Journal of Molecular Structure, 250 (1991) 395-401
Elsevier Science Publishers B.V., Amsterdam

A model for low frequency Raman scattering in hydrogen-bonded solids*

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(Received 20 November 1990)

Abstract

We briefly review the properties of the disorder-induced light scattering spectrum observed in Raman scattering experiments from disordered solids; in particular, we concentrate on the region $\omega \rightarrow 0$. From this analysis it appears that ice I_h shows an anomalous behaviour which may be ascribed to the contribution of multiphonon terms; in this paper these are introduced via an explicit non-linear coupling between radiation and matter. The results of this model are reported, and the underlying physical mechanism examined in some detail. Even if the results are somewhat qualitative in character, they give indirect evidence for the presence of activated hexagonal hydrogen loops in ice I_h.

INTRODUCTION

All disordered solids exhibit a wide Raman band, say in the range $\omega = 0$–300 cm^{-1} [1–4]. This band is due to a disordered contribution in the effective polarizability modulation ("electrical" disorder) which gives rise to the observed incoherent light scattering spectrum. If the "electrical order" is defined on a length scale Λ (typically a few ångströms), then all phonons with $\lambda > \Lambda$ are allowed to appear in the observed Raman intensity giving rise to the disorder-induced light scattering (DILS) spectrum.

On quite general grounds, the low-frequency behaviour of the spectrum may be predicted to be

$$I(\omega) \approx \rho(\omega) C(\omega, \Lambda) (n(\omega, T) + 1)/\hbar\omega \qquad (1)$$

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*Presented at the International Symposium on Hydrogen Bond Physics held at Il Ciocco, Barga, Italy, 11-14 September 1990.

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where $\rho(\omega)$ is the density of states and $n(\omega,T)$ the population factor. The coupling of radiation with the different frequency modes is described by the coefficients $C(\omega,\Lambda)$, where Λ-dependence is explicitly indicated. Since for $\omega\to 0$ one has $\rho(\omega)\approx\omega^2$ (having supposed a Debye-like behaviour) and $n(\omega,T)\approx KT_B/\omega$, the entire frequency dependence in $I(\omega)$ is carried by $C(\omega,\Lambda)$; in the limit $\omega\to 0$ this is the quantity of interest. Furthermore, it should be noted that one of the basic physical ingredients underlying the polarizability modulation is the dynamic correlation between different scattering units.

Disordered systems may be then sorted into two broad classes: (a) solids having a high degree of dynamic correlation between atomic or molecular components; (b) solids with at least partially uncorrelated constituents.

In this context, we now briefly summarize the situation concentrating in the region of the spectrum where $\lambda\gg\Lambda$; this condition allows one to neglect the Λ-dependence of the $C(\omega,\Lambda)$ coefficients. For details about the case of $\lambda<\Lambda$ the reader is referred to a previous work [5].

In the first class mentioned $C(\omega,\Lambda)$ scales like ω^2 for $\omega\to 0$; this is easily established noting that the modulation of the effective polarizability induced on each molecule by the surrounding ones may be expanded in series of relative displacements retaining the linear term only (one-phonon approximation); in this case, since $C(\omega)$ contains the correlation function of the relative displacements, it must be $C(\omega)\approx k^2\approx\omega^2$. Comparing this prediction with experimental data, the agreement is fair at low temperature [6] (Fig. 1); raising the temperature, the situation is as if there is "more" scattering than predicted by the simple ω^2 scaling; this is called light scattering excess (LSE). A number of different mechanisms have been proposed to deal with this anomalous feature [7,8]. Here it suffices to note that within all these interpretation schemes both DILS and LSE are explained in terms of dynamics.

The second class of systems is best described by taking a particular system as a reference, e.g. AgI in its α phase. This system is characterized by an ordered iodine lattice while the Ag^+ ions are topologically disordered and free to diffuse from site to site; thus their dynamics are almost totally uncorrelated

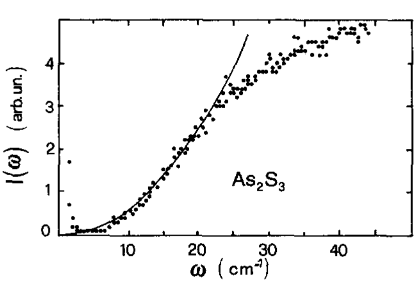

Fig. 1. Low-frequency Raman spectra measured by Nemanich [6] in As_2S_3 at low temperature ($T=8$ K). The full line is the expected ω^2 behaviour.

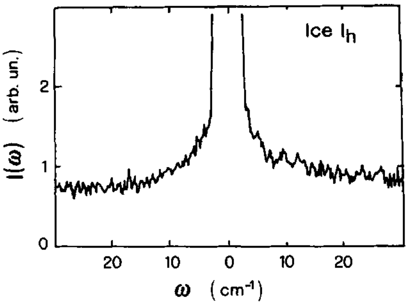

Fig. 2. Low frequency Raman spectrum of ice I_h.

from those of the iodine ions. The light scattering spectrum will thus reflect both the dynamics of the iodine ions and the diffusive motion of the Ag^+ ions. As a matter of fact, the only observable contribution comes from the AgI relative motion. This means that the $C(\omega)$ coefficient will be ω-independent, at least for $\lambda \gg \Lambda$, i.e. the scattered intensity does not depend on frequency in the limit $\omega \rightarrow 0$.

As sometimes happens with classification schemes, ours is far from being exhaustive; there are solids where DILS cannot be explained by either theory. In this context, the most interesting systems to us are hydrogen bonded (HB) solids. Several measurements on such systems (ice I_h, KDP) established that $I(\omega)$ is indeed ω-independent in the low-frequency region (Fig. 2). This is in strong contrast with the high degree of dynamic correlation present in HB systems. This apparent failure can be found in the following fact, tacitly assumed in the above discussion; the mechanism of induced polarizability is well described by regular and smooth functions of the distance between different scattering units ("regular" mechanisms). In this case the renormalized atomic (or molecular) polarizability expansion in terms of displacements can be truncated at the one-phonon term, higher-order terms being negligible. However in HB solids, due to the rearrangement of electronic states, the effective polarizability of a given unit is drastically changed even for a small displacement of the atoms from their equilibrium positions, where the polarizability of the unit is thought to attain its maximum (or minimum) value. This clearly leaves room for multiphonon terms, whose existence may significantly alter the shape of $I(\omega)$ in the low-frequency region.

Along these lines we now present an explicit model to treat $I(\omega)$ in the long-wavelength limit in HB solids. In the following we shall confine ourselves to the statement of the problem and to the final result of the calculation. All formal matters will be left aside, being part of a separate paper [5].

FORMULATION OF THE MODEL

The model is formulated with reference to a system composed by incoherent scatterers; the polarizability is very strongly dependent on the relative distance between units, in agreement with the qualitative picture sketched at the end of the Introduction. We consider the following form for the mutual induced polarizability between units i and j

$$\Pi_{\alpha\beta}(t)=\Delta\Pi_{\alpha\beta}\exp[-(\bar{u}^{ij}(t)\cdot\hat{R}^0)^2/2\sigma^2] \tag{2}$$

where $\bar{u}^{ij}(t)=\bar{u}^i(t)-\bar{u}^j(t)$ is the relative displacement and $\bar{R}^0=\bar{x}^i-\bar{x}^j$ is the relative distance between the equilibrium positions of the units. In eqn. (2) the hat indicates a unit vector.

Besides the fact that it gives a reasonable description at a phenomenological level, this particular functional form was forced on us by computational necessity; it should be noted that it allows the existence of multiphonon even terms only.

The link with experiment is via the Fourier transform (FT) of the classical polarizability auto-correlation function

$$I_{\alpha\beta}(\omega)=\int dt\,\exp(i\omega t)\langle\Pi_{\alpha\beta}(t)\Pi_{\alpha\beta}(0)\rangle=[\Delta\Pi_{\alpha\beta}]^2\int\exp(i\omega t)c(t)dt \tag{3}$$

where $\langle\ \rangle$ denotes thermal average.

The calculation may be summarized in the two following steps: (i) within the harmonic approximation one uses the normal mode expansion to rewrite the arguments in the exponential factors in a more tractable form; and (ii) by means of successive linear transformations the thermal average is reduced to the calculation of gaussian integrals.

The final result for $c(t)$ is

$$c(t)=\frac{1}{\sqrt{[1+f(0)]^2-[f(t)]^2}} \tag{4}$$

with

$$f(t)=4K_B T\sum_{\bar{k}\chi}\frac{|\Gamma_{\bar{k}\chi}|^2}{\omega_\chi(\bar{k})}\cos[\omega_\chi(\bar{k})t] \tag{5}$$

where $|\Gamma_{\bar{k}\chi}|^2$ contains the dynamics [5]. Note that no approximations have so far been made in the calculation, apart from the harmonic hypothesis. We now assume a dispersion relation of the Debye form and consider only longitudinal acoustic phonons in the long wavelength-limit $k\to 0$. The above relation simplifies to

$$f(t)=\frac{1}{5}\frac{K_B T}{Mc_L^2}\frac{|\bar{R}^0|^2}{\sigma^2}3(\omega_D t)^{-3}\{2\omega_D t\cos(\omega_D t)+[(\omega_D t)^2-2]\sin(\omega_D t)\} \tag{6}$$

The basic role is played by the parameter $A=(K_B T/Mc_L^2)(|\bar{R}^0|^2/\sigma^2)$ through the product of two adimensional quantities: $(K_B T/Mc_L^2)$, the square of the ratio of the thermal velocity to the sound velocity of the system, and $|\bar{R}^0|^2/\sigma^2$,

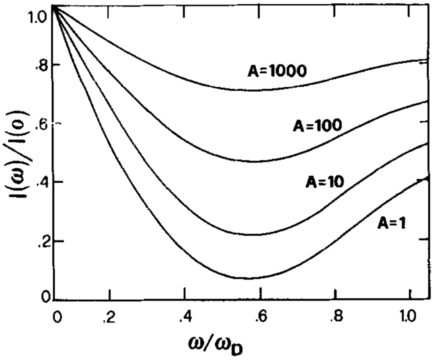

Fig. 3. Low frequency part of the spectrum of the scattered light calculated according to our model. The different curves refer to different values of the parameter A (see text). All the spectra have been purified from the $\delta(\omega)$ contribution and have been normalized to $I(0)$.

the ratio of the nearest-neighbour distance to the length scale of the induced polarizability function. $I(\omega)$ curves calculated via eqn. (6) are plotted in Fig. 3 for different values of A. It is immediately apparent that for $\omega \to 0$, $I(\omega)$ increases; adding this contribution to the one-phonon term (coming from "regular" mechanisms) we see that the two could well conspire to give a constant behaviour in $I(\omega)$ for $\omega \to 0$. Thus we have found a mechanism, at least on a qualitative basis, to account for the existing low-frequency data. However, the use of this model must be justified on a more sound physical basis: this will be the subject of the next section.

APPLICATION TO ICE I_h

We shall now focus our attention on a particular system, that is ice I_h. In the structure of ice in the hexagonal phase the oxygen atoms form an ordered sublattice with each oxygen atom surrounded, at a distance of about 3 Å, by four equivalent oxygens in a tetrahedral coordination (see Fig. 4). On the contrary, as established from X-ray diffraction measurements, the hydrogen sublattice is disordered. The hydrogen atoms are localized off-centre on each O–O bond, at a distance of about 1 Å from one of the two oxygens. All the protons are arranged so as to preserve the molecular character of the crystal, i.e. on the four bonds pertaining to a given oxygen there are two hydrogen atoms "close" and two "far" from that oxygen. Therefore within each O–O bond there are two possible equilibrium positions for hydrogen, but in order to preserve the molecular integrity, there is no possibility of displacing any proton from one equilibrium position to the other without getting other protons involved. However, it should be noted that there are situations where the rearrangement of six protons (all belonging to the same hexagon formed by the oxygen atoms in the ice I_h structure) will be independent from all other protons. A rough eval-

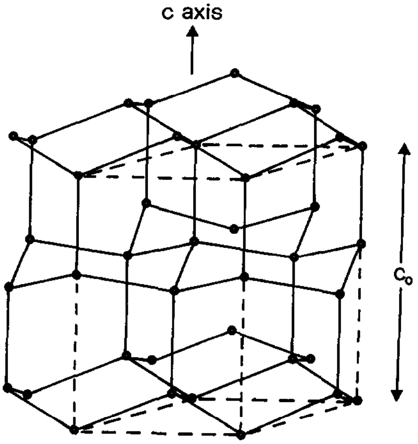

Fig. 4. Arrangement of the oxygen atoms in ice I_h.

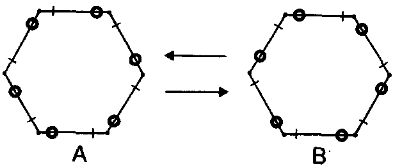

Fig. 5. The two possible arrangements of hydrogen atoms in a "hexagon" which give rise to delocalization of the proton wavefunction. The oxygen atoms are at the corners of the (non-planar) hexagons while the hydrogen atoms (●) occupy one of the two equivalent positions (+). Going from situation A to B all the protons shift counterclockwise.

uation shows that this happens with probability $p \approx 0.01$. This fraction of the total number of hexagons we shall refer to as "activated" units.

It is interesting to calculate the potential energy that the whole crystal acquires when the six protons of an activated unit move together, each along its bond (Fig. 5). We have calculated the energy of a single hexagonal loop of water molecules; the six oxygen atoms are placed at the sites of the ice I_h lattice and the protons are placed in an activated configuration, as a function of the parameter ρ, i.e. the (common) distance along the bond of all the protons from one of the nearest oxygens. The calculation has been performed in the Hartree–Fock scheme. This has been accomplished using the GAUSSIAN 88 program [9] with the STO-3G basis set for the radial functions. The result is shown in Fig. 6, where the double-well structure is clearly visible with two minima at $\rho = 1$ Å and $\rho = 1.75$ Å.

The above picture is entirely classical: the correct picture is one in which tunnelling amongst the two different equilibrium configurations occurs. Protons are delocalized with wavefunctions either symmetric or antisymmetric; as a consequence the electronic clouds are also more delocalized and therefore

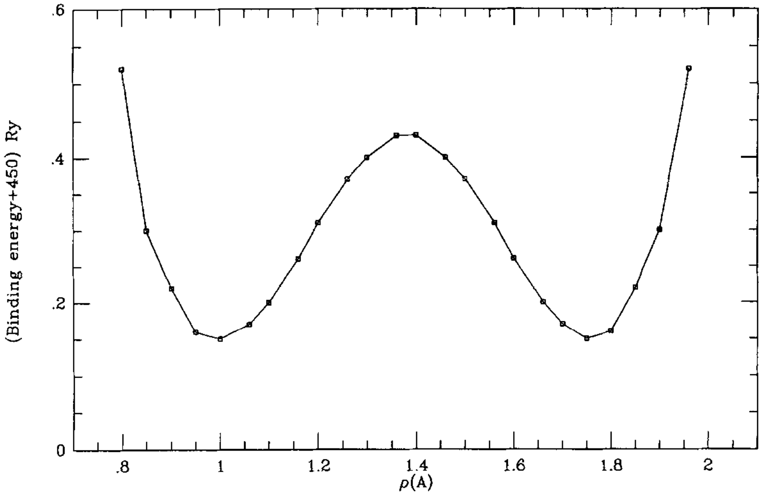

Fig. 6. Binding energy of a single hexagonal loop as a function of the ρ distance (see text). The full line drawn through the points serves merely as a guide for the eye.

more "polarizable". If we now add phonons to this picture the symmetry of the proton hamiltonian is broken; even small displacements from the equilibrium position cause the six protons to be projected into localized states on one side of the bonds reducing the polarizability of the units. Thus the polarizability of the whole unit is drastically modulated by the thermal motion and this is the physical mechanism underlying our model.

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