



# Dynamics of relaxation processes in liquids: Analysis of oscillation and orientation spectra



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## ABSTRACT

Based on the spectra of molecular (Rayleigh) scattering of light, we investigate relaxation dynamics in the molecules of para-, meta-, and ortho-xylenes which are confined in a container and heated from room through critical temperature  $T_c$ . We experimentally elucidate the successive transitions from hindered to absolutely-free rotations at temperatures up to a pre-critical temperature  $T^* (< T_c)$  and then from individual to collective motions (macroscopic vibrations) of the molecules at higher temperatures above  $T^*$  up to  $T_c$ . Close to  $T_c$ , the inner field anisotropy is the same along three axes of inertia of the ellipsoid, and the depolarization degree is universal and independent of the specific nature of xylene isomers. A marked deviation from the Rayleigh's theory is also found in the spectral intensity of scattering light.

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## 1. Introduction

Knowledge of the spectral shapes of molecular (Rayleigh) scattering of light (MSL), particularly their temperature dependence, will reveal a mechanism for anisotropy fluctuations in liquids, intermolecular interaction and its local intermolecular field [1].

Despite a great number of experimental and theoretical works in literature [2], the puzzle on the relaxation in liquids has not been solved so far. While the behaviors in the vicinities of the freezing and boiling temperatures at constant pressure are more-or-less examined, global studies on the phase above the vapor pressure curve in such liquids (confined in a container) heated from room through critical temperatures are very limited and are highly desirable.

Oscillation and orientation spectroscopy is one of the most informative experimental methods of investigating a liquid state of substances and allows us to obtain information not accessible by other experimental methods.

The present work is a logical and nontrivial continuation of our preceding works [3,4] and is devoted to systematic analysis of the dependence of MSL spectra on intermolecular interactions of xylene isomer molecules in a liquid state confined in a container in the temperature range (293 K–593 K) between the room temperature

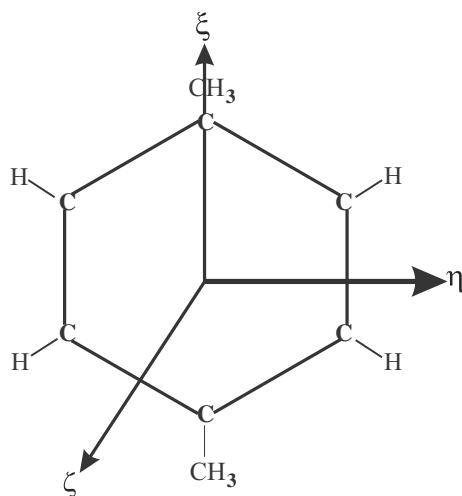
(slightly above the freezing temperature  $T_f$ ) and the critical temperature  $T_c$  which equals to 616 K, 617 K and 630 K for para-, meta- and ortho-xylenes, respectively. Because of the confinement with the use of the saturated vapor, substances keep a liquid state above the vapor pressure curve, showing no phase-transition to gas.  $T_c$  itself cannot be reached in our experiment because of a large pressure which breaks the container.

The molecules of xylene isomers are described by a model, where a pair of hydrogen atoms in the benzene ring is replaced by a pair of methyl groups with each including one hydrogen atom located in the ring plane and the other two located symmetrically relative to both sides of this plane. See Fig. 1 in the case of para-xylene. Each xylene plays as an ellipsoid with three axes of inertia, whose polarizability is responsible to the oscillation and orientation spectra. The dominant contribution to the spectra comes from the rotation around  $\xi$  axis which has the smallest moment of inertia, while the rotation around  $\zeta$  axis is the most massive, giving little contribution to the spectra. On the other hand, the rotation around  $\eta$  axis is marginal and its contribution to the spectra has a possibility to show a strong temperature dependence.

The model slightly differs in configuration of the methyl groups in the benzene ring. The para-xylene molecule belongs to the group of  $C_{2h}$  symmetry and the molecules of meta- and ortho-xylenes to the group of  $C_{2v}$  symmetry. Among xylenes, the para-xylene is the most suitable because of its symmetry, for synthesizing stable long polymers.

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**Fig. 1.** Choice of axes for a molecule of para-xylene.  $\eta$  and  $\xi$  axes lie on the ring plane and  $\zeta$  axis is perpendicular to it.

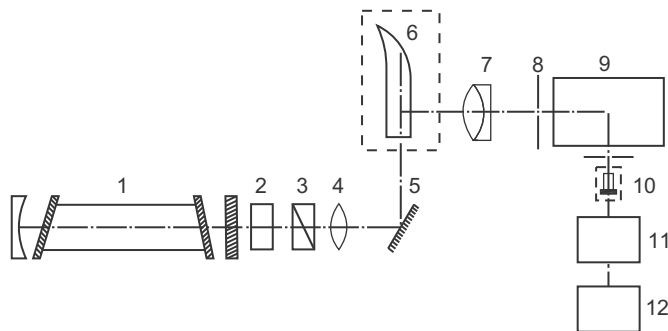
## 2. Experimental setup

The method of measurement stems from that described in Ref. [5]. MSL spectral data to be presented below are obtained using the diffraction spectrometer DFS-4. The experimental setup as a whole is shown in the schematic diagram in Fig. 2.

Concerning the photoelectric recording of spectra, we have regularized receiver-recording and kinematic parts. Since the experiment is accompanied with insufficient time resolution, adjustments to improve the time resolution are essential for line shape analyses. As well-recognized, the resolution of the device depends not only on properties of the optical system of the monochromator, but also is limited by the inertia of the receiver-recording device, and the insufficient time resolution appears in such a way as, the higher the scanning rate is, the bigger the discrepancy is in the observed spectra. The time resolution can thereby be improved by decreasing the scanning rate. We adjusted the scanning rate in a spectrometer to the minimal one, 8 Å/mm.

Optical properties of the spectrometer DFS-4 are quantified as follows: 1) the dispersion for the grating lattice is 1200 grooves/mm, which corresponds to a periodicity of 6.4 Å/mm; 2) the luminosity is 1:10.4; 3) the resolution (to the first order) is  $1.2 \times 10^{-5}$  (see Ref. [6]).

Dispersion of the spectrogram for the line 488 nm is  $0.22 \text{ cm}^{-1}/\text{mm}$ . Width of the instrumental function consisting of width of a slit  $1.08 \text{ cm}^{-1}$  and that of excited line is  $1.5 \text{ cm}^{-1}$ , and the shape of the function is dispersive. The statistical error on the intensity of molecular scattering spectra falls between 2 and 4%.

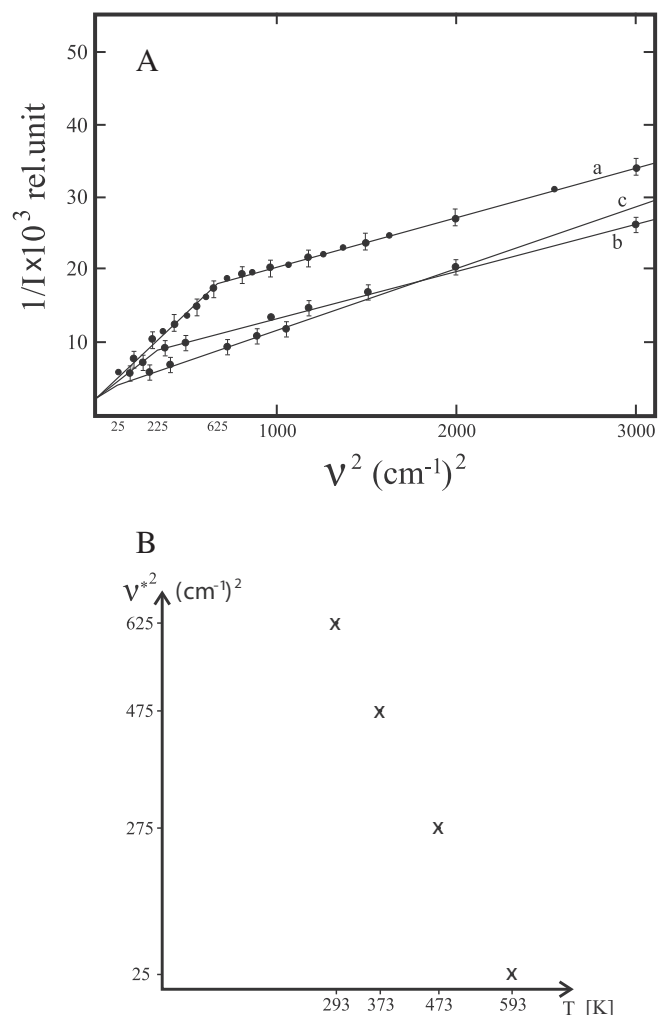


**Fig. 2.** Experimental setup for photoelectric recording of regions nearby the center of the spectra for the depolarized MSL: (1) Argon laser LG-106M; (2)  $\lambda/4$  plate; (3) Nicol prism; (4) focusing lens; (5) rotating mirror; (6) a vessel with test liquid; (7) condenser; (8) diaphragm; (9) spectrometer DFS-4; (10) photoelectric multiplier; (11) amplifier; (12) recorder.

## 3. Line spectra for depolarized parts of MSL

The scattering line shapes for para-xylenes are given by  $1/I$  – versus  $\nu^2$  spectrum (see Fig. 3) with  $\nu$  the frequency and  $I$  the density of the line spectra (the Fourier transform of a time correlation function of the macroscopic polarizability tensor of the substance) for the depolarized part (the case that directions of incident and scattered electric fields are mutually vertical) of MSL. The spectrum in the low-frequency range  $0 \leq \nu < 50 \text{ cm}^{-1}$  is observed to be a superposition of two independent Lorentzian curves, i.e., the “narrow” and “broad (or wing)” components with each center taken as  $\nu = 0$ . Two Lorentzians, i.e., the “narrow” and “broad (or wing)” components, are joined at the inflection point  $\nu^*$  near  $25 \text{ cm}^{-1}$  at room temperature. When the liquid is heated towards  $T_c$ , the inflection point is monotonically shifted to a lower frequency and is located near  $5 \text{ cm}^{-1}$  at  $T = 593 \text{ K}$  (see the lower panel of Fig. 3). On the other hand, the spectrum in the high-frequency range  $\nu \geq 50 \text{ cm}^{-1}$  is composed of a single “broad (or wing)” component. From the observation of temperature dependence the gradient of the spectra in Fig. 3, the narrow component is very sensitive against the temperature variation, while the broad one is almost independent of temperature.

A detailed observation shows that the central part of the  $T$ -sensitive narrow component first becomes wider with increasing temperature. The maximal widening is realized at  $T^* \sim 513 \text{ K}$  for para-xylenes, at



**Fig. 3.** Panel (A): Line spectra for depolarized parts of MSL of para-xylene molecules as a function of squared frequency. Ordinate and abscissa are  $1/I$  and  $\nu^2$ , respectively. Temperature values are: (a) 293 K, (b) 473 K and (c) 593 K. Panel (B): Temperature dependence of the inflection point  $\nu^*$  evaluated from panel (A).

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