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Depolarized Raman scattering in normal and supercooled antimony trichloride

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Depolarized low frequency Raman spectra obtained for molten antimony trichloride are discussed. Measurement has also been performed on the supercooled liquid down to 53.2° below the melting point ($t_m = 73.4^\circ\text{C}$). The experimental results indicate that the spectral contributions, in the range 2–100 cm^{-1} of Stokes shift from the exciting line are due to: (1) a central Lorentzian line, whose width and intensity are connected to the dynamics of the break-up of intermolecular chlorine bridges; and (2) a solidlike contribution that furnishes an effective density of states, which corresponds to a convolution of “acoustical” and “optical” modes in a coupled linear chain structure with middle range order.

I. INTRODUCTION

Recently, much attention has been focused on the structure of crystalline^{1,2} and molten SbCl_3 .^{3–5} The solid crystalline phase⁶ is molecular in nature with pyramidal basic units, having a mean Sb–Cl distance of 2.36 Å and a Cl–Sb–Cl bond angle of 95° . These values are very similar to those found for liquid^{4,5} and gaseous SbCl_3 .⁶ Near the melting point (73.4°C), this compound is an associated liquid with high relative dielectric constant,⁷ low autoionization constant and a low electrical conductivity.⁸ For these properties, in the liquid state, SbCl_3 behaves like the liquid water, and in addition acts as a good solvent for organic solutes.

The structural arrangement of molten SbCl_3 is far from being random. In fact recent x-ray and neutron diffraction experiments⁴ have been interpreted on the basis of the reference interaction site model⁵ in terms of pyramidal molecules that are attached by means of chlorine bridges to form a chain structure. The intermolecular mean Sb–Cl distance is about 3.4 Å and the dipole axes of the molecules are strongly correlated, up to 2–3 molecular diameters. Such a correlation is probably responsible for the high dielectric constant of molten SbCl_3 near the melting point. Furthermore, the chains interact through van der Waals forces, and this implies a middle range connectivity for the system.

The dynamical properties of crystalline and liquid SbCl_3 have been studied recently² by means of Raman spectroscopy. In particular, the intensity and the frequency of the optical phonons have been analyzed near the solid–liquid transition. Furthermore, for the liquid phase, the intramolecular stretching modes in the region 250 to 450 cm^{-1} (of frequency shift), and the corresponding bending modes in the region 100 to 200 cm^{-1} ,

have been shown to be in agreement with previous measurements.^{9,10} Finally, we have shown² that in molten SbCl_3 in the region 10 to 100 cm^{-1} of Stokes shift, there is a contribution to the anisotropic spectra that is typical of a vibrational density of states.

The aim of the present work is to investigate in detail the very low frequency region of anisotropic Raman spectra, as a function of temperature both in the normal liquid and in the supercooled liquid phases. It will be shown that a Rayleigh central component is present in the depolarized (or anisotropic) spectra. The latter can be described in terms of a Lorentzian component whose intensity and width are temperature dependent. Moreover these spectral contributions can be interpreted as due to the kinetics of the process of breaking and forming chlorine bridges between SbCl_3 molecules. In addition to this dynamic structural contribution, there is also a projected density of states that is the convolution of the true density of states $g(\omega)$ with the mode dependent matrix elements. This Raman effective density of states^{11,12} (typical of amorphous materials), is temperature independent in the case of liquid SbCl_3 and, in the very low frequency region, shows an “acoustic”-like (ω^2) behavior.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The Raman measurements were performed on ultra-pure SbCl_3 samples prepared similarly to the one used for the previous work.² The sample was thrice-sublimated and sealed in an optical quartz tube under low Ar pressure (~ 0.5 atm). The measurements, performed with the Raman apparatus described in detail elsewhere,^{2,13} have been made by using a specially built optical thermostat. Measurements were performed at 180.0, 130.2, 80.1, 78.9, 31.0, and 20.1°C , while the temperature was constant, in all the range studied,

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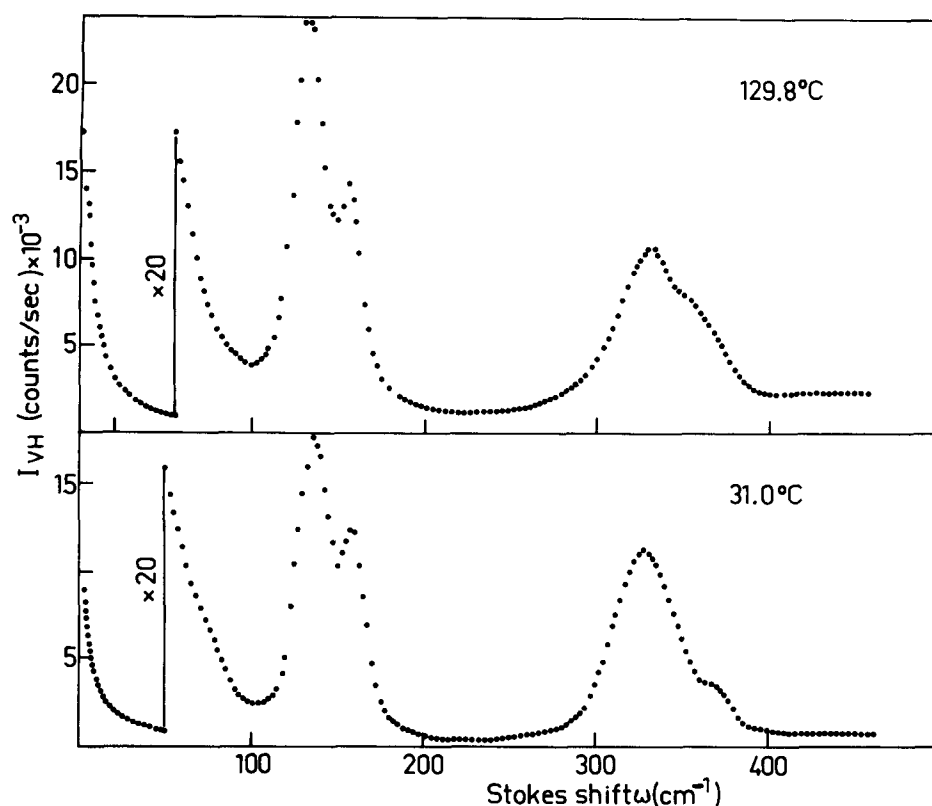


FIG. 1. Typical depolarized Raman spectra for molten SbCl_3 at 129.8°C (normal region) and 31.0°C (supercooled region).

within 0.02°C. As exciting source we have used the 5145 Å line of an Ar^+ ion laser with 500 mW of optical power. Because of the high optical purity of the sample we could record spectra down to 2 cm^{-1} of Stokes shift for both VV and VH polarization in a 90° scattering geometry. For all the spectra the resolution was 0.4 cm^{-1} in the range 2–20 cm^{-1} and 2.5 cm^{-1} in the range 15–450 cm^{-1} . The digitalized experimental data were processed by means of a PDP MINC 11 system. The high chemical purity of the salt has allowed us to perform measurements down to 53.3° below the melting point. The experimental data were normalized to the intensity of the incident beam, which was continuously monitored. Furthermore, the spectra were corrected for the temperature dependence of the density and for refractive index and internal field.^{14,15} (A detailed description of the correction procedure can be found in Ref. 30.) The values of the densities and of the refractive indexes were taken from the literature.⁸

Figure 1 shows typical examples of depolarized Raman spectra for molten and supercooled SbCl_3 . It will be noted that in addition to the contribution of the intramolecular stretching modes at 300–400 cm^{-1} and the contribution of intramolecular bending modes at 100–200 cm^{-1} , there is also a large contribution in the low frequency region.

We will now discuss this last spectral contribution within the framework of current theories.

III. ANALYSIS OF THE DEPOLARIZED SCATTERING MECHANISM

In order to understand how the structural properties influence the dynamics of the vibrational modes in mol-

ten and supercooled SbCl_3 , it is important to note that in disordered systems such as liquids and amorphous materials, although the isotropic component of the spectrum is directly connected with the eigenmodes of the system, the anisotropic component $I_{\text{anis}}(\omega)$ may be interpreted in terms of a vibrational density of states.^{16,17} In fact, due to the breakdown of the crystalline momentum selection rule, the Raman (or IR or inelastic incoherent neutron scattering) spectra give rise to a density of states similar to the one-phonon density of states of the corresponding crystal,¹¹ although somewhat broader. Once the contribution $I_{\text{anis}}^{(v)}(\omega)$ of the collective modes to the Raman spectrum is known, a Raman effective density of states^{12,13} $g_{\text{eff}}^R(\omega)$ can be obtained through the equation

$$g_{\text{eff}}^R(\omega) = (\omega_0 - \omega)^{-4} \omega \cdot \frac{1}{n(\omega, T) + 1} I_{\text{anis}}^{(v)}(\omega), \quad (1)$$

where ω is the Stokes frequency shift and ω_0 is the frequency of the incident beam; $(\omega_0 - \omega)^{-4} \omega$ takes into account the Stokes extraradiation factor and the dielectric fluctuation correlation factor in the quasiharmonic approximation, while

$$n(\omega, T) + 1 = \left[\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right]^{-1} + 1$$

is the appropriate Bose-Einstein population factor. The $g_{\text{eff}}^R(\omega)$ is also related to the true density of states $g(\omega)$ through the relation

$$g_{\text{eff}}^R(\omega) = P(\omega)g(\omega), \quad (2)$$

where $P(\omega)$ is a Raman mode dependent¹¹ coupling function.

Raman spectra of disordered materials such as mo-

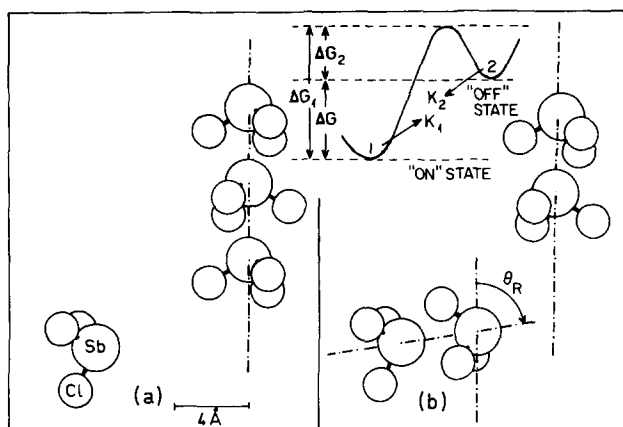


FIG. 2. Schematic view of the intermolecular arrangement in molten SbCl_3 . The insert shows the transition between bound and free molecules (see Sec. IV for details).

lecular crystals,^{17,18} amorphous semiconductors,¹¹ superionic,^{19,20} and structured liquids^{2,13,21-23} have been successfully analyzed in this framework. In particular, for liquids like B_2O_3 ²² and ZnCl_2 ¹³ in which only a small number of bonds are broken upon melting, or for liquids like concentrated electrolytic solutions^{24,25} in which the structural arrangement is similar to that of the corresponding hydrated crystals, the vibrational modes seem to be collective in character.²⁵

The concepts mentioned above, as already stressed,² can be applied to molten SbCl_3 . In this system near the melting point, the bond connectivity due to chlorine bridges^{4,5} allows the existence of collective excitations. In addition, in the spectral range $2.0\text{--}20\text{ cm}^{-1}$, due to the relaxation of hydrodynamic modes (structural relaxation, reorientational motions, etc.), we find an anisotropic quasielastic contribution that is typical of many liquids.¹⁴ This quasielastic component of the spectrum is related to the temporal correlation function of the anisotropic part of the polarizability tensor.¹⁴ Depending on the various mechanisms (jump diffusion, extended diffusion, small step diffusion, etc.) involved in the scattering process, $C_\beta(t)$ and its Fourier transform $I_{\text{anis}}(\omega)$ are characterized by various relaxation times. It has been shown^{14,16} that for "structure limited" or "associated" liquids, e.g., H-bonded liquids, there exists a structural relaxation time τ_s that can be related to the energy of the bonds. The value of τ_s is generally lower or at most of the same order of magnitude as the reorientational relaxation time τ_R .

As we have seen, the physical properties of molten SbCl_3 are such⁵ that the structural contributions to the Raman spectra can be analyzed in the same framework of the associated liquids.²⁶ In fact, one can expect that only a free molecule can easily reorient itself. A pictorially simple representation of the process is shown in Fig. 2 for the case of SbCl_3 . In the insert of the same Fig. 2, the energy path for the activated process for the breaking of the chlorine bridge is shown. We will discuss this process in detail in the next section. The relaxation and reorientational contributions to the intensity are therefore given by two Lorentzian compo-

nents $\mathcal{L}_s(\omega)$ and $\mathcal{L}_R(\omega)$ centered at zero, with HWHM Γ_s and Γ_R equal to $(2\pi c\tau_s)^{-1}$ and $(2\pi c\tau_R)^{-1}$, respectively. In conclusion we can write the anisotropic Raman scattering in the form

$$I_{\text{anis}}^{\text{tot}}(\omega) = \mathcal{L}_R(\omega) + \mathcal{L}_s(\omega) + I_{\text{anis}}^v(\omega) \propto \omega_0^4 \left(\frac{A_R \Gamma_R^2}{\Gamma_R^2 + \omega^2} + \frac{A_s \Gamma_s^2}{\Gamma_s^2 + \omega^2} \right) + (\omega_0 - \omega)^4 \cdot P(\omega) g(\omega) \cdot \frac{[n(\omega, T) + 1]}{\omega}. \quad (3)$$

It is important to notice that in the $2.0\text{--}20\text{ cm}^{-1}$ region of Stokes shift, both the quasielastic and the collective contributions to the Raman intensity are present; the component due to the density of states becomes equal to a constant (C), under the assumptions that $P(\omega)$ is ω independent (as suggested in Ref. 22 for molten B_2O_3 and in Ref. 13 for molten and glassy ZnCl_2) and that $g(\omega) \sim g_{\text{acoustic}}(\omega) \sim \omega^2$ [the $g_{\text{opt}}(\omega)$ contribution lies in the higher spectral range].

IV. DISCUSSION OF THE EXPERIMENTAL DATA

In our spectra, only one simple Lorentzian contribution seems to be present in the low frequency region. The existence of two Lorentzian contributions has been reported in the literature for other systems. For example in the case of liquid H_2O , Montrose *et al.*²⁷ have fitted the low frequency region of the depolarized Rayleigh wing, with two Lorentzians: one, \mathcal{L}_R , due to the reorientation of the molecules, and another, much broader \mathcal{L}_s , due to the breaking and forming the H bonds. The relaxation times τ_R and τ_s associated with the two processes as expected, obey the inequality $\tau_s < \tau_R$. In those cases when $\tau_s \ll \tau_R$ the line might be so narrow as to be undetectable with a conventional Raman spectrometer. The above mentioned inequality will hold more and more the heavier the molecule is and, hence, the larger the moment of inertia. In the case of SbCl_3 , it is reasonable to assume that the moment of inertia is large enough to make the line \mathcal{L}_R very narrow. We are currently performing experiments with a Fabri-Perot scanning interferometer to analyze the \mathcal{L}_R contribution. In all those cases when $\tau_s \ll \tau_R$, Eq. (3) can be written

$$I_{\text{anis}}^{\text{tot}}(\omega) \propto \frac{A_s \Gamma_s^2}{\Gamma_s^2 + \omega^2} + C. \quad (4)$$

Equation (4) can be rearranged as

$$(I_{\text{anis}}^{\text{tot}}(\omega) - C)^{-1} \propto \left(\frac{1}{A_s} + \frac{\omega^2}{A_s \Gamma_s^2} \right), \quad (4 \text{ bis})$$

where C assumes the value that makes the left-hand side of (4 bis) a linear function of ω^2 .¹³ The remaining two parameters A_s and Γ_s can be obtained from the intercept and slope. Figure 3 shows the lines obtained at the different temperatures indicated. The numerical values of A_s , Γ_s , and C are shown in the insert of Fig. 3. Once the values of Γ_s are known, the corresponding values of τ_s can be calculated. When these values are plotted versus the corresponding reciprocal absolute temperature, a straight line is obtained; this fact suggests the existence of a thermally activated relaxation process. All these results can be rationalized with a reasonably simple two-state model of liquid SbCl_3 . More specifically we assume the existence of intact and

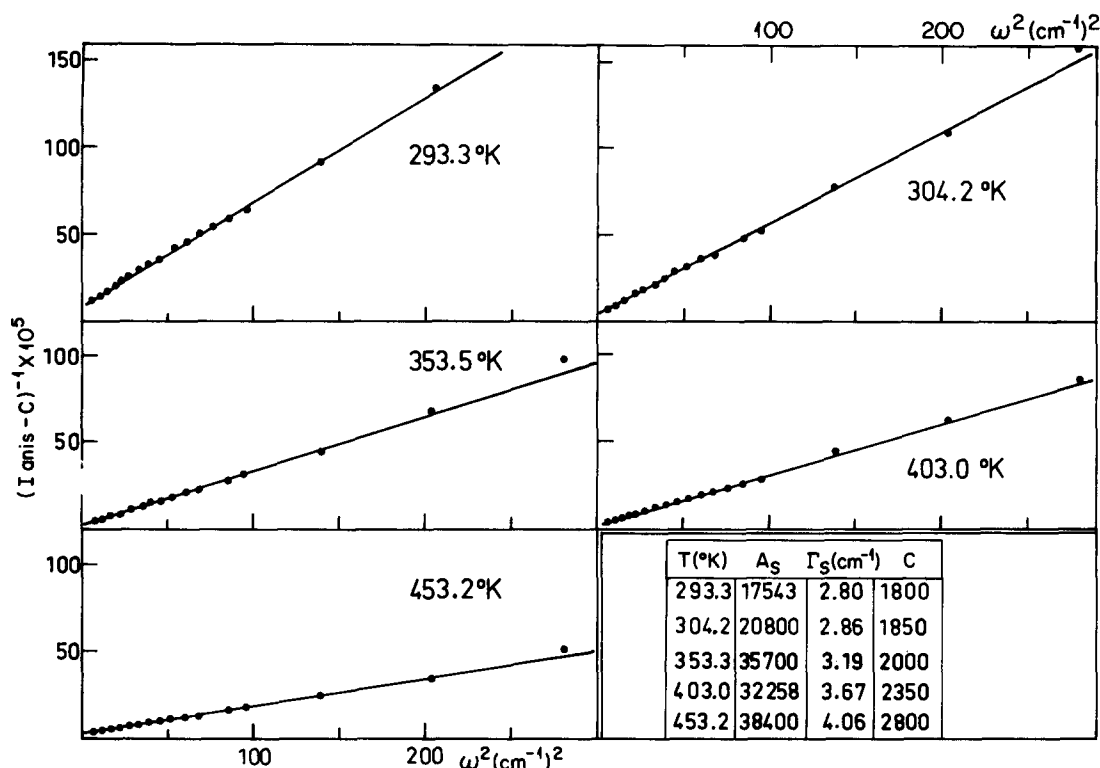


FIG. 3. Plot of the central Lorentzian band [see Eq. (4 bis) of the text] in molten SbCl_3 at different temperatures. The corresponding values of A_s , Γ_s , and C are also reported.

of broken bonds (states “on” and “off” in the insert of Fig. 2). The transition from one state to the other one is considered to be a thermally activated process (i.e., it takes place through a potential barrier ΔG_2). The existence of two possible states for the molecules implies that the anisotropic component of the polarizability tensor is modified according to the level of occupancy of the two states. Furthermore, we assume that the correlation of the fluctuations of the polarizability tensor decays exponentially with time, giving rise to the Lorentzian \mathcal{L}_s previously mentioned. As a consequence the width of the Lorentzian Γ_s will contain information about the activation energy (height of the barrier), while the integrated intensity could be related to the binding energy (difference between the energies of the “on” and the “off” states). An analogous “bond-lattice” model has been successfully used elsewhere to describe the liquid state properties.²⁹

V. DESCRIPTION OF THE MODEL AND INTERPRETATION OF THE DATA

Let us call n_1 and n_2 the number of intact and broken bonds between SbCl_3 molecules in the scattering volume of the sample. The equilibrium between the on and off states can be described in terms of the reaction²⁸



where

$$k_i \sim \exp(-\Delta G_i/RT). \quad (6)$$

We now assume that from the point of view of the

kinetics, the partial “reactions” of (5) are both unimolecular and of the first order. This assumption is not only reasonable, but it is also valid. Then under conditions of equilibrium:

$$\frac{n_2^0}{n_1^0} = \frac{k_2}{k_1} = \exp(-\Delta G/RT). \quad (7)$$

The probability of finding a bond in the “on” state is hence

$$p_B = \frac{n_1^0}{n_1^0 + n_2^0} = \frac{1}{1 + \exp(-\Delta G/RT)}, \quad (8)$$

while the rate of transition will be

$$\frac{dn_1}{dt} = -k_1 n_1 + k_2 n_2. \quad (9)$$

The solution of differential equation (9) is

$$n_1(t) = A \exp(-k_1 - k_2)t + n_1^0, \quad (10)$$

which shows that the fluctuations around the equilibrium value decay exponentially in time, with time constant $\tau_s = (k_1 + k_2)^{-1}$. The magnitude of the fluctuations is given³¹ by

$$\overline{n_1^2} - (\overline{n_1})^2 = \overline{n_2^2} - (\overline{n_2})^2 = \frac{n_1^0 \cdot n_2^0}{n} \propto p_B(1 - p_B). \quad (11)$$

The integrated intensity of the Lorentzian \mathcal{L}_s that is connected to $\overline{n_1^2} - (\overline{n_1})^2$ is therefore suitable for the calculation of p_B and hence the binding energy ΔG . In particular, Eq. (11) shows that I_s is an increasing function of the temperature and is in agreement with the experimental results. It is to be noted that the same behavior

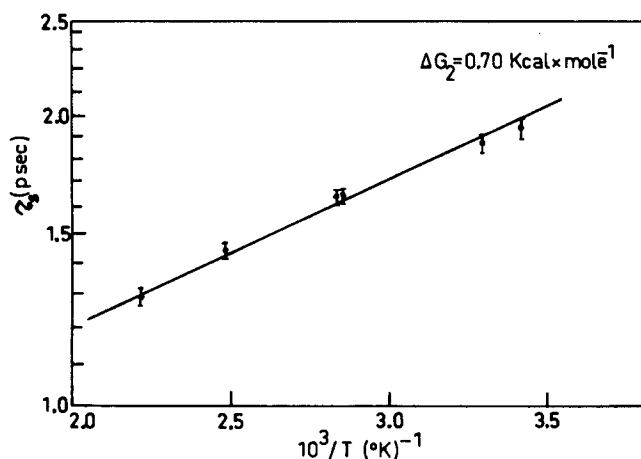


FIG. 4. Relaxation time vs reciprocal absolute temperature for molten SbCl_3 . The solid line is an Arrhenius fit to the experimental data.

has been reported for liquid water.²⁷ The fitting of the experimental data with Eq. (11) is shown in Fig. 5. For the binding energy we obtain the value $\Delta G = 2.4 \text{ kcal mol}^{-1}$. As far as the time constant τ_s is concerned, the experimental data are well fitted (see Fig. 4) with a straight line in a semilog plot. Such a circumstance indicates that $\Delta G_2 \ll \Delta G_1$ and from the slope of the line we obtain the value $\Delta G_2 = 0.7 \text{ kcal mol}^{-1}$. By combining this value with the binding energy ΔG , we obtain $\Delta G_1 = \Delta G_2 + \Delta G = 3.1 \text{ kcal mol}^{-1}$. It is interesting to note that the experimental heat of vaporization for SbCl_3 lies between 2.4 and 3.0 kcal mol^{-1} .⁸ These values match the value of ΔG just found by us.

Taking into account Eq. (3), it is possible to obtain the Raman effective density of states $g_{\text{eff}}^R(\omega)$ by subtracting the \mathcal{L}_s contribution from the experimental $I_{\text{anis}}^{\text{total}}(\omega)$. In the low-frequency region (between 2 and

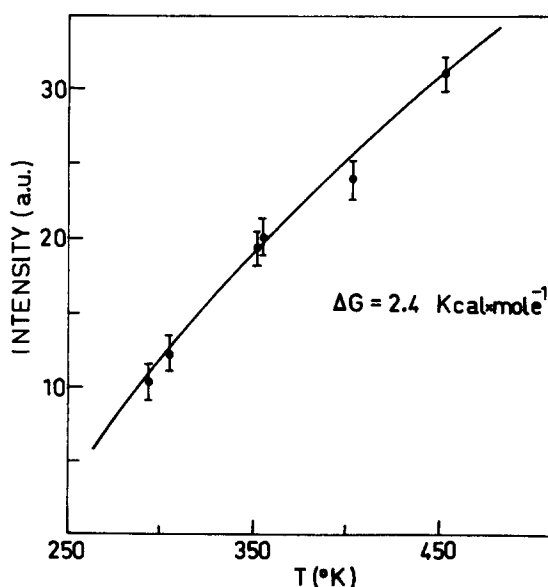


FIG. 5. Temperature dependence of the integrated intensity of the Lorentzian \mathcal{L}_s . The points are experimental data and the solid line is the fit obtained with Eq. (11) of the text.

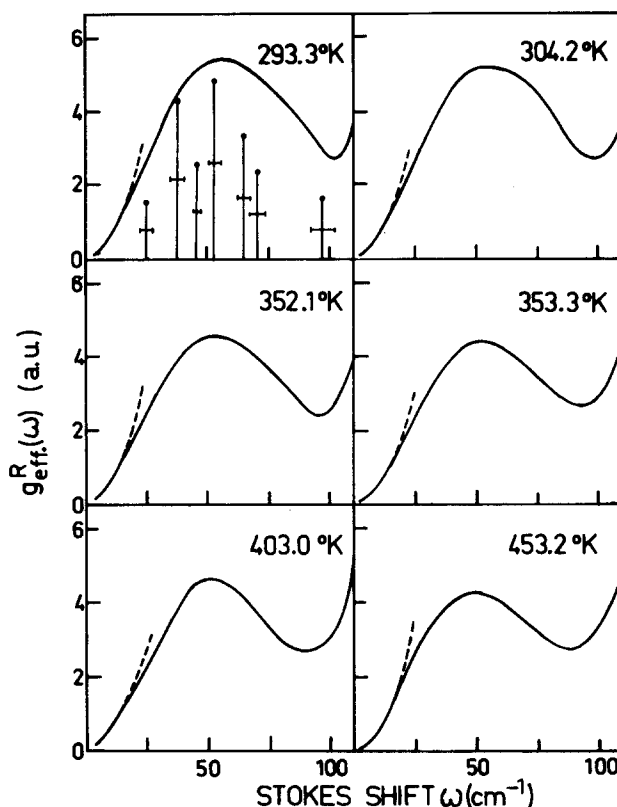


FIG. 6. Low frequency Raman effective density of states $g_{\text{eff}}^R(\omega)$ at various temperatures. In the curve corresponding to $T = 293.3 \text{ K}$, the optical phonons of solid SbCl_3 are shown for comparison.

18 cm^{-1}), the only contribution is furnished by the acoustical mode. Between 18 and 100 cm^{-1} both acoustical and optical modes contribute to the density of the states. Such a spectral region is shown in Fig. 6. For $T = 293.3 \text{ K}$, the low frequency optical phonons of crystalline SbCl_3 are also shown for comparison. The dashed lines are parabolic eye guides, to show that the acoustical contribution is the dominant one in the very low frequency region of the spectrum.

Another interesting feature of the spectra presented in Fig. 6 is the lack of sensitivity of the various curves to the temperature. In other words, the temperature dependence of the spectra is entirely contained in the Bose-Einstein population factor. Such a circumstance, as well as the occurrence of the optical contribution in the liquid in the same frequency region of the corresponding optical phonons of the crystal, strongly support our initial idea that the spectral modes are collective in character, i.e., the liquid is characterized by an effective density of states. Finally, for frequencies larger than about 100 cm^{-1} (Fig. 1), the density of states will contain the higher frequency contributions coming from the bending and the stretching of the units SbCl_3 connected in chains. More details about this point can be found in Ref. 2.

VI. CONCLUDING REMARKS

The analysis of the dynamic properties of molten SbCl_3 in the normal and supercooled region allows us to

draw the following conclusions:

(1) A quasielastic (Rayleigh) component is present, that is Lorentzian in shape and whose HWHM and intensity are related to the dynamic fluctuations in the number of chlorine bridges in a linear chain coordination. The experimental data are discussed in terms of a simple thermodynamic model that allows the evaluation of the main parameters implied. We have shown that the process of breaking a bond in a chain is thermally activated. The binding energy has been calculated to be 2.4 kcal mol⁻¹, while the reverse barrier height has been shown to be 0.7 kcal mol⁻¹. The resulting model agrees well with the structural arrangement previously proposed^{4,5} on the basis of scattering experiments. The remarkable agreement between the binding energy here obtained (2.4 kcal mol⁻¹) and the reported value⁸ of the heat of evaporation (2.7 ± 0.3 kcal mol⁻¹) is very interesting.

(2) A collective contribution is also present in the total intensity $I_{\text{anis}}^{\text{tot}}(\omega)$; this becomes evident when the Lorentzian \mathcal{L}_g is subtracted from the spectra. We obtained a Raman effective density of states which, in the low frequency region, is a convolution of acoustical and optical modes. By comparison between the spectra of molten and crystalline SbCl₃, it is evident that the $g_{\text{eff}}^R(\omega)$ for the disordered phase is a smooth version of the one-phonon density of states of the ordered phase. Finally, under the assumption that the acoustical contribution behaves like a Debye continuum elastic, the 2.0–18 cm⁻¹ region is very well fitted by a ω^2 law, strongly supporting the idea that collective vibrations are present in the system. We believe that an appropriate inelastic neutron scattering experiment could detect more directly this cooperative behavior.

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