

Molecular Reorientations in Liquid and Solid Cyclohexane

Interpretation of Relaxation Functions from Raman Line Profiles

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Going out from the recorded line shapes, the true profiles of the vibrational band $\nu_{22}(E_g)$ of cyclohexane and their half-widths are calculated in dependence of the temperature. The influence of the intrinsic line width turns out to be so small as to lie practically within the tolerance. The correlation functions of the true line profiles are found to be Lorentzian in good approximation. They are within the tolerance in conformity with the correlation functions of the orientational line shapes. Rotations of the C_6H_{12} -molecules around their C_2 -axes are supposed to be the cause for the occurring of a plastic phase.

1. Introduction

The Raman-spectroscopy beside the IR- and NMR-spectroscopy is an important method of molecular physics for the investigation of molecular motions and intermolecular correlations of condensed phases. A clarification of the mechanisms of these intermolecular forces can contribute to the interpretation of the structure of liquids. Debye¹ with his model of rotational diffusion describes the reorientation of approximately spherical molecules in viscous substances. During the past years a few theoretical works²⁻⁵ about the movement of linear and spherical molecules in liquids have been published. The theories mentioned, on the whole are in conformity with the corresponding experiments^{6, 7} and show that Debye's model in many cases describes the molecular rotations inadequately. Recently a few works^{8, 9} have been published, which are concerned with extending these new theories to symmetrical tops and antisymmetrical molecules. A completion and improvement of the existing experimental material appears to be necessary in order to check upon the validity of the model ideas and the theoretical assumptions.

For cyclohexane older NMR-measurements of the spin-lattice relaxation times¹⁰ and half-width determinations of some Raman- and IR-vibrational lines¹¹⁻¹³ are published, which indicate considerable rotations of the molecules in the liquid as well as in their plastic solid phase. Recently some authors have ascertained the vector-correlation functions

from IR-measurements¹⁴ and the relaxation functions from Raman-measurements⁸ for some rotation vibrational bands. As the vector-correlation function¹⁴ practically only exists for one line and one temperature, and since with the relaxation functions⁸ a Lorentz profile has been assumed as a true line profile, it appears useful to study both types of correlation functions in dependence on the temperature more closely.

In the present work the profiles of some Raman-rotation vibrational lines of cyclohexane are evaluated. The profiles are recorded as a function of the temperature. Special importance is given to the line shapes, as these as a rule supply more information than their half-widths. The ascertainment of the relaxation functions of a suitable band from the recorded profiles takes place after the known methods¹⁵ with the help of Fourier-transformations. The influence of the intrinsic line width upon the correlation functions is estimated.

2. Experimental Arrangement

The line shapes of the rotation vibrational bands $\nu_5(A_{1g})$, $\nu_{22}(E_g)$, $\nu_{21}(E_g)$ and $\nu_{19}(E_g)$ of cyclohexane were recorded in the liquid and plastic solid phase in the range of 193.5 K up to 345.5 K and for comparison in the rigid solid phase at appr. 78 K. The recording of the bands was made with a Cary-Model 81 Raman-Spectrophotometer¹⁶. A 90° scattering arrangement was used. Excited- and scattered light were not polarized. Cyclohexane p.a. of Messrs. E. Merck was used as sample substance, which for the Raman-investigations was distilled and dried via sodium. All measurements were made with the same sample. A temperature constancy of appr. ± 1 K, which was sufficient for the present

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measurements, could be achieved by using a suitable cooling agent, which was streaming around the sample substance.

The line shapes were recorded several times always for one band at a certain temperature. Then they were corrected, normalized and averaged¹⁶. Thereby profiles are obtained which at different temperatures have the same peak intensities but still contain the instrumental profile. The true line shapes result from Fourier-transformation according to known methods^{15, 16}.

3. Experimental Results

In Fig. 1–4 the corrected, normalized and averaged line shapes still containing the instrumental

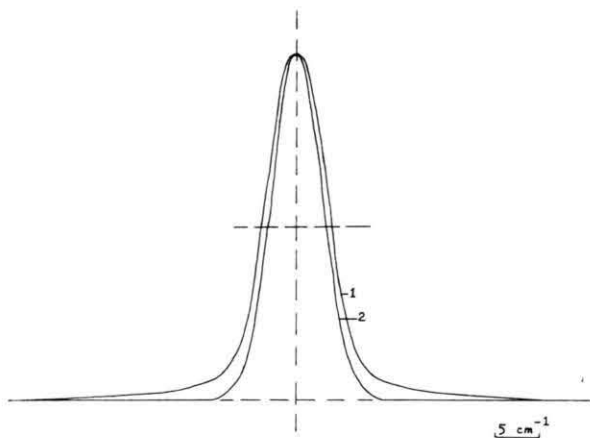


Fig. 1. Temperature dependence of the corrected, normalized and averaged profiles for $\nu_5(A_{1g}) = 802 \text{ cm}^{-1}$.

1 193.5 K up to 345.5 K; 2 78 K.

profile have been drawn. The line contour of $\nu_5(A_{1g})$ within the tolerance in the entire plastic and liquid range remains independent of temperature. If the line shape in these ranges is compared to the shape at appr. 78 K, a slight narrowing of profile still is to be recognized.

The degenerated Raman bands with decreasing temperature become distinctly narrower. During change from liquid to plastic phase no essential modification of the line contour can be noted. Whereas at 193.5 K (plastic phase) and at appr. 78 K (rigid phase) the profiles differ very distinctly. As the range between 193.5 K and 78 K was not studied, from these measurements it can not yet be determined, whether the profile narrowing at the transition point (186 K) shows a jump or not.

The change of the line shapes is once more shown in Fig. 5 and 6a with the help of their half-widths as a function of temperature. In completion of the narrowing of the profiles it is found that the decrease of the half-widths of the degenerated vibrations with diminishing temperature is appr. of the same order of magnitude. The widths of $\nu_{21}(E_g)$ and $\nu_{22}(E_g)$ at the corresponding temperatures differ only very slightly, whilst the width of the $\nu_{19}(E_g)$ band — obviously because of the disturbance through $\nu_3(A_{1g})$ — lies appr. 1–2 cm^{-1} above the other widths. At the melting point no point of discontinuity is noticed. At appr. 78 K the half-width of ν_{22} within the tolerance corresponds to the width of the appertaining instrumental profile. Whilst the half-width of ν_{21} in that

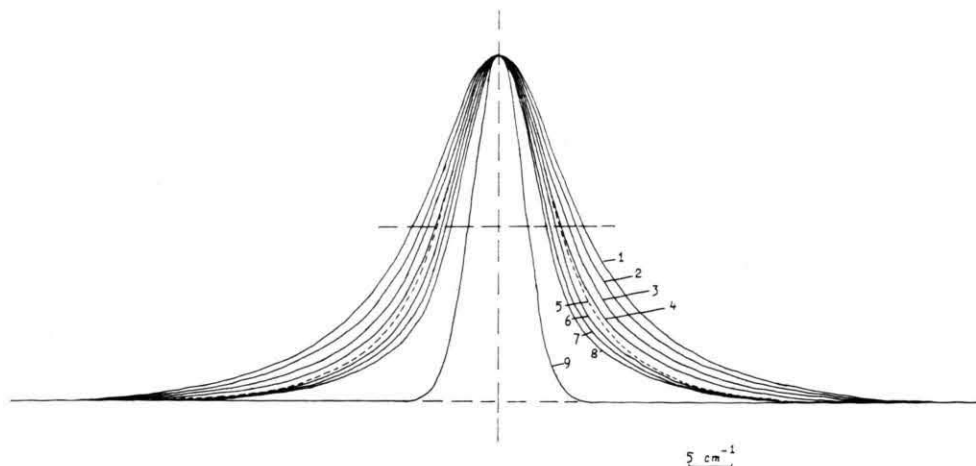


Fig. 2. Temperature dependence of the corrected, normalized and averaged profiles for $\nu_{22}(E_g) = 1031 \text{ cm}^{-1}$.

1 345.5 K 2 325.5 K 3 303.5 K 4 281.5 K 5 276.0 K 6 259.5 K 7 237.5 K
8 193.5 K 9 78 K.

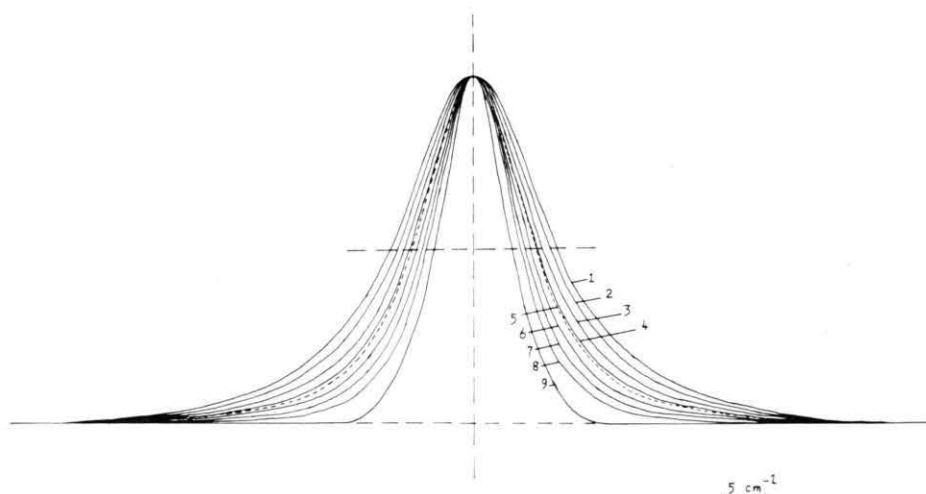


Fig. 3. Temperature dependence of the corrected, normalized and averaged profiles for $\nu_{21}(E_g) = 1270 \text{ cm}^{-1}$.
 1 345.5 K 2 325.5 K 3 303.5 K 4 281.5 K 5 276.0 K 6 248.5 K 7 226.5 K
 8 193.5 K 9 78 K.

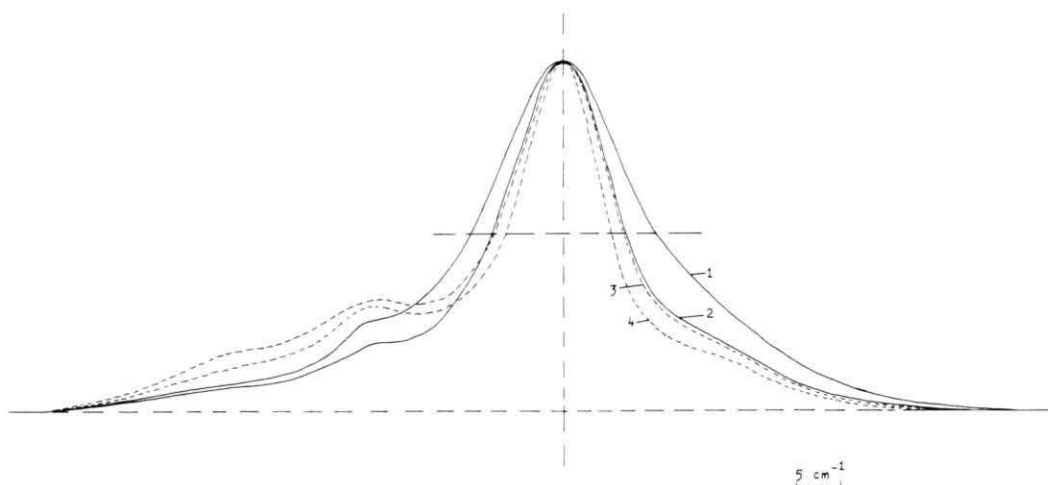


Fig. 4. Temperature dependence of the corrected, normalized and averaged profiles for $\nu_{19}(E_g) = 1443 \text{ cm}^{-1}$.
 1 345.5 K 2 281.5 K 3 276.0 K 4 193.5 K.

range lies slightly above, which can be explained by a slight splitting of the degeneracy¹³.

The tendency of profile narrowing at decreasing temperature at the three 2-fold degenerated vibrations is appr. alike. It, therefore, is sufficient to study the profile of one of these lines more closely. In this region ν_{22} offers itself, as this vibration shows an almost undisturbed symmetric line shape, and no splitting of degeneracy of any importance could be ascertained.

The line shapes of the true profiles¹⁶ $\varphi(\nu)$ of $\nu_{22}(E_g)$ in Fig. 7 are represented in their depen-

dence on temperature. This graph differs from Fig. 2 in as much as after elimination of the instrumental profile by Fourier-transformation¹⁵ all lines have become narrower. At appr. 78 K the profile practically may be described as a delta-function. — The corresponding half-widths are shown in Fig. 6 b vs the temperature.

4. Relaxation Functions

The relaxation function $C_q(t)$ is obtained by Fourier-transformation of the true line profile

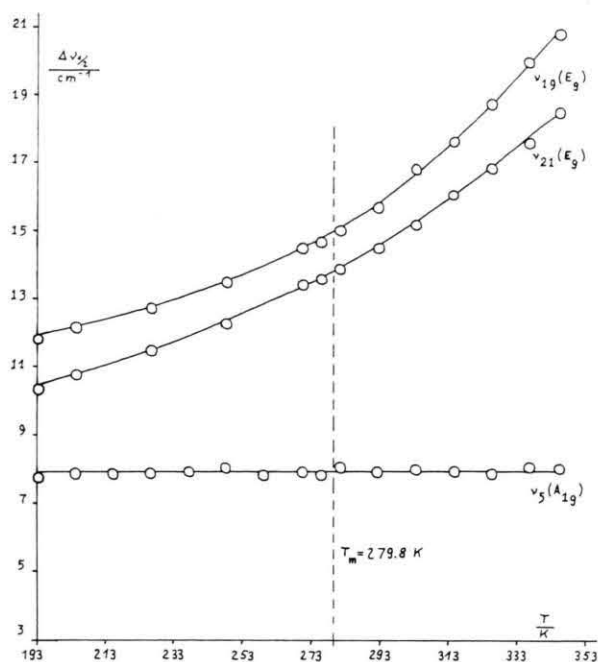


Fig. 5. Half-width vs temperature of the corrected, normalized and averaged profiles for $\nu_5(\text{A}_{1g})$, $\nu_{19}(\text{E}_g)$ and $\nu_{21}(\text{E}_g)$.

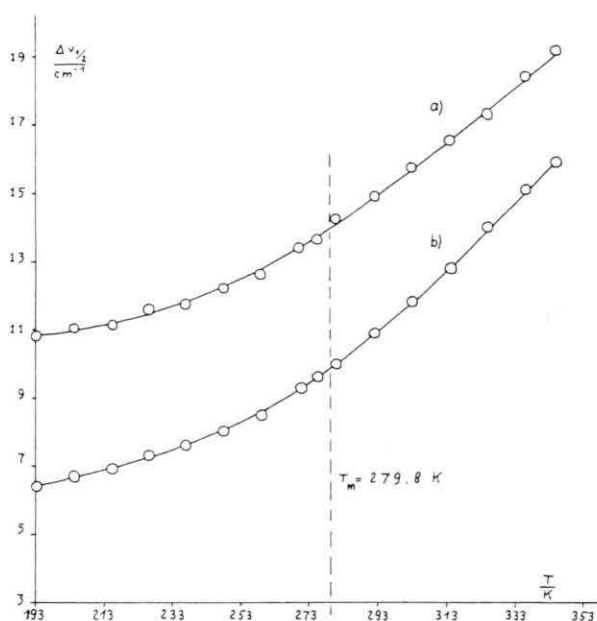


Fig. 6. a) Half-width vs temperature of the corrected, normalized and averaged profiles for $\nu_{22}(\text{E}_g)$. b) True half-width vs temperature for $\nu_{22}(\text{E}_g)$.

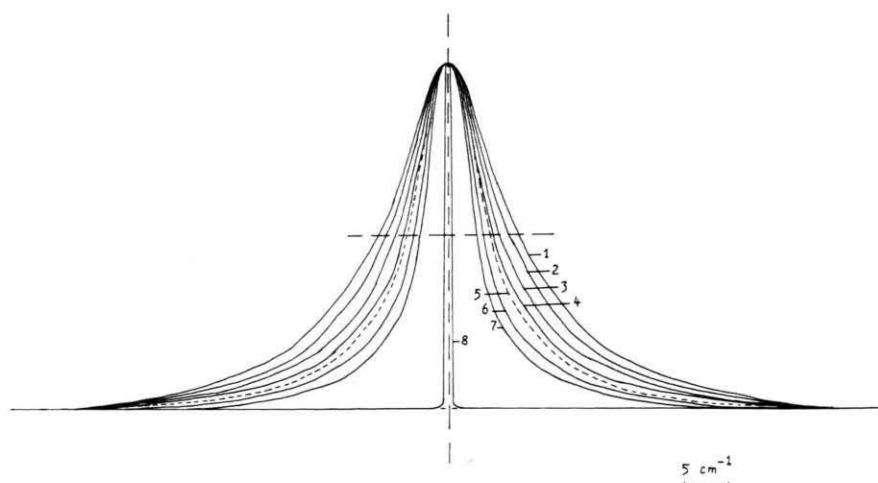


Fig. 7. Temperature dependence of the true line shapes for $\nu_{22}(\text{E}_g)$.

1 345.5 K 2 325.5 K 3 303.5 K 4 281.5 K 5 276.0 K 6 248.5 K 7 193.5 K 8 78 K.

$\varphi(\nu)$ ¹⁶. In Fig. 8 $\ln C_q(t)$ for the different temperatures is plotted vs the time. The tolerance of the function depends upon the resolving power $\Delta\omega_A$ of the spectrograph. After Ref. 3 a computation of the functions only up to a time $\tau_A = 1/\Delta\omega_A$ is sensible. For the present measurements τ_A amounts to appr. 2 ps.

The computed functions due to the effect of truncation¹⁷ show deviations which were compensated. The course of the curves for $t > \tau_A$ has been drawn as a broken line. In good approximation $\ln C_q(t)$ turns out to be straight lines, meaning $C_q(t)$ and thereby $\varphi(\nu)$ practically are Lorentzian. This result is in conformity with that of the authors in Ref-

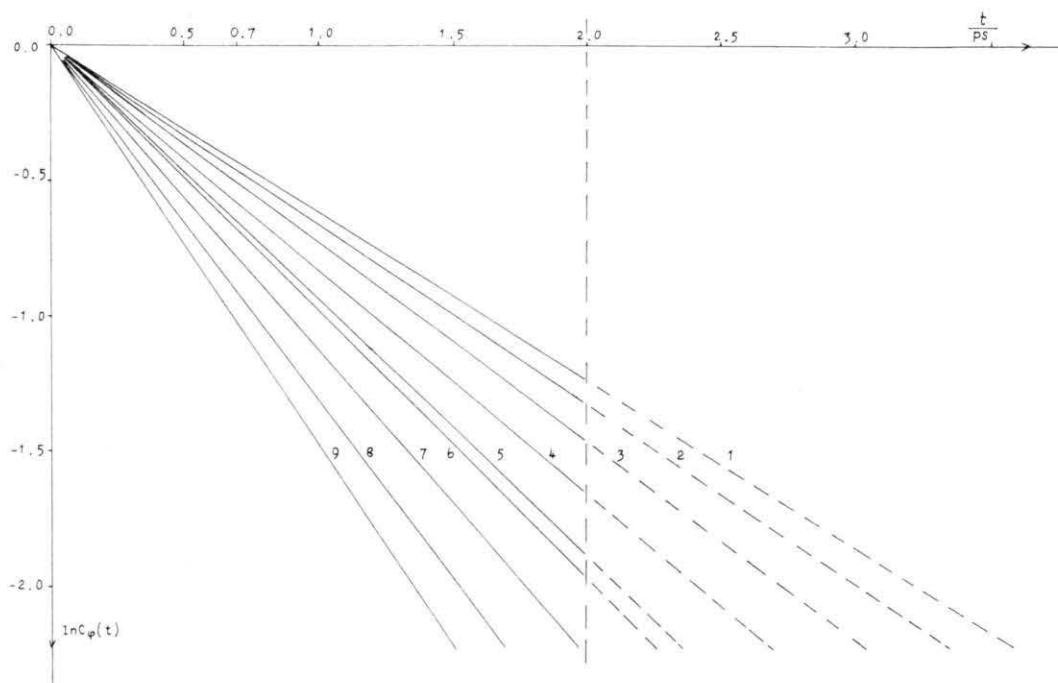


Fig. 8. Temperature dependence of $\ln C_\varphi(t)$ vs time t for $\nu_{22}(E_g)$.

1 193.5 K 2 215.5 K 3 237.5 K 4 259.5 K 5 276.0 K 6 281.5 K 7 303.5 K 8 325.5 K
9 345.5 K.

The straight lines are drawn through up to the origin, as model computations have shown that a deviation from the exponential course for short times is caused by the truncation.

erence 8. For short periods a minor deviation from the exponential course in the range of 0.0 to 0.1 ps cannot be excluded.

The true line profile $\varphi(r)$ respectively the appropriate relaxation function $C_\varphi(t)$ contain the influence of the intrinsic and orientational line width^{8, 20}. It is

$$C_\varphi(t) = C_v(t) \cdot C_{or}(t), \quad (1)$$

$C_v(t)$ and $C_{or}(t)$ being the components of the relaxation functions of the profile $\varphi(r)$, which are caused by the intrinsic resp. orientational line width. For $\ln C_\varphi(t)$ it is

$$\ln C_\varphi(t) = \ln C_v(t) + \ln C_{or}(t). \quad (2)$$

It is to be clarified how the components $\ln C_v(t)$ and $\ln C_{or}(t)$ enter into $\ln C_\varphi(t)$. To this end the intrinsic line width $\Delta\nu_{1/2\text{intr}}$ belonging to $C_v(t)$ is to be estimated.

5. Estimation of Influence of the Intrinsic Width

After Ref. 20 it is for $C_v(t)$ for $t \gg t_c$

$$C_v(t) = \exp\{-\langle\omega^2\rangle t_c t\} = \exp\{-t/t_{c\text{rv}}\}, \quad (3)$$

ω being frequency shift through intermolecular interactions,

t_c being correlation time of the function $\langle\omega(0) \cdot \omega(t)\rangle$,

$t_{c\text{rv}}$ being vibrational relaxation time.

The intrinsic line width is depending upon temperature, particularly when orientation-sensitive interaction potentials become effective²⁰. In the present case an increase of temperature should lead to a line narrowing. The influence of the intrinsic line width upon $\varphi(r)$ respectively $C_\varphi(t)$, if the effect lies outside the accuracy of measurement at all, should be more strongly apparent at lower temperatures.

The influence of the orientational line width also at low temperatures in the plastic phase should be considerable, as reorientations around the C_2 -axes after Heuse¹⁸ and Rozental¹⁹ are absolutely plausible, as for instance the specific volume of rigid cyclohexane is by 18% less than the value at the melting point. At the latter the increase amounts to 5%. The corresponding values for benzene which — as well known — has no plastic

phase, are 10% and 13%. It results therefrom, that the change of volume for cyclohexane at the transition point amounts to appr. 8%. The heat of transition is appr. 2.5 times greater than the melting heat. The corresponding entropies are even 4 times different from one another. By these reasons already in the plastic phase the potential barriers must have become essentially lower, also making reorientations around the C_2 -axes probable.

Qualitative IR-measurements²¹ are supporting this hypothesis. A reorientation around the C_3 -axis by sterical reasons is even more probable, if not C_6H_{12} in good approximation can even be called a spherical top.

It can be assumed, therefore, that also at low temperatures in the plastic phase the component of the orientational line width is considerable, and supposedly surpasses the component of the intrinsic line width. For higher temperatures this assumption, because of the narrowing of the intrinsic line width, is still more strictly valid.

During transition from the plastic to the rigid phase for ν_{22} a shifting of the band maximum of appr. 2 up to 3 cm^{-1} occurs. According to the above mentioned ideas²⁰ $\langle\omega^2\rangle$ is of the same order of magnitude as this shifting. Therefore it is

$$\langle\omega^2\rangle \approx (\pi c \Delta\nu)^2. \quad (4)$$

Assuming the probably existing orientation-sensitive interaction potentials, for t_c approximately the orientational line width $\Delta\nu_{1/2\text{or}}$ can be taken. With $\Delta\nu_{1/2\text{or}} \approx 6.5\text{ cm}^{-1}$ it is $t_c \approx 1.6\text{ ps}$. After (3) it is $t_{c\text{rv}} \approx 4.3\text{ ps}$. This corresponds to a value of $\Delta\nu_{1/2\text{intr}}$ of appr. 2 cm^{-1} . As the determination of $\langle\omega^2\rangle$ is an estimation upwards, it can be assumed that the contributions of the intrinsic line width are still smaller and in first approximation are negligible.

6. Discussion

By reason of the experimental results and the — by estimation proven — small influence of the intrinsic line width upon the true line profile it can be concluded, that the correlation function $C_q(t)$ in good approximation is Lorentzian and that $C_q(t) \approx C_{\text{or}}(t)$. The latter result is not in conformity with that of Bartoli and Litovitz⁸, who for instance for room temperature assume an intrinsic line width of 6.0 cm^{-1} . The estimation of the

intrinsic line width in this work for the plastic phase yields a value of not more than 2 cm^{-1} . Because of the line narrowing at increased temperature the value at room temperature will be even lower, meaning that the value of 6.0 cm^{-1} of the authors in Ref. 8 is not tenable.

In determining the intrinsic line width the authors are using the well known Racov-Arrhenius-formulation¹², which takes for granted a — in connection with this observation inadmissible — intrinsic line width, which is independent of temperature. The value of the intrinsic line width is obtained through extrapolation into the rigid phase. At the transition point from the plastic to the rigid phase, however, a jump in the half-width will very probably occur. The measurements available in this regard at appr. 78 K show a half-width of less than 1.0 cm^{-1} . The true line profile $\varphi(\nu)$ in consequence practically is a delta-function. At the transition point from the plastic to the rigid phase molecular interactions apparently do not show up as an intrinsic half-width $\Delta\nu_{1/2\text{intr}}$ any longer, but as a shifting of the band maximum, so that $\langle\omega^2\rangle \approx (\pi c \Delta\nu)^2$. This assumption is probably more justified than the Racov-Arrhenius extrapolation, carried out in the afore mentioned manner. Due to the authors in Ref. 8 assuming other intrinsic line widths than in the present paper, for instance at room temperature they find a correlation time of 1.7 ps \pm 0.3 ps, while the here presented measurements show a value of 1.0 ps \pm 0.3 ps. At lower temperatures the differences become still more distinct.

Bartoli and Litovitz⁸ by changing from liquid to plastic phase find for ν_{22} a jump in the half-width of the true line profile of appr. 2 cm^{-1} . The point of discontinuity within this work could not be reproduced. Such a jump could neither be explained by a narrowing of the intrinsic line width of 2 cm^{-1} . Instead, the decrease of the intrinsic line width should result in an increase of the temperature. A discontinuous decrease of the orientational line width at the melting point by comparison of thermodynamic data at the phase transitions liquid-plastic resp. plastic-rigid does not appear justifiable. The experimental results of this work support this assumption.

Concluding, it can be stated that — because of the assumption of an intrinsic line width of 6.0

cm^{-1} — the stated correlation times by Bartoli and Litovitz⁸ for $\nu_{22}(\text{E}_g)$ as a function of tempera-

ture have proved to be too high, if compared to the results presented here.

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