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RAYLEIGH SCATTERING FROM PIVALIC ACID

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Résumé. — Les spectres de diffusion Rayleigh polarisés et dépolarisés de l'acide pivalique ont été mesurés avec une grande précision. Le temps de relaxation de réorientation moléculaire et l'énergie d'activation sont déduits directement de ces mesures pour les phases plastiques et liquides du cristal.

Abstract. — Both the polarized and depolarized spectra of Rayleigh scattering from pivalic acid have been measured with high precision. The relaxation time for molecular reorientation and the energy of activation are deduced directly from these measurements for both the liquid and plastic phases of the crystal.

1. Introduction. — A high resolution study of the spectrum of light scattered quasi-elastically by succinonitrile [1], [2] has recently permitted us to observe scattering from fluctuations in anisotropy and from fluctuations in entropy in an ordered system. The combined spectrum Σ , shown in figure 1, is the sum of three components. Spectrum (a) is depolarized and arises from fluctuations in anisotropy, these fluctuations have been attributed to the rotation of the nitrile group. The profile (s) is polarized and arises from

entropy fluctuations ; (δ), also polarized, is caused by elastic scattering from static imperfections. The widths of these lines are related to the relaxation time of the process responsible for the scattering.

This type of experiment thus allows us to obtain quantitative information about the rotational motion of radicals or molecules in plastic crystals, and also to measure the coefficient of thermal diffusivity.

The object of this paper is to present the results of similar investigations of pivalic acid ($(\text{CH}_3)_3\text{CO}_2\text{H}$). This substance exists in a plastic phase between the temperatures 7 °C and 37 °C.

The molecules, which are globular in shape, occupy the sites of a face centered cubic lattice. Dielectric measurements [3] have shown that the molecules are coupled by hydrogen bonds to form dimers. Rupture of the hydrogen bond permits the reorientation of the molecule along any of the twelve equiprobable directions. The fluctuations in anisotropy are thus related to a step-like rotation of the whole molecule [4].

The depolarized spectrum was first observed by Bird *et al.* [5]. In this present work we study the complete Rayleigh spectrum with a higher spectral resolution.

2. Polarized scattering : measurement of the coefficient of thermal diffusivity. — The light scattered by entropy fluctuations is polarized. The profile of the spectrum has lorentzian shape of half-width Γ_s , where : $\Gamma_s = DK^2$, D is the thermal diffusion coefficient and

$$K = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2};$$

FIG. 1. — Typical spectrum of plastic crystals. The spectral density $S(\nu)$ is plotted against the frequency ν of the scattered light. ν_0 is the frequency of the light source. The width of the line (s) is always about 10 MHz (backward scattering), whereas the width of the profile (a) is typically 10^2 or 10^3 MHz. (δ) can be assimilated to a Dirac function.

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θ is the scattering angle in the medium, λ the wavelength of the incident light and n the refractive index.

The spectrum was analysed using an optical heterodyne technique at small forward angles ($40' < \theta < 1^\circ 35'$). The experimental apparatus has already been described in a previous paper [2]. The sample is a single crystal of excellent optical quality. It was grown in a sealed cell by H. Fontaine (*) using a Bridgmann-Stockbarger technique.

Figure 2 shows the dependence of Γ_s on K^2 . We find :

$$D = (6.7 \pm 1) 10^{-4} \text{ cm}^2 \text{ s}^{-1}.$$

FIG. 2. — Variation of Γ_s vs K^2 at room temperature.

3. Depolarized scattering : studies of molecular motion. — The scattering arising from fluctuations in anisotropy is depolarized and the width of the spectrum does not depend on the scattering angle. These properties permit us to distinguish it from the spectrum caused by entropy fluctuations.

In the plastic phase, the half-width of the depolarized spectrum is typically 20 MHz and was analysed by means of a spherical Fabry-Perot interferometer whose free spectral range was 213 MHz and instrumental half-width 2.1 MHz [6]. Fitting and deconvolution by computer of the experimental data enabled us to calculate the Rayleigh coefficient and half width Γ_a of the spectrum (Fig. 3a).

Measurements in the liquid phase were continued using plane Fabry-Perot interferometers with spacings of 5 and 2.5 mm. The instrumental half-widths were 0.25 and 0.63 GHz respectively. Figure 3b shows a spectrum recorded at 50 °C.

The ratio of the depolarized Rayleigh coefficient R_θ for pivalic acid to the (polarized) coefficient for benzene at 20 °C was measured in the temperature interval

FIG. 3. — a) Spectrum obtained at 36 °C using the spherical interferometer. b) Spectrum obtained at 50 °C with a plane Fabry-Perot interferometer. In both cases the apparatus function W has been recorded.

8 °C to 36 °C. This ratio is roughly independent of temperature within experimental precision. We obtain

$$\frac{R_\theta \text{ piv}}{R_{bz}} = 0.21 \pm 0.05.$$

The reorientation time τ_a , deduced from the measurements of Γ_a ($\tau_a = 1/2 \pi \Gamma_a$) is plotted as a function of temperature in figure 4. The reorientation time follows an Arrhenius-type law with activation energy :

$$\begin{aligned} 0.32 \pm 0.04 \text{ eV} & \text{ in plastic phase} \\ 0.16 \pm 0.01 \text{ eV} & \text{ in liquid phase.} \end{aligned}$$

FIG. 4. — Relaxation time as a function of temperature.

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4. **Conclusion.** — Our experiments have enabled us to measure directly the activation energy and the relaxation time of the rotational movements in pivalic acid.

In the liquid phase the reorientation time (10^{-10} s) is much greater than in a non-associated liquid with an equivalent molecular weight (10^{-12} s) [7]. We may conclude therefore that even in the liquid state the molecules are associated by hydrogen-bonding.

It is interesting to compare the results of measurements made in the plastic phase with the values deduced indirectly from measurements made by NMR [4] and radio-active tracer techniques [4]

(Table I). The excellent agreement between the three sets of values confirms the description of the crystal which was presented in the introduction.

TABLE I

Type of measurement	$E(\text{eV})$	$\tau (\times 10^8 \text{ s})$ at 286 K	Ref.
NMR	0.37 ± 0.04	1.0	Jackson-Strange [4]
Radio-active tracer	0.39	1.3	id.
Light scattering	0.32 ± 0.04	1.3	Our result Bird <i>et al.</i> [5]
	0.62 ± 0.08	3.2	

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