FIZIKA 6 (1974) 1—7

IR CORRELATION FUNCTION ANALYSIS OF BENZENE RING ROTATIONS IN LIQUID CRYSTALS

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Received 25 october 1973

Abstract: The IR correlation functions $C(t)$ of liquid crystal diheptyloxyazoxybenzene have been calculated for benzene ring rotations in the smectic, nematic and isotropic phases. It has been found that the benzene ring rotates in random angular jumps of 30° in the smectic phase and of 60° in the nematic and isotropic phases. The rotational correlation times (R. C. T.) are of the order of 10^{-12} s and appear to be comparable with R. C. T. of benzene ring rotations in ordinary organic liquids.

1. Introduction

A number of studies appeared recently describing translational and rotational motions in liquid crystals on the basis of NMR, Rayleigh and neutron scattering[1-6] measurements. Nevertheless, the details of the molecular motions and the motions of its structural elements, like alkyl chains, azoxy groups and benzene rings are still rather poorly understood.

Paying attention to the Raman and IR spectra, which can be expressed in terms of the rotational-vibrational correlation function, i. e. relaxational function[7], detailed information on the internal molecular motions can be obtained.

Correlation function analysis appears to be a very powerful method for analysing molecular dynamics of liquids. This method was first developed by Gordon[8] and

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widely applied by Rothschild[9], Bratosh[10] and many others[11]. On the other hand it has not yet been applied to liquid crystals, so this paper seems to be the first approach of this kind.

It has been generally assumed for liquids that the rotation occurs through random angular steps which are short in comparison with the period of free rotation. According to Rothschild many organic molecules rotate in angular jumps between 20° and 60°, and even higher than 60° in very viscous media[12]. During a jump which is completed in $0.4 \cdot 10^{-12}$ s (a usual value for many organic liquids), the molecules were found to rotate freely. In the case of liquid crystals Samulski et al.[13] have found that the molecules of p-oxyazoxyanizole (PAA) rotate around the long axis in large jumps also. By using proton-spin lattice relaxation they have found that the rotational and translational motions were strongly coupled in the nematic phase. From comparison of rotational correlation times with results of dielectric studies the reorientational jumps were found to be higher than 60°.

In this letter a correlation function analysis of benzene ring rotations obtained from the free rotor model is given. This function is compared with the experimental IR correlation function of liquid crystal diheptyoxyazoxybenzene (HOAB). In this way the subject of our study is not a whole molecule, but one of its structural elements. However, the conclusions have been extended to the behaviour of the whole molecule. The IR spectra of HOAB have been taken in the solid, smectic, nematic and isotropic phases. The general conclusions regarding the temperature dependence of the IR lines are in agreement with Bulkin et al.[14].

2. *Theory and results*

In every molecule two motions are present at the same time: the rotational and vibrational ones, the result of which is the rotational-vibrational spectrum. However, it has to be taken into account that the structural elements of the molecule have their own motions (CH_3-rotation around the C-O axis, the benzene ring-rotation and deformation vibration, alkyl chain twisting vibration). To find out what really happens it is necessary to calculate the correlation function of the related IR spectral band.

The IR absorption intensity $I(\omega)$ is given by the fluctuation-dissipation theorem

$$I(\omega) = \int_{-\infty}^{\infty} \mathrm{e}^{-i\omega t} < \vec{\mu}(0) \vec{\mu}(t) > \mathrm{d}t =$$

$$= \int_{-\infty}^{\infty} C(t)\, \mathrm{e}^{-i\omega t} \mathrm{d}t,$$

where $\vec{\mu}(t)$ is a unit vector pointing into the direction of the transition dipole moment, and $C(t)$ is the correlation function. Once $I(\omega)$ is known, $C(t)$ can be obtained by means of Fourier inversion i. e.

$$C(t) = \int I(\omega - \omega_0)\, e^{-(\omega - \omega_0)t}\, d(\omega - \omega_0),$$

where ω is the centre of the IR band under consideration.

A contribution to the spectral line shape will arise due to the time dependence of changes in the normal coordinate associated with the transition. It is known that the rotations and vibrations are correlated. However, the normal coordinate will become uncorrelated due to the interactions of the vibrator with neighbouring molecules as well as with other groups in the same molecule[17]. The more quickly this loss of correlation occurs, the less certain we will be about the vibrator's interaction with its environment and the corresponding power spectrum will be broader. Assuming that the vibrational and rotational motions have to be uncorrelated $C(t)$ can be separated into two parts, C and C_R[7].

One finds

$$\langle \vec{\mu}(0) \vec{\mu}(t) \rangle = \langle \mu(0) \mu(t) \rangle \cdot \langle \hat{\mu}(0) \hat{\mu}(t) = \\ = C_V(t) \cdot C_R(t).$$

The principal question arising here is, how the vibrational part of the correlation function has to be taken into account. It is difficult to extract $C_V(t)$ from the band contour, but in the cases of symmetrical profiles this problem becomes relatively easy, because the free-rotor model is the most natural approach.

Assuming the free-rotor model in which the vibrational relaxation is neglected, one finds[9])

$$C(t) \equiv C_R(t).$$

For reasons of symmetry the persisting rotational correlation function must be real part, so that only the cosine transform has to be taken into account.

Since orientational motions occur through random steps, a Gaussian form of the correlation function is to be expected, and assuming a short-time behaviour it can be expanded into the power series of $\omega_M t$, as Bliot et al.[15]) have shown

$$C_R(t) = 1 - \frac{1}{2}\omega_M^2 t^2 + \frac{1}{12}\left(1 + \frac{1}{4}\frac{B}{C}\right)\omega_M^4 t^4 + \ldots,$$

where $\omega_M^2 = \frac{2\,KT}{I}$ and I is the moment of inertia of the magnitude of

$$I \sim 2 \cdot 10^{-32}\ \mathrm{gcm}^2.$$

The ratio $\frac{B}{C}$ gives the form of the ellipsoid of inertia (in the case of linear molecules $\frac{B}{C} = 0$, and in the spherical one $\frac{B}{C} = 1$). This formula has been used to fit the experimental correlation function of the benzene ring deformation vibration (540 cm^{-1}) in the smectic, nematic and isotropic phases. A very good fitting with the Gaussian form has been obtained in all the cases, which means that the free rotation of benzene rings in HOAB molecules is an important relaxational mechanism. For the rotational correlation times of the benzene ring which are given by[11])

$$\tau = \int \langle \mu(0) \mu(t) \rangle \, \mathrm{d}t$$

one finds*

$$\begin{aligned} &\text{smectic } \tau = 8.2 \cdot 10^{-12} \text{ s}, \\ &\text{nemastic } \tau = 5.3 \cdot 10^{-12} \text{ s}, \\ &\text{isotropic } \tau = 4.1 \cdot 10^{-12} \text{ s}. \end{aligned}$$

The calculated and the experimental $C(t)$ are identical (Fig. 1) until the correlation function decreases to

$$\begin{aligned} \langle \mu(o) \mu(t) \rangle \text{ smectic } &= 0.85, \\ \langle \mu(o) \mu(t) \rangle \text{ nematic } &= 0.5, \\ \langle \mu(o) \mu(t) \rangle \text{ isotropic } &= 0.45, \end{aligned}$$

one finds that the average angular jumps of rotations are:

$$\begin{aligned} &\text{arc cos } 0.83 \sim 30^\circ \text{ (smectic)}, \\ &\text{arc cos } 0.50 \sim 60^\circ \text{ (nematic)}, \\ &\text{arc cos } 0.45 \sim 63^\circ \text{ (isotropic)}. \end{aligned}$$

If the benzene ring rotates with the whole molecule, the molecule rotates in angular jumps of 30° in the smectic phase, and 60° in the nematic and isotropic phases which is in agreement with Rothschild[9, 11, 12]) and Samulski et al.[13]).

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* Strictly speaking, the rotational correlation time τ average $< \tau >$ for all rotations around the symmetry axis and around the x and y axes. In this case the general expressions for the rotational correlation function is:

$$C(t) \sim e^{-\left[\frac{a}{Ix} + \frac{b}{Iy} + \frac{c}{Iz}\right] t^2},$$

where I_x, I_y and I_z are the corresponding principal moments of inertia. Here the experiment gives information about the R.C.T. which is average over τ_x, τ_y and τ_z.

For the rotational times of the whole molecule Samulski found a period of 10^{-9} s. From our calculations the rotational correlation times of benzene rings are of the order of 10^{-12} s, indicating that the benzene rings rotate between 10^2 and 10^3 times faster than the whole molecule. However, their jump angles are equal.

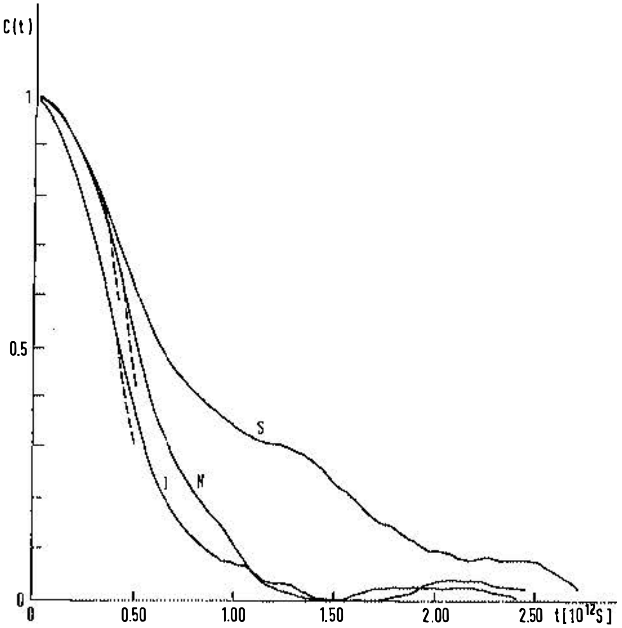

Fig. 1. Correlation function of the liquid crystal HOAB in the smectic (S), nematic (N) and isotropic (I) phases. The dotted lines denote free rotor decay in every phase.

According to Spence et al.[16], the benzene groups rotate around the C-N axis more easily than the whole molecule can rotate about any axis. Our results confirm this. In the smectic phase, where the matching of benzene rings of neighbouring molecules causes a cooperative effect, a very hindered rotation is a general feature. The molecular forces need only about $0.25 \cdot 10^{-12}$ s to cause an observable effect on the molecular motion which is reflected as a loss of correlation.

However, in the nematic phase the situation is rather different. Generally speaking, besides the effect of nematic order are also due to the cybotatic clusters which appear in the nematic phase as a result of residual order from the smectic phase[18]. Nevertheless their role is highly reduced, and rotation is less hindered than in the smectic phase. The intermolecular forces need about $0.48 \cdot 10^{-12}$ s to cause an observable effect, as in the isotropic phase, which is of the same order as in ordinary organic liquids[9].

3. *Conclusions*

It has been found that the benzene rings rotate in angular jumps of 30° in $8.2 \cdot 10^{-12}$ s, of 60° in $5.3 \cdot 10^{-12}$ s, and higher than 60° in $4.1 \cdot 10^{-12}$ s, in the smectic, nematic and isotropic phases, respectively.

For comparison, the rotational correlation time of the benzene ring in liquid toluene is about $3.5 \cdot 10^{-12}$ s[19].

It can be concluded that the benzene ring rotates about 10^2 to 10^3 times faster than the whole molecule of the liquid crystal does. The time of the order of 10^{-12} s is in agreement with the benzene ring rotation in many organic liquids.

Acknowledgement

It is a pleasure to acknowledge valuable conversations with Prof. R. Blinc and Dr. M. Schara, as well as to Dr. B. Borštnik for the help in numerical calculations.

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ANALIZA ROTACIJE BENZENSKOG RINGA U TEKUĆIM KRISTALIMA POMOĆU KORELACIJSKIH FUNKCIJA INFRACRVENOG SPEKTRA

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Sadržaj

Izračunate su korelacijske funkcije IC spektra tekućeg kristala diheptiloksiazoksibenzena za rotacije benzenskog prstena u smektičkoj, nematskoj i izotropnoj fazi. Nađeno je da prsten rotira skokovito, po 30° u smektičkoj fazi, a po 60° u nematskoj i izotropnoj fazi. Rotacijska korelacijska vremena su reda veličine 10^{-12} s, što je komparabilno sa rotacijskim korelacijskim vremenima benzenskog prstena u običnim organskim tekućinama.