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## The role of molecular structure in temperature effects of light scattering in liquids

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**Abstract** In this paper we study depolarization components of the molecular scattering of light (DCMSL) within the wide spectral range ( $0-200\text{ cm}^{-1}$ ) and in the temperature intervals ( $20-200^{\circ}\text{C}$ ) in such liquids as toluol  $\text{C}_6\text{H}_5\text{CH}_3$  and aniline  $\text{C}_6\text{H}_5\text{NH}_2$ . It is shown that when liquid is heated and temperatures approaches to the critical value, contribution to DCMSL by the vibrational motion of molecules becomes significant. The temperature-frequency behavior of DCMSL spectra are discussed from the view point of hindered molecular rotation.

**Keywords** Light scattering, molecular liquids, depolarization component, vibrational motion of molecules, temperature effects

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### Introduction

Light scattering is a part of electromagnetic field interaction with matter which provides information about its structure, relaxation processes and molecular configuration changes. All this information can be extracted from the shape of the depolarization components of molecular scattering of light (DCMSL) contours.

Modern theoretical molecular spectroscopy is mainly the spectroscopy of isolated (non-interacting) molecules while in the experimental studies the optical and other physical properties of molecules are studied in condensed media (solutions, liquids, and solids) where intermolecular interaction is important. In such systems a molecule to be studied is subjected into the action of not only a light wave, but environmental intermolecular strengths, too. In this case the experimentally observed spectra characterize not a molecule itself, but molecule-medium system, too. Therefore the study of the effect of intermolecular interactions on the spectroscopic properties of liquids and their molecular constituents is of importance.

It is known that the DCMSL contour in liquids covers wide spectral range, from 0 to  $200-250\text{ cm}^{-1}$ . The most well studied part of the spectrum covers the range from 0 to  $50-60\text{ cm}^{-1}$ . According to the literature data, in this spectral range the DCMSL contour in liquids is a superposition of two dispersion contours, narrow and wide ones. However, the mechanisms responsible for the narrow and wide contours are different. In [1], the narrow part of was explained by the rotational motion of polarizability-anisotropic molecules and the wide one with vibrations.

If the central part of DCMSL contour ( $0-60\text{ cm}^{-1}$ ) is a superposition of two dispersion contours and explained by rotation and vibration degrees of freedom [2], then the far parts of DCMSL ( $60-200\text{ cm}^{-1}$ ) can be described by the dispersion dependence. Despite the considerable progress made in the study of DCMSL in liquids, the problem is still far from being completely investigated. Moreover, the experimental data on the shape of far wings are still contradicting [3, 4]. Such a contradiction can be explained by the fact that signal at wings is weak and the noises are comparable with the level of a signal. A model of hindered rotation of liquid molecules was proposed in [5]. According to this model, both contour components are caused by the re-orientation of the liquid molecules with respect to main axes of inertia. Due to the different shapes of molecules (different length along the different axes of inertia) and the local internal field anisotropy in liquid the hindered rotation along the axes



should be different. In strong deceleration the rotation occurs in the form of jump-like turnings from one quasi-stable position into another one. This causes the different relaxation times for each type turning. Within this model, the DCMSL contour depending on a molecule symmetry group consists of superposition of two (symmetrical gyroscope) or three (asymmetrical gyroscope) dispersion contours.

In [6] the integral intensity of depolarized scattered light in benzene within the temperature range 25-60°C was experimentally studied in [6]. It was found that the temperature dependence of the integral intensity is non-monotonic. By the comparing experimental data with the theoretical results obtained on the basis of molecular dynamics modeling, the conclusion on the role of transitions between the local structures of liquid benzene was made.

Despite the existence of the broad variety of experimental data on the behavior of different physical characteristics in liquids [7-16], there is no universal idea about the underlying mechanism of the processes occurring at the molecular level. In this paper we address the role of the temperature effects in the behavior of the DCMSL contour in organic liquids consisting of asymmetrically polarized molecules within the wide range of temperature and frequencies.

## Experiment

An experimental setup on the basis of spectrometer DFS-12 for DCMSL spectra registration was constructed. The setup was intended for producing the weak light spectra in automatic mode (the setup was described in [11]). The working range of the setup is 360-650 nm; relative hole-collimator is 1:5.3 and the linear dispersion at output slit is 5 Å/mm. He-Ne laser (radiation wavelength is 628 nm) with power of about 50 mW was used as a radiation source. The DCMSL spectrum is registered with a cooled photo-cathode FEU-79 operating in a mode of photon count. The count characteristic for different values of voltage was measured to select a FEU-79 working voltage. It was found that the plateaus of the count characteristic are within the range 1.800-1.850 V. The dark count for FEU voltage 1.800 V was 52.2 pulses a second at room temperature. Great attention was paid to dish-making because our goal was to study the DCMSL contour for high temperatures. Therefore, the standard (ordinary) dishes cannot be used for such measurements. The solid-drawn dishes made of the thick-walled molybdenum glass (with the wall thickness, 2.5 mm) were used [12]. Every substance was cleaned depending on its initial product quality [13]. Toluene and aniline were dust-removed and degassed by double vacuum refining into a dish. The dish with a substance was placed in a thermostat and its electronic scheme allowed temperature stabilization with accuracy  $\pm 0.5^\circ\text{C}$ . The DCMSL spectra were studied within the temperature range from 20 to 200°C. Each temperature was maintained for not less than 2 h.

## Results and Discussion

The liquids containing the molecules having close structure and symmetry but with different chemical bonds have been selected for our experiment. In particular, we selected toluene and aniline, whose molecules have the same symmetry  $C_{2v}$  and the same base (benzene ring) but differ in bonds.

Molecules of toluene and aniline have the shape of asymmetric top (rotator). The DCMSL contour for molecules is a superposition of three dispersion contours whose half-widths ( $\sigma_i$ ) are defined by three relaxation times,

while their weights ( $\alpha_i$ ) are given by

$$\alpha_i = \frac{(a_k - a_j)}{2g^2} \quad (1)$$

Where  $g^2 = \frac{1}{2}[(a_1 - a_2)^2 + (a_2 - a_3)^2 + (a_3 - a_1)^2]$  is the anisotropy coefficient,  $a_1, a_2, a_3$  are the components of polarizability tensor of molecule.

The weights  $\alpha_1^{theor}$ ,  $\alpha_2^{theor}$ ,  $\alpha_3^{theor}$  calculated with (1) are presented in Table 1. The principal values are taken from [7].

Since the weight of the third contour  $\alpha_3$  (Table 1) for the both substances is very small (2%-4%), the scattering contour for each liquid can presented as the sum of two dispersion contours (narrow and wide). The narrow



contour is related to the rotation of molecule with respect to axes 2 and 3. The axes for the toluene molecule were selected as presented in Figure 1.

The half-widths of the constituent contours ( $\sigma_i$ ) are defined by the characteristic times of jump-like transitions from one quasi-stationary position into another one. The molecules of toluene and aniline rotate with respect to axes 2 and 3 (see, figure 1) by their elongated part, so that these rotations will be more hindered. Hence the relaxation time along these axes will be longer than that along axes 1. The wide contour is associated with rotation relative to axis 1—the axis of facilitated turn.

The analysis of our experimental data (Table 2) shows that the DCMSL contour observed for toluene and aniline (in coordinated  $1/I$  on  $\nu^2$  where  $I$  being the spectral density of the DCMSL contour line) is a sum of two dispersion contours within the range from 0 to  $60 \text{ cm}^{-1}$  at room temperature. With liquid heating the bend border shifts to low frequencies.

The experimental data for the contours of the dispersion components ( $\alpha_1$ ,  $\alpha_2$  and  $\sigma_1$ ,  $\sigma_2$ ) obtained in our study are presented in Table 2. The data are obtained by expansion of the experimental contour in terms of components using the method of successive approximations

**Table 1:** The weights  $\alpha_1^{theor}$ ,  $\alpha_2^{theor}$ ,  $\alpha_3^{theor}$  calculated using (1)

Substance	$\alpha_1^{theor}$	$\alpha_2^{theor}$	$\alpha_3^{theor}$
$\text{C}_6\text{H}_5\text{CH}_3$	0.61	0.35	0.04
$\text{C}_6\text{H}_5\text{NH}_2$	0.58	0.40	0.02

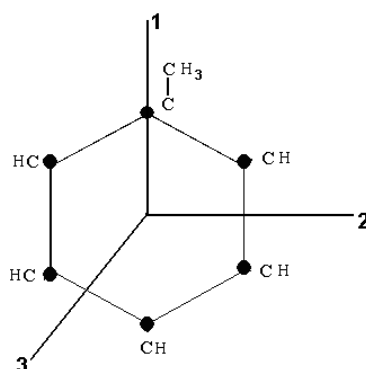


Figure 1: The axes selected for the toluene molecule

**Table 2:** The experimental contours

Substance	$T$ ( $^{\circ}\text{C}$ )	$\alpha_1$	$\alpha_2$	$\sigma_1$ ( $\text{cm}^{-1}$ )	$\sigma_2$ ( $\text{cm}^{-1}$ )
$\text{C}_6\text{H}_5\text{CH}_3$	20	0.67	0.33	1.20	7.40
	100	0.60	0.40	2.60	12.50
	150	0.54	0.46	4.60	12.20
	200	0.51	0.49	4.60	12.20
$\text{C}_6\text{H}_5\text{NH}_2$	20	0.74	0.26	0.80	13.0
	100	0.60	0.40	2.50	13.30
	150	0.55	0.45	3.40	12.50
	200	0.44	0.56	3.10	11.80

As shows the analysis of the experimental data (see, Table 1), the character of the temperature dependence of the contour components is the same for both liquids. The narrow contour ( $\sigma_1$ ) has the sharp temperature dependence; the half-width of the wide contour ( $\sigma_2$ ) weakly depends on the temperature. Such temperature dependence can be explained by hindered internal rotation of a molecule. Namely, the narrow contour is caused by rotation with respect to the axes 2 and 3 which is hindered. Therefore one can expect that by increasing of



temperature (liquid heating) “defrosting” of the motion along these axes occurs. The half-width of the wide contour which is related to the rotation with respect to axis 1 (passing through the carbon point of the ring) weakly depends on the temperature that is caused by almost free rotation.

Consider the weight values and their temperature dependence. When liquid is heated the intensity of the narrow contour (intensity at the center) decreases, while the intensity of the wide contour (peripheral parts) increases. Comparison of the theoretical and experimental weights of the contour components (Tables 1 and 2) shows that at the room temperature the weight values  $\alpha_1$  and  $\alpha_2$  for the both substances differ from  $\alpha_1^{theor}$  and  $\alpha_2^{theor} + \alpha_3^{theor}$ . Such discrepancy decreases as temperature increases, e.g., for 100°C the calculated  $\alpha_1^{theor}$  and experimental  $\alpha_1$  values are almost identical. Further increasing of the temperature leads to the discrepancy again. This can be caused by the role of other types of molecular motion, e.g. vibrational one [1]. It should be noted that there is no universal explanation of the nature of DCMSL contour wings. In [3] the narrow contour was explained by the role of orientation fluctuation and the wide one by the vibrational motion. In [14] the wide contour was explained by the effect of the rotational Brownian motion, while the narrow one to the Maxwell effect arising under action of thermo-elastic waves. Some authors (see, e.g., [15, 16]) this part of the wing is explained as caused by the rotational oscillations of molecules. The difference in the values  $\alpha^{theor}$  (see Table 1) calculated using (1) and those experimentally obtained (see Table 2) can be caused by the contribution of the vibrational mechanism to DCMSL. This mechanism will contribute to the peripheral parts of the contour since the characteristic time of vibration motion is not less than that of hindered rotation and the vibration mechanism weight increases by increasing of the temperature.

For anisotropic molecules the contribution by vibration mechanism can be estimated in terms of the principal values of the molecule polarizability components,  $\alpha_i$  and the calculated weights of the DCMSL contour components,  $\alpha_1$  and  $\alpha_2$ .

Since the vibrational mechanism contributes to the wide contour only, one can show that the weights of rotational ( $\alpha_{rot}$ ) and vibrational ( $\alpha_{vib}$ ) motions can be written as

$$\alpha_{vib} = \frac{\gamma}{1 + \gamma}, \alpha_{rot} = \frac{1}{1 + \gamma} \quad (2)$$

where

$$\gamma = \frac{1}{\alpha^{theor}} \left( \frac{\alpha_1^{theor}}{\alpha_1^{exper}} - 1 \right), \text{ and } \alpha_1^{theor}, \alpha_2^{theor} \text{ are the weights of the contour components (narrow and wide)}$$

calculated from the principal values of the polarizability tensor components  $\alpha_i$ , and  $\alpha_1^{exper}$  is the weight of the narrow contour obtained from experiments (Table 2).

From the data of Tables 1 and 2 for 200°C, we obtain  $\alpha_{vib} = 0.49$  for toluene and  $\alpha_{vib} = 0.44$  for aniline, i.e., the values are slightly less than the half of the wide contour which is caused by the vibrational mechanism.

## Conclusions

There is another experimental indication that when the temperature becomes closer to the critical one, a new mechanism starts to play role in DCMSL. For toluene and aniline the DCMSL contour approximation with two dispersion contours at the room temperature is rather good. However, by increasing of the temperature the approximation becomes worse, mainly at the peripheral parts. This fact indicates that the contribution by vibrational motion of molecules at low temperatures is rather small.

The above study of the temperature-frequency behavior of the DCMSL spectrum shows the existence of effects caused by structural re-configuration in the light scattering in liquids.

Our model for the molecule thermal motion in molecular liquids well explains the experimentally observed peculiarities both in contour numbers and in the temperature behavior of the contour component parameters for objects with variable structures of molecules.



Finally, it is important to note that in different studies the DCMSL contour is associated with such processes as Brownian rotational motion, hindered rotation, vibration, shift deformation etc. Apparently, all these mechanisms make their contributions to the DCMSL spectra and the objective is to establish the principal mechanisms under specific conditions of experiments.

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