\underline{W}\underline{\Omega}^{-1})]=\exp[\mathrm{Tr}\ln(\underline{Q})] \end{aligned} \tag{A13}$$

with

$$[\underline{Q}]_{ss'}=\delta_{ss'}+\frac{1}{\beta\sqrt{\omega_s\omega_{s'}}}[\gamma_s(t)\gamma_{s'}(t)+\gamma_s(0)\gamma_{s'}(0)]\ . \tag{A14}$$

Defining now

$$g_s^1=\frac{\gamma_s(t)}{\sqrt{\beta\omega_s}}\ ,\qquad g_s^2=\frac{\gamma_s(0)}{\sqrt{\beta\omega_s}}\ , \tag{A15}$$

and the Q matrix has elements

$$Q_{ss'}=\delta_{ss'}+\sum_{i=1,2} g_s^i g_{s'}^i\ . \tag{A16}$$

Our aim is now to diagonalize the $6N\times 6N$ matrix $\underline{Q}$. Defining $\underline{X}=\underline{Q}^{-1}$ and multiplying Eq. (A16) for the $\underline{X}$ matrix, we can write

$$\delta_{ss'}=X_{ss'}+\sum_t X_{st}\left[\sum_{i=1,2} g_t^i g_{s'}^i\right]\ ,\quad \forall s,s'\ . \tag{A17}$$

Now, defining $f_s^i=\sum_t X_{st}g_t^i$ (so that $X_{ss'}=\delta_{ss'}-\sum_{i=1,2}f_s^i g_{s'}^i$) we can write Eq. (A17) in terms of the quantities g_s^i and f_s^i only, i.e.,

$$\sum_{i=1,2} g_{s'}^i\left[g_s^i-f_s^i-\sum_{j=1,2} f_s^j\sum_t g_t^j g_t^i\right]=0\ ,\quad \forall s,s'\ . \tag{A18}$$

For the system in Eq. (A18) to have nontrivial solutions then, for a given i, the coefficients of each $g_{s'}^i$ must vanish, that is

$$\sum_{j=1,2} f_s^j\left[\delta_{ij}+\sum_t g_t^j g_t^i\right]=g_s^i\ . \tag{A19}$$

If we now introduce the 2×2 $\underline{\alpha}$ matrix as

$$\alpha_{ij}=\delta_{ij}+\sum_s g_s^i g_s^j\ , \tag{A20}$$

then

$$\sum_{j=1,2}\alpha_{ji}f_s^j=g_s^i\ , \tag{A21}$$

and therefore,

$$X_{ss'}=\delta_{ss'}-\sum_{i,j=1,2}\beta_{ij}g_s^i g_{s'}^j \tag{A22}$$

with $\underline{\beta}=\underline{\alpha}^{-1}$. Notice that so doing the calculation of the elements of the $\underline{X}$ matrix has been reduced to the diagonalization of the 2×2 $\underline{\alpha}$ matrix. We are now in condition to perform the trace calculation:

$$\begin{aligned} \mathrm{Tr}\ln(\underline{Q})&=\mathrm{Tr}\sum_{n=1}^{\infty}\frac{1}{n}[\underline{I}-\underline{Q}^{-1}]^n\\ &=\mathrm{Tr}\sum_{n=1}^{\infty}\frac{1}{n}[\underline{I}-\underline{X}]^n=\sum_{n=1}^{\infty}\frac{1}{n}\mathrm{Tr}[\underline{Y}]^n \end{aligned} \tag{A23}$$

with

$$Y_{ss'}=\sum_{i,j=1,2}\beta_{ij}g_{s'}^j g_s^i\ . \tag{A24}$$

Now

$$\begin{aligned} \mathrm{Tr}[\underline{Y}]=\sum_{ss'}\delta_{ss'}Y_{ss'}&=\sum_{i,j=1,2}\beta_{ij}\sum_s g_s^i g_s^j\\ &=\sum_{i,j=1,2}\beta_{ij}\eta_{ji}=\mathrm{Tr}[(\underline{\beta}\underline{\eta})]\ , \end{aligned} \tag{A25}$$

where $\eta_{ij}=\alpha_{ij}-\delta_{ij}$. In the same way one can show that

$$\mathrm{Tr}[\underline{Y}^n]=\mathrm{Tr}[(\underline{\beta}\underline{\eta})^n]\ . \tag{A26}$$

Notice that $\underline{Y}$ is a $6N\times 6N$ dimensional matrix whereas $\underline{\beta}$ and $\underline{\eta}$ are 2×2 matrices. After this lengthy calculation the final result is now at hand: in fact, using the defining equation for $\underline{\eta}$, we have

$$\begin{aligned}\mathrm{Tr}[\ln(\underline{Q})] &= \sum_{n=1}^{\infty} \frac{1}{n}\mathrm{Tr}[(\underline{\beta\eta})]^n \\ &= \sum_{n=1}^{\infty} \frac{1}{n}\mathrm{Tr}[(\underline{I}-\underline{\beta})]^n \\ &= \mathrm{Tr}[\ln(\underline{\beta}^{-1})] = \mathrm{Tr}[\ln(\underline{\alpha})] = \ln \det\underline{\alpha} \; . \qquad \text{(A27)}\end{aligned}$$

Finally, the correlation function reads

$$\begin{aligned}c(t) &= \exp\{-\tfrac{1}{2}\mathrm{Tr}[\ln(\underline{Q})]\} \\ &= \exp[-\tfrac{1}{2}\ln \det\underline{\alpha}] = \frac{1}{\sqrt{\det\underline{\alpha}}} \; . \qquad \text{(A28)}\end{aligned}$$

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[*] Author to whom correspondence should be addressed.

[†] Present address: Dipartimento di Fisica, Università di Roma "Tor Vergata", via E. Carnevale, Roma, I-00173, Italy.

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