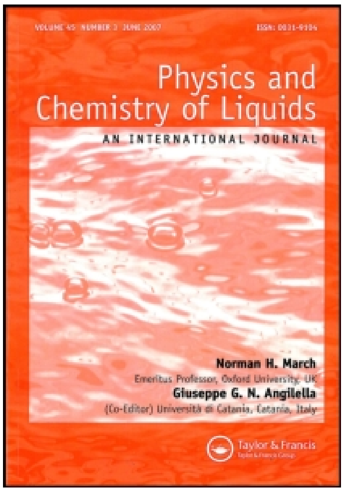

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Raman scattering studies of ionic → molecular transitions in $AlCl_3$, near the melting point

F. Aliotta[a]; G. Maisano[a]; P. Migliardo[a]; C. Vasi[a]; F. Wanderlingh[a]; R. Triolo[b]; G. P. Smith[c]
[a] Istituto di Fisica dell'universita di Messina and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Richerche, Messina, Italy [b] Istituto di Chirnica Fisica dell'Universita di Palerrno, Palermo, Italy [c] Oak Ridge National Laboratory, Tennessee, USA

To cite this Article Aliotta, F. , Maisano, G. , Migliardo, P. , Vasi, C. , Wanderlingh, F. , Triolo, R. and Smith, G. P.(1983) 'Raman scattering studies of ionic → molecular transitions in $AlCl_3$, near the melting point', Physics and Chemistry of Liquids, 12: 3, 225 — 235
To link to this Article: DOI: 10.1080/00319108308084556
URL: http://dx.doi.org/10.1080/00319108308084556

Phys. Chem. Liq., 1983, Vol. 12, pp. 225-236
0031-9104/83/1203-0225$18.50/0

Raman Scattering Studies of Ionic → Molecular Transitions in $AlCl_3$ Near the Melting Point

F. ALIOTTA, G. MAISANO, P. MIGLIARDO, C. VASI, and F. WANDERLINGH

Istituto di Fisica dell'Universita di Messina and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Richerche 98100 Messina, Italy.

R. TRIOLO

Istituto di Chimica Fisica dell'Universita di Palermo 90123 Palermo, Italy.

and

G. P. SMITH

Oak Ridge National Laboratory, Oak Ridge, Tennessee, 37830, USA.

(*Received September 25, 1982*)

Raman spectroscopic studies of solid $AlCl_3$ as a function of the temperature were performed up to the melting point ($T = 193.3°C$). Measurements were also performed on molten $AlCl_3$, known to be a molecular liquid. In particular, the evolution of the dynamical properties of the system was studied near and through the solid-liquid transition. The temperature evolution of a phonon mode centered at 196 cm^{-1} seems to herald the melting transition, and we identify this phonon as the soft mode theoretically foreseen by March and Tosi.(2)

Furthermore, our analysis of the Raman data in the melt provided an interpretation of the quasi-elastic central component (Rayleigh wing); its width gave an indication about the mean life time of intermolecular bonds. Finally, we detected a phonon-like contribution that gives an effective Raman density of states.

I GENERAL CONSIDERATIONS

The investigation of the vibrational properties of systems undergoing a structural phase transition represents one of the most challenging problems in lattice dynamics.(1) Very recently,(2, 3) the ionic to molecular transition was analyzed from a theoretical point of view for systems such as $AlCl_3$,

HgI_2, etc. in which a change takes place just after the transition occurs. In particular, as far as the aluminum chloride system is concerned, March and Tosi(2) investigated in some detail the melting transition from the ionic solid to molecular liquid, the molecule being $(AlCl_3)_2$. These authors, among other things, give a theoretical prediction of the possibility of a softening of a particular phonon mode that heralds the melting transition.

The physical and chemical properties of $AlCl_3$ have been extensively studied especially in the liquid phase. In fact, liquid mixtures of $AlCl_3$ and $SbCl_3$ are used as catalytically active solvents(4,5,6) for chemical reactions of polycyclic arenes; in addition $AlCl_3$ is used in technological applications.(7)

Crystalline $AlCl_3$ is an ionic compound with a layered structure.(8) The solid is monoclinic with four Al and twelve Cl per unit cell. Furthermore, an octahedral coordination of Cl around the aluminum ion with shared faces forms the above mentioned layered structure. However, it is to be noted that nuclear quadrupole resonance measurements(9) show a sizable degree of covalence in the Al–Cl bond. At the melting point, the aluminum atoms move from octahedral to tetrahedral sites in such a way that dimeric Al_2Cl_6 units are formed.

Near the melting point, the electrical conductivity(10,11) of solid $AlCl_3$ shows an anomalous behaviour as a function of the temperature. A large increase in the conductivity with increasing temperature is in fact observed in the 140 ÷ 190°C range, followed by a sharp drop at the melting transition. This anomalous behaviour has been explained on the basis of a jump diffusion of chlorine ions from octahedral to unoccupied tetrahedral sites randomly distributed. Such an abrupt drop of conductivity is due to the molecular nature of the liquid phase. Other authors,(12) however, suggest that this effect may be induced by the presence of impurities in the solid matrix.

As stressed above, molten $AlCl_3$ is a molecular liquid having $AlCl_3$ dimers as basic units. X-ray diffraction measurements(13) on molten $AlCl_3$ near the melting point show that the melt consists of $(AlCl_3)_2$ units in which each Al atom is surrounded by a tetrahedral arrangement of chlorine atoms and the two tetrahedra share an edge. It should be noted, however, that this structure is far from being regular, just as in vapor phase. The $(AlCl_3)_2$ molecules appear to be stretched in the Al–Al direction. This distortion from a regular double tetrahedron is interpreted in terms of interactions between intermolecular chlorine atoms. In fact, two maxima in the radial distribution function at high values of r (>7Å) (See Ref. 13 for details) seem to be due to intermolecular coordination.

The dynamical properties of $AlCl_3$ have been extensively studied in the gaseous(14,15) and liquid states, particularly in mixtures with alkali halides(16, 17) and with antimony trichloride.(18, 19) As far as the vibrational modes of dimer $(AlCl_3)_2$ are concerned, experimental Raman and IR data are fully explained by a normal coordinate analysis of the D_{2h} symmetry group. The aim of the present work was to perform a careful experimental analysis of the vibrational dynamics in solid $AlCl_3$ near the melting transition, together with the investigation of intramolecular effects in the liquid phase. It will be shown that there is a phonon mode that seems to go soft in accordance with March and Tosi's hypothesis.(2) Its center frequency, width and strength depend strongly on temperature (compared with other modes in the solid phase). Furthermore, the Raman spectrum of molten $AlCl_3$ shows all the intramolecular vibrational modes typical of the Al_2Cl_6 units present in the disordered phase. The anisotropic component of the spectrum in the low-frequency region indicates the presence of a central mode that can be assigned to the mean life time of the intermolecular bonding. In addition to this contribution, there is a projected density of states in the translational region(20) that takes into account the intermolecular connectivity of the system under examination.

II EXPERIMENTAL SECTION

The Raman experiments were performed on ultrapure $AlCl_3$ samples prepared at the Chemistry Division of the Oak Ridge Laboratory according to a procedure elsewhere described;(21) the only difference was that in the preparation of this sample HCl of electronic grade purity was used. In order to avoid any chemical contamination, the samples were handled in an argon atmosphere and sealed under vacuum in fused quartz optical cells. The purified salt was composed of clear colorless crystals, and the corresponding colorless melt was of very good optical quality. All measurements were performed in our laboratories with a Raman apparatus described in detail elsewhere(22, 23) and with the same cylindrical cell. Also measurements were performed as a function of the temperature both in the solid and the liquid phases. Temperature was controlled to within 0.02°C in all the ranges studied by means of a specially built optical thermostat. In the ordered phase we performed measurements at 53.3, 117.0, 171.3, 179.2, 184.2, 186.1, 189.2, 190.2, 190.9, 191.9, and 193.2°C. Because of the very small temperature range of liquid phase existence(24) (the melting and boiling points are practically coincident), and because of the high vapor pressure (>2 atm at 200°C), Raman spectra of the melt were measured only at 200.1°C, just above the melting point. Our sample melted at 193.3°C, in good agreement with literature data.(21) In order to avoid local heating, we used the 4880 Å line of an Ar^+ ion laser working with an optical power less than 50 mW for the crystal and less than 200 mW for the melt. The reproducibility of the measurements was checked by performing various runs as a function of temperature and, as the melting point was approached, we found it necessary to wait in order to reach thermodynamic equilibrium. Unpolarized Raman spectra were taken for the polycrystalline solid sample in the range of 10 → 450 cm^{-1} of Stokes shift with a resolution of 1.5 cm^{-1}. For the liquid state we recorded both I_{VV} and I_{VH} spectra in a 90° scattering geometry, with 2.5 cm^{-1} spectral resolution in the range 10 → 700 cm^{-1} of Stokes shift. In order to study very carefully the low frequency contribution in the liquid state, we took I_{VH} spectra with 0.25 cm^{-1} resolution in the $-10 \rightarrow +10\ \text{cm}^{-1}$ of the spectral range; with a resolution of 0.5 cm^{-1} in the $-15 \rightarrow +15\ \text{cm}^{-1}$ range, and with a resolution of 1 cm^{-1} in the $-25 \rightarrow +25\ \text{cm}^{-1}$ range. The digitized Raman data were automatically normalized for the incident beam intensity and were sent to a Digital MINC 11 system where all processing was performed.

In Figure 1 we report a typical unpolarized Raman spectrum for the solid sample near the melting point. Figure 2 shows the isotropic (2a) and

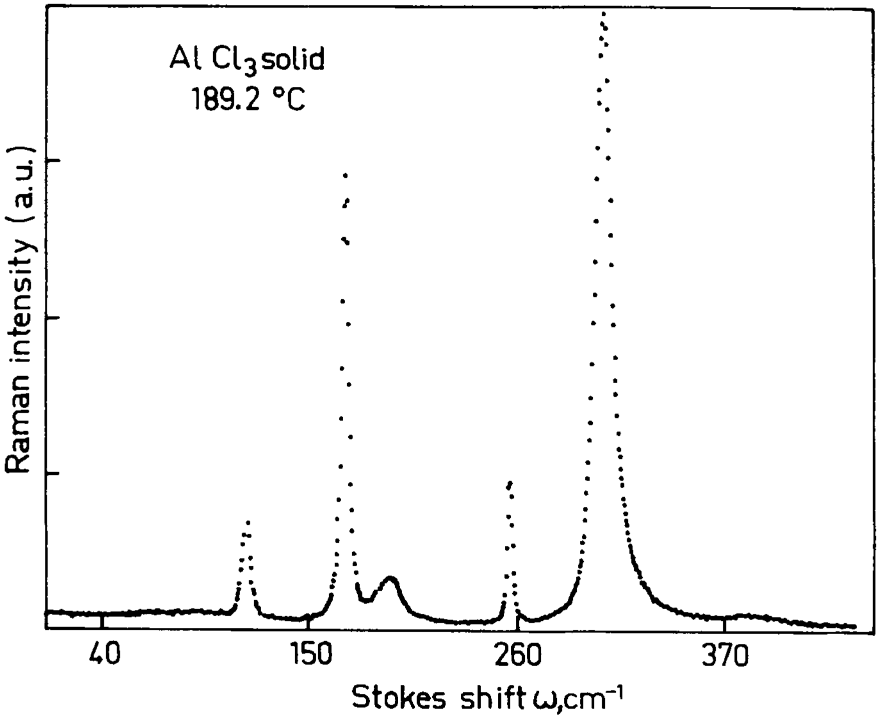

FIGURE 1 Unpolarized Raman spectrum in crystalline $AlCl_3$.

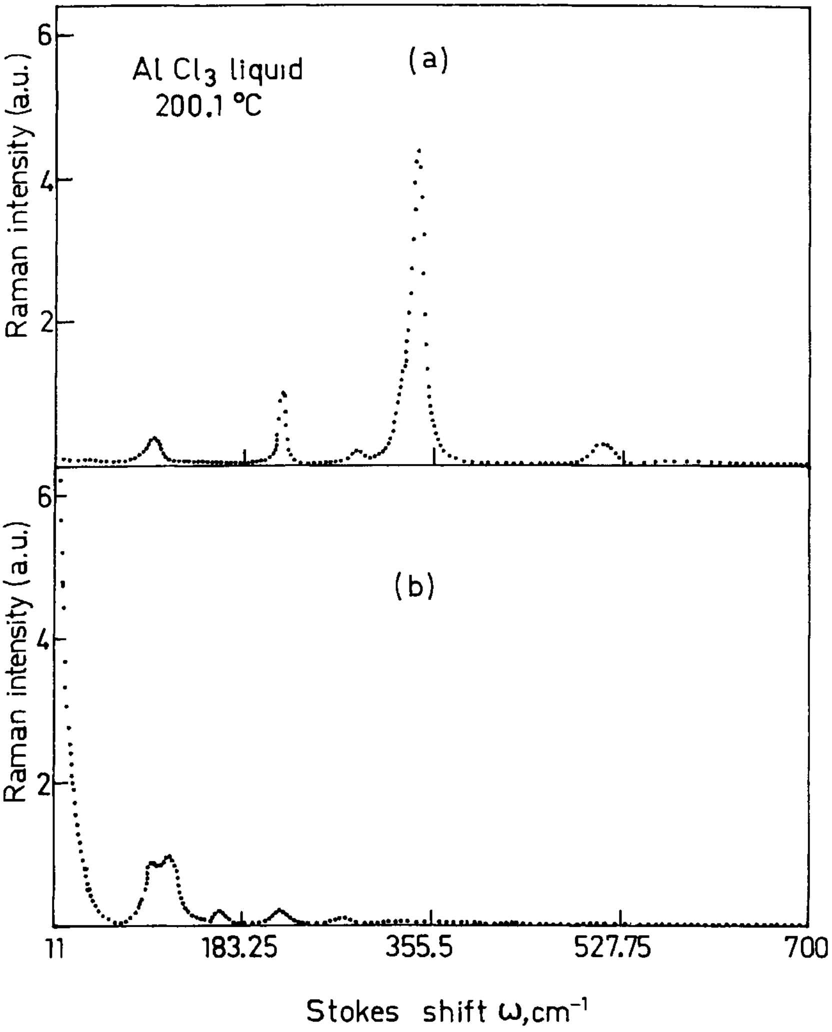

FIGURE 2 Isotropic (a) and anisotropic (b) Raman spectra for molten $AlCl_3$.

the anistropic (2b) Raman spectrum for 200.1°C. The isotropic spectrum, which is in essence due to a partially coherent light scattering(25) process, is obtained through the well-known relation $I_{IS} = I_{VV} - \frac{4}{3}I_{VH}$, and shows all 9 of the low modes of the Al_2Cl_6 dimeric units. The anisotropic Raman spectrum $I_{VH}(\omega)$ shows, among other things (see Figure 2b), a large Rayleigh wing in the low frequency spectral region.

III DISCUSSION OF THE EXPERIMENTAL DATA AND CONCLUSION

A comparison of Figure 1 and Figure 2 allows a qualitative identification of the optical phonon modes of the crystalline salt. As previously mentioned, calculations of force constants(15) performed on Al_2Cl_6 (regular double tetrahedron) allows us to assign the entire intramolecular spectrum for the melt with a suitable account of the distortion of the regular tetrahedron in the liquid. Then, by taking into account the local arrangement of the crystal, it is possible to find a correspondence between the optical modes of the melt and those of the crystal. Then it is possible to assume that the vibrations centered at 115 cm^{-1} ($\upsilon_4 - A_g$) and 169 cm^{-1} ($\upsilon_7 - B_{1g}$) of the Al_2Cl_6 structure with D_{2h} symmetry are present in the solid phase without large differences. The strong peak centered at 307 cm^{-1} can be identified with the highly symmetric ν_2–A_{1g} stretching mode present at 340 cm^{-1} in the molecule. Similarly, the mode centered at 285 cm^{-1} in the liquid corresponds to the 255 cm^{-1} mode of the solid. It is to be noted that at the melting point, both the 307 cm^{-1} and the 255 cm^{-1} optical modes suffer the same amount of frequency shift. This occurrence indicates that the assignment(15) of the 285 cm^{-1} vibrational mode in the liquid (i.e., $\nu_4 + \nu_7$ combination band) must be revised. In the liquid we have an additional vibrational mode centered at 217 cm^{-1} that cannot exist in the solid phase. In fact, such a mode is mainly due to a stretching–stretching interaction at the angle between the aluminum and the two shared chlorines (See Ref. 15 for details).

In the ordered phase we have a peak centered at 196 cm^{-1} (for $T =$ 53.3°C) which is absent in the liquid. Such a phonon mode is strongly temperature dependent; it shifts towards lower frequencies as the temperature increases and at the same time its width increases and its area decreases. In Figure 3a, we show the behaviour of the intensity of such a peak as a function of the temperature, and in Figure 3b the behaviour of the ratio $\omega_{196}/\Delta\omega$ between the center frequency and the width of the 196 cm^{-1} phonon mode is shown. The temperature behaviour of such a mode and its disappearance at the melting point suggests the identification

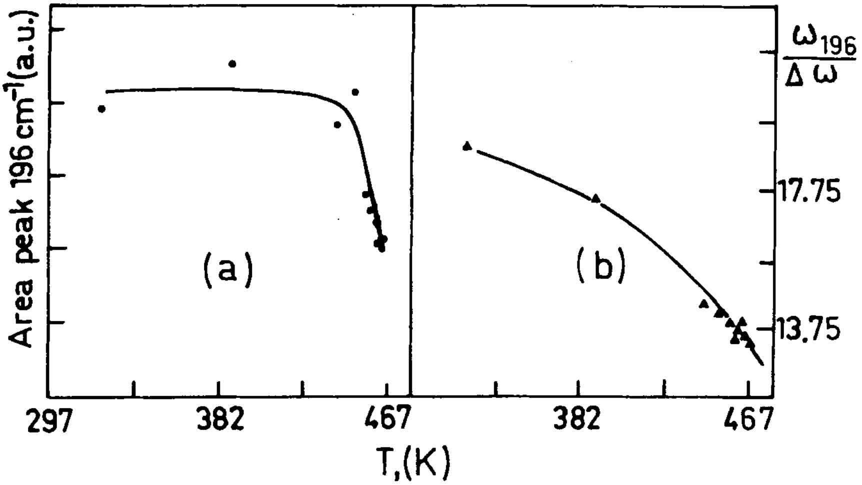

FIGURE 3 Area (a) and Q-factor (b) of the 196 cm^{-1} phonon *vs.* temperature. The continuous lines are a guide for eye.

of this phonon as the soft mode that heralds the phase transition. It is to be noted that the abrupt change towards higher frequencies of the two modes centered at 255 cm^{-1} and 307 cm^{-1}, as the melting point is approached, can be also connected to the disappearance of the 196 cm^{-1} optical phonon. If in fact, such a mode is identified with the one theoretically predicted by March and Tosi,(2) it is possible to evaluate the angle (~60°) between the vibrational direction of such a mode and that of the Al–Cl stretching mode.(26) Then, if the force constant of the disappearing phonon is transferred to that of the contiguous mode, it is possible to recover exactly the above mentioned frequency jump of the stretching mode. This working hypothesis has been verified for the antimony trichloride melting process,(23) where the energy transfer process between vibrational modes(22) was evident. In order to understand the vibrational dynamics of molten AlCl$_3$, it is important to stress that for liquids two alternative points of view exist for explaining the nature of the dynamic contribution to the scattered radiation. In the first one, the spectrum is interpreted in terms of a gas-like model in which the system is collision dominated. Such a model can be applied to liquids in which only a weak first-neighbor coordination is present. In the second one the behaviour of this disordered phase appears to be structure dominated. In such a case the liquid more closely resembles an amorphous material, at least in the very short (10^{-11} sec) temporal domain. This may be true, for example, for liquids like concentrated(28, 29) electrolyte solutions in which the structural arrangement is similar to that of the corresponding hydrated crystals, or for liquids like B_2O_3(30) and $ZnCl_2$(22) in which only a small number of bonds are broken upon melting, or of liquids like $SbCl_3$(20) in which a polymeric chain exists. Therefore, for those "structure limited" liquids,(31) the vibrational modes are identified as "quasi-phononic" excitations for times that are orders of magnitude shorter than the diffusional times. In any case, while the isotropic component of the spectrum is connected with the eigen modes of the system, the anisotropic spectrum $I_{\text{anis}}(\omega)$, due to the breakdown of the crystalline momentum selection rule, is interpreted in terms of a vibrational density of states. The above concepts, although first developed for amorphous materials and glasses(32,33) have been applied successfully to the above mentioned liquids. Furthermore, there is also present a quasi-elastic component (Rayleigh wing, which is depolarized) characteristic of the liquid state that can be connected to various scattering mechanisms(34) as reorientational relaxation, jump diffusion, structural relaxation, and so on. Taking into account the above mentioned contributions, $I_{VH}(\omega)$ can be written as follows:

$$I_{VH}(\omega) = I_{\text{anis}}^{\text{total}}(\omega) = L_R + L_S + I_{\text{anis}}^{\text{vibr}}(\omega) \tag{1}$$

where L_R and L_S are Lorentzian components due to the reorientational and structural relaxation processes, respectively, and $I_{\text{anis}}^{\text{vibr}}(\omega) \propto P(\omega) \cdot n(\omega, T) \cdot \omega^{-1} \rho(\omega)$ is the solid-like contribution; for the meaning of the symbols see Refs. 20, 22. We have analyzed the Raman data on molten $AlCl_3$ in the frame of the concepts described above. The melt is composed of dimeric units Al_2Cl_6 that are connected together, as revealed by x-ray diffraction experiments,(13) giving rise to a structured liquid. In this case we have a structural relaxation time τ_S that is smaller than the reorientational relaxation time τ_R and which gives a FWHM Γ_S of the Lorentzian L_S that is the only component detectable in this measurement. This component is convoluted, in the low frequency range, with the Raman effective density of states

$$\rho_{\text{eff}}^{R}(\omega) = P(\omega) \cdot \rho(\omega) = I_{\text{anis}}^{\text{vibr}}(\omega) \frac{\omega}{n(\omega, T) + 1}$$

Then following a previously applied procedure(20,22) Eq. (1), for $\omega \leq 25\ \text{cm}^{-1}$ becomes:

$$I_{\text{anis}}^{\text{total}}(\omega) = \frac{A_S \cdot \Gamma_S^2}{\omega^2 + \Gamma_S^2} + C \tag{2}$$

The results of fitting our $I_{VH}^{\text{exp}}(\omega)$, in the low frequency region, with Eq. (2) is shown in Figure 4. The points are the experimental data, the continuous line represents a central Lorentzian with $\Gamma_S = 3.91\ \text{cm}^{-1}$ and $A_S = 5125$.

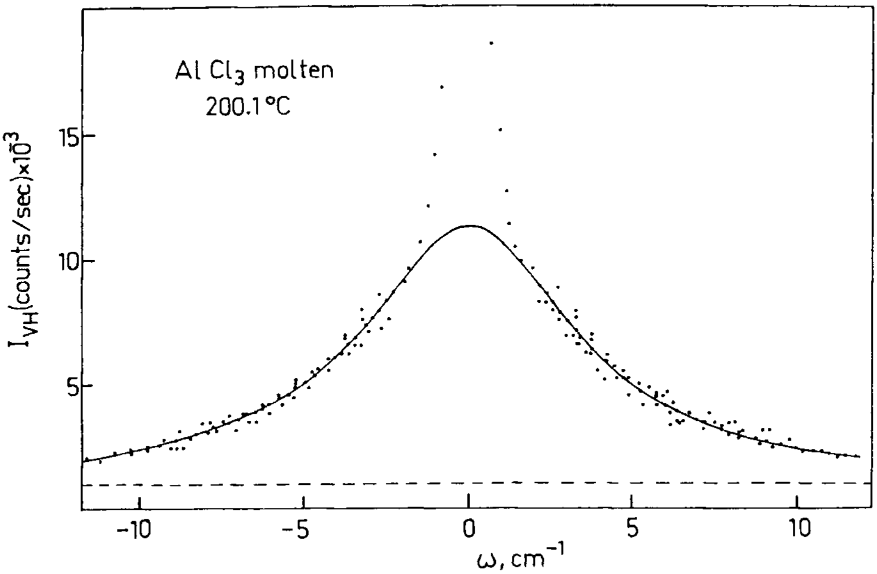

FIGURE 4 Quasi-elastic contribution to anisotropic spectrum in molten $AlCl_3$. The dots represent the experimental data. The continuous line is a Lorentzian curve fitting. The dashed line is the value of the constant C (see text for details).

The dashed line represents the value of the constant contribution $C = 530$, under the assumption that $P(\omega)$ is ω independent, that $\rho(\omega)$ behaves like $\rho_{acoust}(\omega)$, i.e. like ω^2, and the $\rho_{opt}(\omega)$ contributes only at higher frequencies. Finally, the anomalously high experimental data near the zero frequency shift are due to spurious elastic contributions that also mask the reorientational spectrum. The value of $\Gamma_S(3.91\ \mathrm{cm}^{-1})$ gives a characteristic microscopic time $\tau_S = (2\pi C\Gamma_S)^{-1} = 1.36$ psec. This value, in the frame of the existing models for the melt, can be connected to the mean-life of the intermolecular bonds. Unfortunately the difficulty of performing measurements on the liquid as a function of temperature precludes a detailed examination of the dynamics of the break-up of this intermolecular bond.

Taking into account Eq. (1), it is possible also to construct the Raman effective density of states $\rho^R_{eff}(\omega)$ for our system by removing the Lorentzian contribution L_S from the experimental $I^{total}_{anis}(\omega)$.

Figure 5 shows the $\rho^R_{eff}(\omega)$ for molten $AlCl_3$ in the $2 \rightarrow 200\ \mathrm{cm}^{-1}$ of Stokes shift region. An inspection of the figure shows that for very low frequencies an ω^2 behaviour exists as obtained through the fitting procedure. This contribution is convoluted with optical modes for $\omega \geq 15\ \mathrm{cm}^{-1}$, giving rise to a broad band. Finally, intramolecular contributions to $\rho^R_{eff}(\omega)$ are present for $\omega > 70\ \mathrm{cm}^{-1}$. It is to be noted that qualitatively the $\rho^R_{eff}(\omega)$

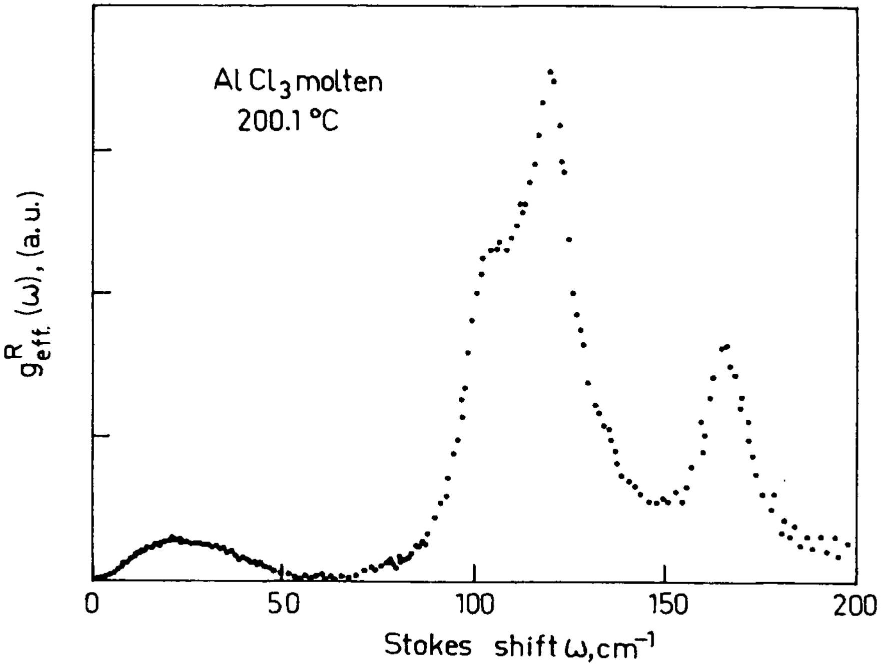

FIGURE 5 Raman effective density of states $\rho^{R}_{eff}(\omega)$ for molten $AlCl_3$.

in our system closely resembles the same spectral density obtained for molten $SbCl_3$(20) and for molten and glassy $ZnCl_2$.(22) We would like to stress that in the latter systems a convincing comparison has been performed between the effective Raman density of states and the information obtained with neutron scattering experiments. Unfortunately such a comparison cannot be made for the system under examination because of the lack of dynamical information in the literature. However, similarities between the spectral behaviour of molten $AlCl_3$ and the above mentioned systems allows us to give the same interpretation in terms of the concept of density of states.

Finally, to better clarify the short-time dynamics in molten $AlCl_3$, Raman measurements in liquid mixtures of $AlCl_3$ with $SbCl_3$ are in progress in our laboratories.

Acknowledgements

We are deeply indebted to Mr. F. Mento of the graphic art dept. of the Institute of Physics for his drawings, to Mr. S. Interdonato for his skillful construction of the electronic part of the optical thermostat, and to Dr. G. M. Begun of O.R.N.L. for critically reading the manuscript. G.P.S. acknowledges financial support from the U.S.D.O.E. under contract No. W-7405-eng-26. This work has been partially supported by C.R.R.N.-S.M.

References

1. G. Niklasson and A. S. Sjolander in "Anharmonic Lattices, Structural Transitions and Melting." Edited by T. Riste, Noordhoff, Leiden, 1974, pp. 1–22.
2. N. H. March and M. P. Tosi, *Phys. Chem. Liq.* **10**, 39 (1980).
3. N. H. March and M. P. Tosi, *Phys. Chem. Liq.* **10**, 95 (1980).
4. A. S. Dworkin, M. L. Poutsma, J. Brynestad, L. L. Brown, L. O. Gilpatrick, and G. P. Smith, *J. Am. Chem. Soc.* **101**, 5299 (1979).
5. A. C. Buchanan, R. Livingston, A. S. Dworkin, and G. P. Smith, *J. Phys. Chem.* **84**, 423 (1980).
6. A. C. Buchanan, A. S. Dworkin, G. P. Smith, M. V. Buchanan, and G. Olerich, Fuel, **60**, 694 (1981).
7. Most of the chemical-physics properties and industrial applications of $AlCl_3$ were reviewed by C. R. Boston, in "Advances in Molten Salt Chemistry." Edited by J. Braunstein, G. Mamantov, and G. P. Smith, Vol. 1. Plenum, N.Y., 1971, pp. 129–163.
8. J. A. A. Ketelaar, C. H. MacGillavry, and P. A. Renes, *Rec. Trav. Chim.* **66**, 501 (1947).
9. P. A. Casabella and N. C. Miller, *J. Chem. Phys.* **40**, 1363 (1964).
10. W. Blitz and A. Voigt, *Z. Anorg. Allg. Chem.* **126**, 39 (1923).
11. K. N. Semenenko and T. N. Naamova, *Zh. Neorg. Khim.* **9**, 1316 (1964).
12. C. R. Boston, S. J. Yosim, and L. F. Grantham, *J. Chem. Phys.* **51**, 1669 (1969).
13. R. L. Harris, R. E. Wood, and H. L. Ritter, *J. Am. Chem. Soc.* **73**, 3151 (1951).
14. W. Klemperer, *J. Chem. Phys.* **24**, 353 (1956).
15. V. H. Maroni, D. M. Gruen, R. L. McBeth, and E. J. Cairns, *Spectr. Acta*, **26A**, 418 (1970).
16. E. Rytter, M. H. Øye, S. J. Cyvin, B. W. Cyvin, and P. Klaebol, *J. Inorg. Nucl. Chem.* **35**, 1185 (1973).
17. G. Torsi, G. Mamantov, and G. M. Begun, *Inorg. Nucl. Chem. Lett.* **6**, 553 (1970).
18. K. W. Fung, G. M. Begun, and G. Mamantov, *Inorg. Chem.* **12**, 53 (1973).
19. R. Huglen, G. Mamantov, G. M. Begun, and G. P. Smith, *J. Raman Spectr.* **9**, 188 (1980).
20. F. Aliotta, G. Maisano, N. Micali, P. Migliardo, C. Vasi, F. Wanderlingh, R. Triolo, and G. P. Smith, *J. Chem. Phys.* **76**, 3987 (1982) and references cited therein.
21. N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.* **6**, 1167 (1967).
22. F. Aliotta, G. Maisano, P. Migliardo, C. Vasi, F. Wanderlingh, G. P. Smith, and R. Triolo, *J. Chem. Phys.* **75**, 613 (1981).
23. M. Fontana, G. Maisano, P. Migliardo, C. Vasi, and F. Wanderlingh, *Opt. Acta* **27**, 1087 (1981).
24. G. W. Mellor, Inorganic and Theoretical Chemistry. Longmans, London, 1960, pp. 312–318.
25. S. Bratos and G. Tarjus, *Phys. Rev. A*, **24**, 1591 (1981).
26. R. Wyckoff, "Crystal Structures." Interscience, N.Y., 1964, Vol. 2, p. 55.
27. A. T. Kozulin, *Opt. Spectrosc.* **32**, 374 (1972), see also A. T. Kozulin, A. V. Gogolev, and N. I. Noskov, *Ibid.* **40**, 518 (1976).
28. M. Fontana, G. Maisano, P. Migliardo, and F. Wanderlingh, *J. Chem. Phys.* **69**, 676 (1978).
29. F. Aliotta, G. Maisano, P. Migliardo, and C. Vasi, "Dynamical Properties of $CuBr_2$ Aqueous Solutions by Inelastic Light Scattering," To appear on *Phys. Chem. Liq.* (1982).
30. R. Shuker and R. Gammon, *J. Chem. Phys.* **54**, 3846 (1971).
31. J. A. Bucaro and T. A. Litovitz, *J. Chem. Phys.* **56**, 413 (1972).
32. See, e.g., M. H. Brodsky in "Light Scattering in Solids." Edited by M. Cardona, Springer, Berlin, 1975, pp. 204–251.
33. G. A. N. Connell, *Physics Status Solidi B* **69**, 9 (1975).