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Citation: *The Journal of Chemical Physics* **75**, 613 (1981); doi: 10.1063/1.442077

View online: <http://dx.doi.org/10.1063/1.442077>

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Vibrational dynamics of glassy and molten ZnCl_2

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(Received 9 March 1981; accepted 8 April 1981)

Polarized Raman spectra of ZnCl_2 were obtained in the liquid phase near the melting point ($T = 598$ K), and in the glassy phase ($T = 293$ K). Measurements were performed down to a very low frequency shift (2 cm^{-1}) from the exciting line. Our analysis of the Raman data provides an interpretation of the collision-like contribution in terms of a structural relaxation time in the picosecond range, while the phonon-like contribution gives an effective Raman density of states. These results are also discussed in terms of existing structural models.

I. GENERAL CONSIDERATIONS

In recent years^{1,2} the chemistry and the physics of molten and glassy ZnCl_2 have been widely studied because of the unusual structural features of this material. In the liquid phase near the melting point ($T = 591$ K), ZnCl_2 shows a very high viscosity,^{1,3} low ionic mobility,⁴ low electric conductivity.⁵ Moreover, it can easily be supercooled and glassified ($T_g = 375$ K). These peculiarities have often been explained by assuming the existence, in the melt of a polymerlike structure composed of ionic complexes,⁶ or by "lattice fragments" with a middle range bonding order.³ Recent x-ray diffraction measurements on molten ZnCl_2 near the melting point⁷ showed that the melt has an ionic type of structure, similar to that of crystalline ZnCl_2 ,^{8a} in which Zn^{2+} ions occupy tetrahedral holes in a close-packed array of Cl^- ions with a Zn-Cl distance of 2.291 ± 0.002 Å. Furthermore, EXAFS studies¹⁰ by Wong and Lytle in glassy and molten ZnCl_2 yielded a local coordination number for Zn^{2+} ions in amorphous phase of 5.1 ± 0.8 Å and an average Zn-Cl distance of 2.34 ± 0.01 Å. The Debye-Waller factor in ZnCl_2 glass was found to be higher than in GeO_2 glass which also has the same tetrahedral coordination. This feature seems to be due to a distribution of distances induced by the disorder of the melting process before the glassification.

Angell and Wong² carried out extensive studies of ZnCl_2 by means of several techniques including density, x-ray scattering, IR and Raman spectroscopy, probe-ion electronic, applied to the crystalline, liquid and vitreous states. A similarity between the structures of the glassy and polycrystalline (α form) was inferred by comparing the corresponding vibrational spectra. This in turn suggests the existence of polynuclear aggregates,^{11,12} formed with discrete entities of the ZnCl_2^{2-n} type.

The existence of so many different models proposed to explain different features of the structure of disordered ZnCl_2 , prompted us to undertake a refined

Raman study of this substance in the molten and glassy states, with particular emphasis on the low-frequency Raman spectrum. We hoped to explain this part of the spectrum in terms of a vibrational density of states. These states can become Raman active by breaking the momentum conservation selection rule.¹³ Actually the phonon density of states built up in this way becomes an effective Raman density of states,¹⁴ which is the convolution of the true vibrational spectrum with the mode-dependent matrix elements. Furthermore, we have found that the vibrational spectrum of molten ZnCl_2 near the melting point is very similar to that of the glassy phase. This fact allows us to define for the liquid phase a reduced Raman spectrum that resembles a broad density of states in the region between 2 and 180 cm^{-1} .

In the $180\text{--}400\text{ cm}^{-1}$ region the anisotropic reduced Raman spectrum shows more sharp features induced by a flat dispersion curve due to a localization of modes. This feature indicates the existence in the liquid of tetrahedral units decoupled from the remaining network. Finally, at very low frequencies the collision-induced light scattering (CILS)¹⁵ in both the liquid and glassy phases, gives rise to a central Lorentzian component in the spectrum that arises from a structural relaxation process.

II. EXPERIMENTAL PROCEDURE AND RESULTS

High-purity anhydrous ZnCl_2 , prepared from zone refined Zn and HCl, according to the procedure described by Brynestad and Yakel^{8b} was used. In order to avoid any chemical contamination, the sample was contained in a sealed quartz optical cell that was loaded in an Argon-filled dry box. Measurements on molten and glassy ZnCl_2 were performed on the same cylindrical cell. Temperature control, within 0.2 K for the measurements on the liquid and within 0.05 K for the measurements involving the glass, was achieved by means of a specially built optical thermostat. The vitreous phase was obtained by quickly quenching the sealed molten sample in cold ethyl alcohol at 250 K. The glass prepared in this way was perfectly transparent and free of optical defects.

A Spex Ramalog 5 Raman spectrometer with the op-

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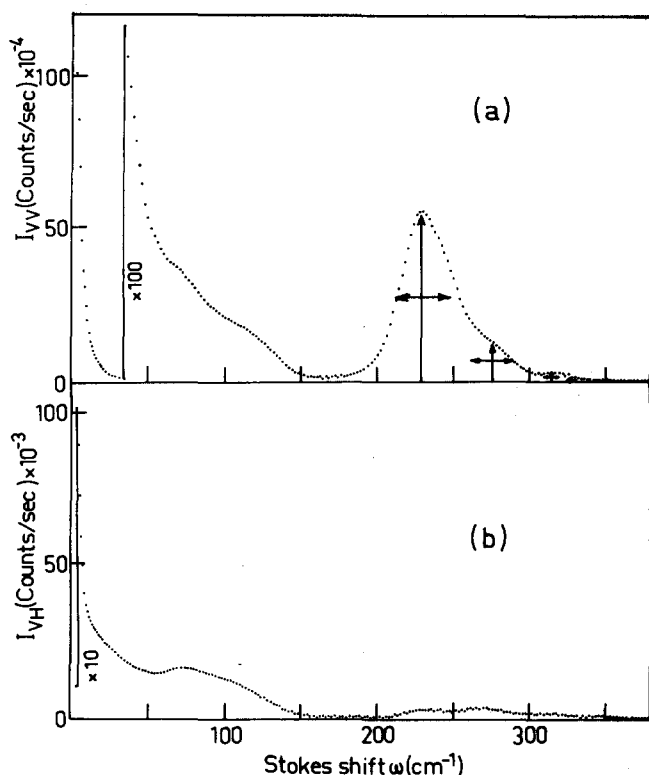


FIG. 1. I_{VV} (a) and I_{VH} (b) Raman spectra for glassy ZnCl_2 at 293 K.

tical thermostat located inside the illumination system was used in a 90° scattering geometry. The laser was a Spectra-Physics Model 170 Ar-ion laser working at 5145 \AA with the beam power continuously monitored and chosen so as to avoid unwanted local heating of the sample. The mean power of the exciting light was about 250 mW for the liquid and about 50 mW for the glass.

The structural stability of the amorphous phase as well as the reproducibility of the measurements was checked at different times by means of duplicate experiments.

The detecting system of the Spex spectrometer consisted of an RCA c-31034 cooled photomultiplier with flat spectral response and dark photon counts less than 10 photons/s. A photocount system allowed the transfer of the data to an MCS. The Raman spectra of ZnCl_2 were measured with both VV and VH polarization geometries. Because of the high spectral purity of the sample and the high rejection efficiency of the experi-

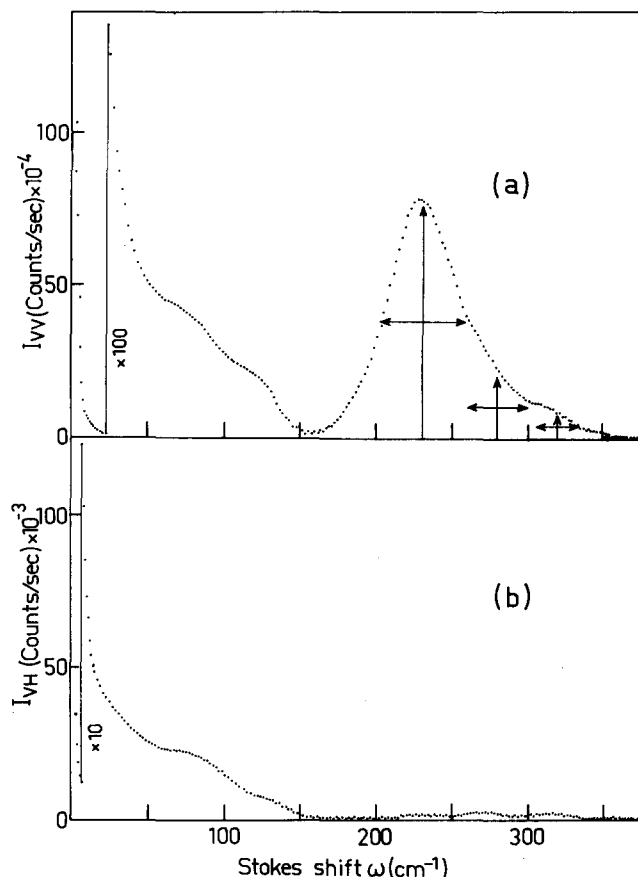


FIG. 2. I_{VV} (a) and I_{VH} (b) Raman spectra for liquid ZnCl_2 at 598 K.

mental apparatus, Raman spectra were obtained starting from a very low frequency shift of 2 cm^{-1} . For all the spectra, the resolution was 0.5 cm^{-1} in the range $2\text{--}15 \text{ cm}^{-1}$ and 3 cm^{-1} in the range $8\text{--}400 \text{ cm}^{-1}$.

I_{VV} and I_{VH} Raman spectra are shown in Fig. 1(a) and in Fig. 1(b) for glassy ZnCl_2 , and in Fig. 2(a) and in Fig. 2(b) for molten ZnCl_2 . The vibrational contribution in VV configuration is related to the isotropic portions of the spectra, and hence to all inter- and intramolecular optical phonons whose wave vector is $q \approx 0.0001 \text{ \AA}^{-1}$; as a consequence, we could perform a suitable deconvolution in symmetric (Lorentz-Gaussian) bands. The results of such a computer calculation are shown as full lines in Figs. 1(a) and 2(a) for the glass and the liquid, respectively. Table I

TABLE I. Bond-stretching bands in molten and glassy ZnCl_2 .

frequency (cm^{-1})	Glass				Melt			
	232	277	315	360	228	280	320	360
height (a. u.)	5441	1452	369	76	7573	1599	792	42
width (cm^{-1})	39	30	20	66	53	39	33	24
area (%)	78.4	17.2	2.7	1.8	81.6	12.8	5.4	0.2
ξ	0.11	0.12	0.6	...	0.03	0.06	0.3	...

summarizes the corresponding center frequencies, widths, heights, percent of area, and depolarization ratios.

III. DISCUSSION

With respect to the structural environment of glassy and molten ZnCl_2 an analysis of Table I shows that the LO and TO phonon contributions are related to a typical tetrahedral coordination geometry for Zn^{2+} . In fact, the fourfold coordination in the bulk network gives rise to a totally symmetric stretching mode centered at 232 cm^{-1} for the melt and 228 cm^{-1} for the glass. The 280 cm^{-1} band for the glass and the 277 cm^{-1} band for the melt, both of high symmetry, might be produced by analogous basic units. According to Angell's "split cell model," vibrational frequency differences are to be expected for tetrahedral units that are near a vacancy due to "broken bonds." The vibrations centered at 315 cm^{-1} for the glass and the 320 cm^{-1} for the melt, may originate from antisymmetric excitations coming from the same elementary units, while the weak 360 cm^{-1} band may be seen as a stretching vibration of ZnCl^+ units¹¹ unbonded to the network.

Inelastic neutron scattering measurements in molten ZnCl_2 ¹⁶ support the idea that the vibrations mentioned above are of a collective type rather than a contribution from isolated molecular entities. In fact, the existence in the dynamic structure factors of well defined k -dependent peaks shows that the vibrational dynamics are cooperative in character, although the modes are very damped in the liquid and glassy state. Let us now discuss the anisotropic part of the spectra, according to this hypothesis. In the context of recent models for the analysis of Raman spectra in amorphous systems,¹⁷ this implies that the anisotropic contribution $I_{\text{anis}}(\omega)$ is directly connected to the vibrational density of states. In fact, due to the breakdown of crystalline momentum conservation selection rules, the Raman (and IR) spectra represent a smoothed out version of the one-phonon density of states of the corresponding crystal. Therefore, from the experimental $I_{\text{anis}}(\omega) \equiv I_{\text{VH}}(\omega)$ we can obtain an effective Raman density of states $\rho_{\text{eff}}^{\text{R}}(\omega)$ through the equation

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

where ω is the Stokes frequency shift and ω_0 and ω_s are the frequencies of the incident and scattered light respectively. In Eq. (1) the term $\omega(\omega_0 - \omega_s)^{-4}$ takes into account the usual extra radiation factor and the dielectric fluctuation correlation function in the quasi-harmonic approximation, while the term

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

is the Bose-Einstein population factor. In turn the effective density of states $\zeta_{\text{eff}}^{\text{R}}(\omega)$ is related¹⁴ to the true density of states $\rho(\omega)$ by the equation:

$$\zeta_{\text{eff}}^{\text{R}}(\omega) = P(\omega) \cdot \rho(\omega). \quad (2)$$

Several models have been developed¹³ to obtain the functional form of $P(\omega)$ in the different phononic branches. Raman spectra of disordered crystalline,^{17,18} amorphous¹³

and superionic¹⁹ solids and structured liquids²⁰⁻²³ have been interpreted very satisfactorily in this framework. It has been shown²⁴ that a direct connection exists between the IR absorption coefficients $\sigma(\omega)$ and $\zeta_{\text{eff}}^{\text{IR}}(\omega)$, where $\zeta_{\text{eff}}^{\text{IR}}(\omega)$ is an effective IR density of states. This point will be discussed below.

The above concepts, although they are developed mainly for amorphous systems, can be applied to the case of liquid systems. In fact, for liquids in which the melting process gives rise to the "breakdown" of only a small percentage of the solid phase bonds,²³ all of the "quasiphononic" excitations (which correspond to the instantaneous local structure of the system) will contribute to the anisotropic scattering. In the case of liquid ZnCl_2 near the melting point, the high viscosity and low ionic mobility indicate that a well-joined structure exists in the melt, in which most of the basic structural units are harmonically bonded. Therefore the anisotropic Raman spectra of both liquid and glass are quite similar.

In liquid ZnCl_2 , basic units bonded together will give rise to a glasslike contribution, while a collisionlike contribution¹⁵ can be due to isolated or weakly interacting ionic species or to reorientational relaxations. In the $2+20\text{ cm}^{-1}$ frequency region, both contributions can be present.

In the sequel we will show a procedure that allows the separation of the two contributions. The CILS contribution is expected to have a Lorentzian shape, centered at zero frequency shift. The contribution from the density of states, in such a low frequency region, comes mainly from the acoustical branch. Accordingly, the corresponding density of states would behave as ω^2 (Debye elastic waves).

Taking into account Eqs. (1) and (2) the above-mentioned contributions will give an anisotropic spectrum of the form:

$$I_{\text{anis}}(\omega) = \frac{A\Gamma^2}{\Gamma^2 + \omega^2} + \frac{n(\omega) + 1}{\omega} (\omega_0 - \omega_s)^4 P(\omega) \rho(\omega). \quad (3)$$

Now, in the range of the frequency of interest, $(\omega_0 - \omega_s)^4 \approx \text{const.}$ and $n(\omega) + 1 \approx (1/\omega)$. If $P(\omega)$ were also ω independent (as suggested in Ref. 23), taking into account that $\zeta_{\text{Acoust.}}(\omega) \sim \omega^2$ as mentioned before, Eq. (3) simplifies to:

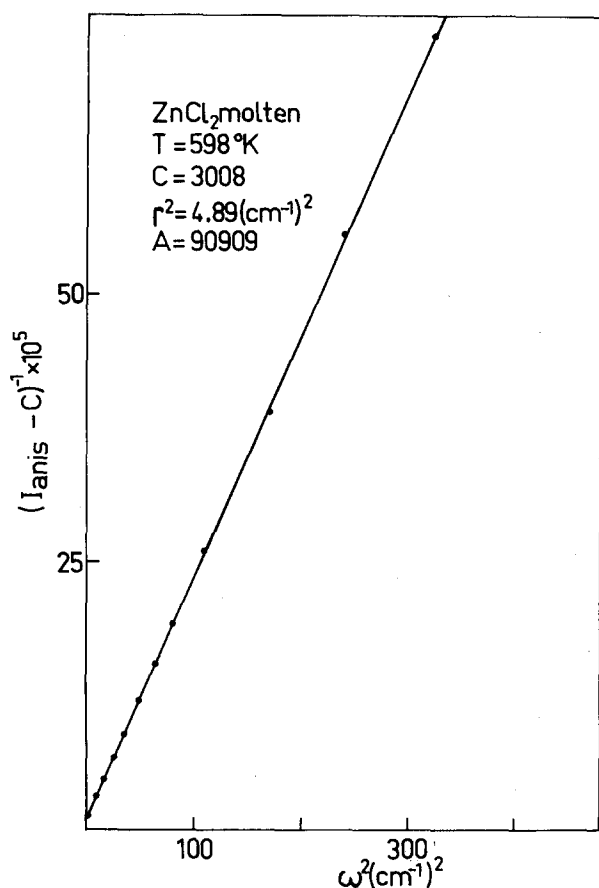
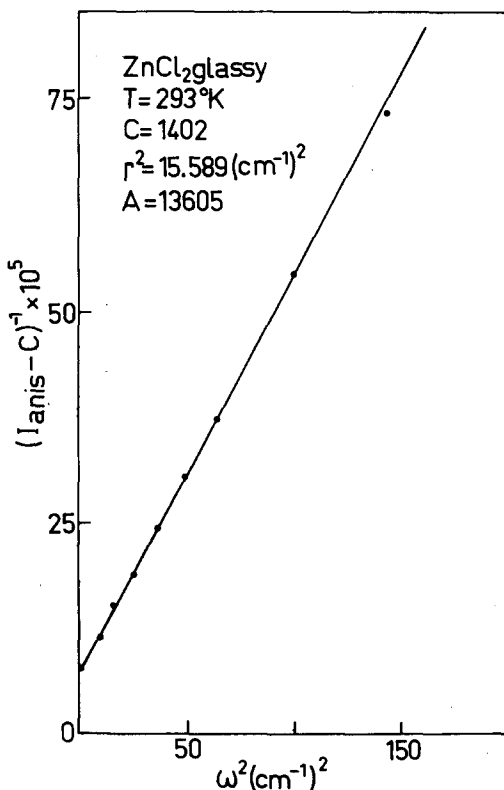
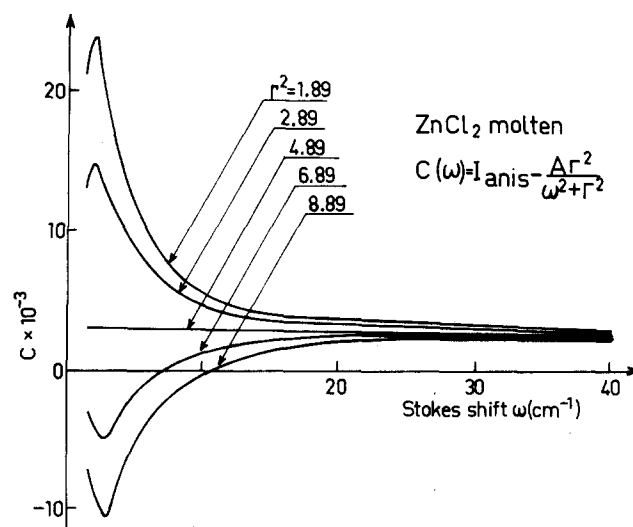
$$I_{\text{anis}}(\omega) = \frac{A\Gamma^2}{\Gamma^2 + \omega^2} + C, \quad (4)$$

where C is a constant.

We tried to fit our experimental data with Eq. (4). The results are shown (for the liquid state) in Fig. 3.

The points are experimental results while the straight line is the calculated curve. It is interesting to note that similar results are obtained by applying the same analysis to the glassy phase as shown in Fig. 4. The goodness of the fit supports the hypothesis implied in Eq. (4).

The analysis can be refined by trying to extract from experimental data the second contribution in the right-hand

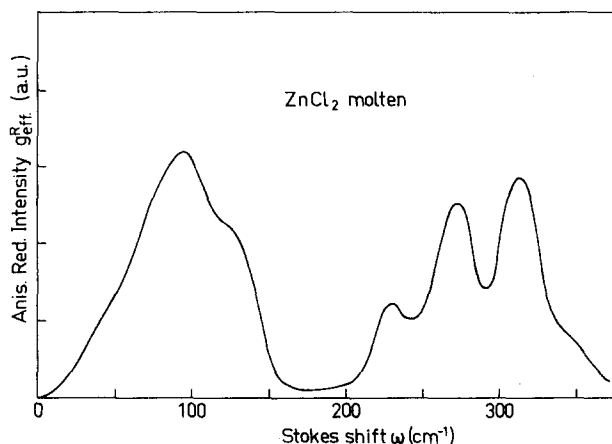
FIG. 3. Plot of the central Lorentzian band in molten ZnCl_2 .FIG. 4. Plot of the central Lorentzian band in glassy ZnCl_2 .FIG. 5. Raman coupling coefficient vs ω for various values of Γ^2 in the melt.

side of Eq. (3). For such a purpose we subtract from $I_{\text{anis}}(\omega)$ a Lorentzian contribution of variable half-width Γ and a constant amplitude $A = 90909$. It is to be noted in fact that the amplitude A of the Lorentzian contribution that dominates as $\omega \rightarrow 0$ is not affected by the behavior of the phononic contribution.

The results are shown in Fig. 5. Obviously for $\Gamma^2 = 4.89 \text{ cm}^{-2}$ a straight line $C = 3008$ is obtained. For different values of Γ^2 the shape of the curve would reflect the behaviour of $P(\omega)$ if such a quantity were not constant.

Lannin²⁵ showed that in amorphous Si and Ge, the function $P(\omega)$ behaves as ω^2 . Such a behavior is clearly excluded in our case: we are left to the conclusion that either $P(\omega) = \text{const}$, according to Ref. 23 or $P(\omega)$ behaves in the unusual way shown in Fig. 5. We believe that the first hypothesis is to be preferred.

Accordingly, taking for Γ the values obtained by the fit with Eq. (4), we obtain two characteristic microscopic times for the system, with a value of $\tau = 2.40 \text{ ps}$ for the melt and $\tau = 1.34 \text{ ps}$ for the glass.²⁶ The value

FIG. 6. Anisotropic reduced Raman intensity of molten ZnCl_2 .

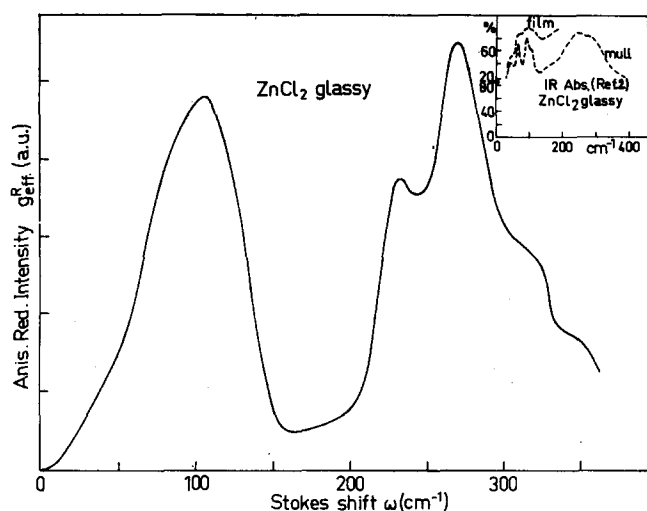


FIG. 7. Anisotropic reduced Raman intensity for glassy ZnCl_2 . The IR adsorption coefficient taken from Ref. 2 is shown in the inset.

of τ found for the liquid is in agreement with that found by Wilmshurst¹⁶ by means of quasielastic neutron measurements, and is of the same order as that found for aqueous ZnCl_2 solutions.²⁷ The existence of this characteristic relaxation time in the picosecond range suggests a diffusion process connected with jumps of the ions in the ordered local structure.

As far as the total phononlike contribution is concerned, the $\rho_{\text{eff}}^R(\omega)$ can easily be obtained directly from the experimental $I_{\text{anis}}(\omega)$. The Lorentzian contribution in fact influences the spectrum only up to $\sim 20 \text{ cm}^{-1}$ and can be subtracted. In such a way the $\rho_{\text{eff}}^R(\omega)$ will behave as ω^2 up to $\sim 20 \text{ cm}^{-1}$ as a consequence of the hypothesis made in Eq. (4). However, the remaining part of the $\rho_{\text{eff}}^R(\omega)$ is independent from any hypothesis.

Figures 6 and 7 show $\zeta_{\text{eff}}^R(\omega)$ for the melt and for the glass, respectively. The form of both functions is quite similar, except for a few minor differences in the optical longitudinal region. Actually, a sharper feature in the $\zeta_{\text{eff}}^R(\omega)$ of the melt, as compared to the glass, indicates a greater degree of "molecularity" of the liquid. This reflects a greater localization of vibrational modes. In the inset of Fig. 7 is shown the IR absorption coefficient vs the wave vector, based on data taken from Ref. 2. It is interesting to note the similarity between $\zeta_{\text{eff}}^R(\omega)$ and $\zeta_{\text{eff}}^{IR}(\omega)$. This indicates that for our system the Raman coupling matrix elements have at least the same frequency dependence. In Fig. 8 we show the average dispersion curves reduced to the first Brillouin zone deduced by Wilmshurst¹⁶ (right) and the $\zeta_{\text{eff}}^R(\omega)$ (left) as deduced by our measurements for molten ZnCl_2 . As can be seen, our $\zeta_{\text{eff}}^R(\omega)$ reflects the main features of the dispersion curves quite well and strongly supports our working hypothesis, i.e., the vibrational dynamics of the system are collective in character.

IV. CONCLUDING REMARKS

The analysis of the Raman spectra of ZnCl_2 for disordered phases leads to the following conclusions: (i)

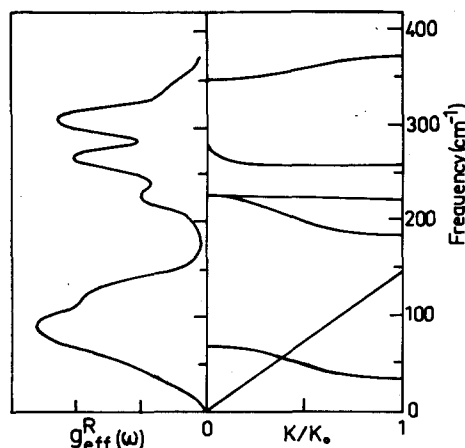


FIG. 8. Representation of "average" dispersion curves (Ref. 16) on the right side and $\zeta_{\text{eff}}^R(\omega)$ on the left side, for molten ZnCl_2 .

The vibrations are connected with the tetrahedral elementary units in a "polymeric network." Such units are present both in the melt and in the glass.

(ii) The frequency contributions to the anisotropic Raman spectra furnish an effective density of states corresponding to collective vibrational modes in a "polymeric network" with middle-range bonding.

(iii) The width of the Lorentzian central line in the anisotropic Raman spectra allows the calculation of a structural relaxation time for both liquid and glassy ZnCl_2 : this time seems to characterize a jump diffusion process for the ions in vacancies originated by broken bonds. Further measurements at various temperatures are in progress to better clarify the microscopic nature of this relaxation time.

ACKNOWLEDGMENT

R. T. and G. P. S. acknowledge financial support from the U.S. Department of Energy under Contract No. W-7405-ENG-26 with the Union Carbide Corporation.

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