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M. Godlewska[a]; J. A. Janik[b]; A. Kocot[c]; X. P. Nguyen[b]; J. Sciesinski[b]; W. Witko[b]
[a] Institute of Physics, Jagiellonian University, 30-059, Kraków, Poland [b] Institute of Nuclear Physics, 31-342, Kraków, Poland [c] Institute of Physics, Silesian University, 40-007, Katowice, Poland

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Far infrared study of molecular reorientation in some alkoxyazoxybenzenes

by M. GODLEWSKA†, J. A. JANIK‡, A. KOCOT§, X. P. NGUYEN‡,
J. ŚCIESIŃSKI‡ and W. WITKO‡

†Institute of Physics, Jagiellonian University, 30-059 Kraków, Poland
‡Institute of Nuclear Physics, 31-342 Kraków, Poland
§Institute of Physics, Silesian University, 40-007 Katowice, Poland

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Far infrared spectra in the frequency range 20 to 200 cm^{-1} for the 4,4′-di-*n*-alkoxyazoxybenzene homologous series are presented for the isotropic and nematic phases and for 0·1 M solution in benzene. In addition some partially deuteriated samples were studied. The spectra consist generally of two broad bands. By comparison of the spectra for different deuteriated compounds it is possible to interpret the higher frequency band as being connected with the intramolecular torsional vibration of the end groups. The band at lower frequencies we associate with the Poley absorption of librating molecules. The confined rotator model calculations performed for this band, for all compounds studied, give the rotational correlation time which is in good agreement with the correlation times as derived from quasi-elastic neutron scattering experiments.

1. Introduction

Vibrational far infrared spectroscopy is a valuable tool to study intermolecular vibrations of polar substances. Some intramolecular motions can also be observed in this region. In the first systematic approach Venugopalan and Prasad presented far infrared spectra for seven members of the homologous series of the 4,4′-di-*n*-alkoxyazoxybenzenes [1]. In the isotropic phase all of these substances exhibit one very broad absorption band. Venugopalan and Prasad consider four factors contributing to the absorption in the far infrared: (i) the tail of the microwave Debye absorption corrected for molecular inertial effects, (ii) the Poley absorption due to librational motion of the molecule as a whole in a temporary cage formed by its neighbours, (iii) the torsional motion of specific polar groups, and (iv) low frequency deformation modes of the molecule. They conclude that for molecules with shorter terminal groups (1 to 3 carbon atoms) the torsional motion dominates, whereas for longer terminal groups (4 to 7 carbon atoms) the Poley absorption prevails [1].

The present paper is a continuation of our earlier far infrared study [2] which was undertaken with the aim to determine absorption coefficients and not simply qualitative spectra. Then, for the Poley absorption a model fitting leading to such molecular parameters as, for example, characteristic times would be possible [3]. The characteristic times obtained in this way can be compared with correlation times resulting from other experiments, e.g. dielectric relaxation, incoherent quasi-elastic neutron scattering (QNS) and Raman scattering [4]. Preliminary results of such model fitting and comparison have already been published by us for two 4,4′-di-*n*-alkoxyazoxybenzenes namely 4,4′-dimethoxyazoxybenzene (PAA) and 4,4′-di-*n*-heptyloxyazoxybenzene (HOAB) [2].

Now we present a similar study for the next three members of the series that is with $n = 2$, 3 and 5. In contrast to [1] we observe in all compounds (except PAA) two broad bands. To elucidate the problem of assignment of these bands the measurements for partially deuteriated species and for benzene solutions were also made. The Poley absorption band should be less sensitive to deuteriation than the torsional band, since its position is inversely proportional to the square root of the moment of inertia of the whole molecule, and this does not change significantly on deuteriation. In contrast, the torsional band frequency should be particularly sensitive to deuteriation of the terminal groups as it is inversely proportional to the square root of the reduced inertia moment of the end groups. In the solution spectra we expect a change in external modes while the internal modes should remain the same. Values for the absolute absorption coefficient for the isotropic and nematic phases of the mesogens are presented and discussed in terms of the confined rotator model.

2. Experimental

The far infrared absorption measurements were performed in the range 20 to $200\,\mathrm{cm}^{-1}$ using a vacuum version of the Digilab FTS–14 Fourier Transform Spectrometer. The resolution of measurements was $4\,\mathrm{cm}^{-1}$. Experimental conditions and preparations were the same as in [2]. The sample was placed between α-quartz windows sealed with indium or teflon spacers. The effective thickness of the sample was established for every sample from the thickness of the sandwich window–spacer–window after it has been mounted. In order to avoid interference between the windows (channel effect), caused by the high refractive index of quartz, one window was shaped ultrasonically to obtain a non-flat surface. Measurements with different spacers were therefore performed to derive correct absolute values of the absorption coefficient. The estimated error of the absolute α values is about 10 per cent. The number of scans for measurements was chosen to be sufficiently high (300 or more) that further increase in the signal-to-noise ratio practically did not improve the spectra. We believe that our procedure of obtaining the α values is correct since in our previous experiments [2] the far infrared measurements fitted well the α values determined in the 2 to $13\,\mathrm{cm}^{-1}$ region obtained by the use of the carcinotrons technique. Since the bands considered in this paper are broad and overlap, the accuracy of their positions is about $5\,\mathrm{cm}^{-1}$.

The 4,4′-di-*n*-alkoxyazoxybenzenes were synthesized in a cooperating organic laboratory [6] and purified until the melting and clearing points were in accord with their literature values [5]. The same procedure was applied for the deuteriated samples and the isotopic substitutions were also checked by mass spectroscopy and N.M.R. [6]. The temperature of the sample was measured by a thermocouple and controlled by the temperature programmer with an accuracy better than $\pm 0.5^\circ$ in the whole range of temperatures for which the spectra were recorded. Benzene solutions corresponding to a mole fraction of 0·1 of the mesogens with $n = 1$, 3, 5, 7 were prepared and their spectra were recorded at a temperature slightly above room temperature.

3. Results and discussion

The absorption coefficients were calculated from the spectra both for isotropic and nematic phases; they are shown in figure 1. The temperatures in which the spectra were recorded are shown in the figure. Comparison of the isotropic phase spectra

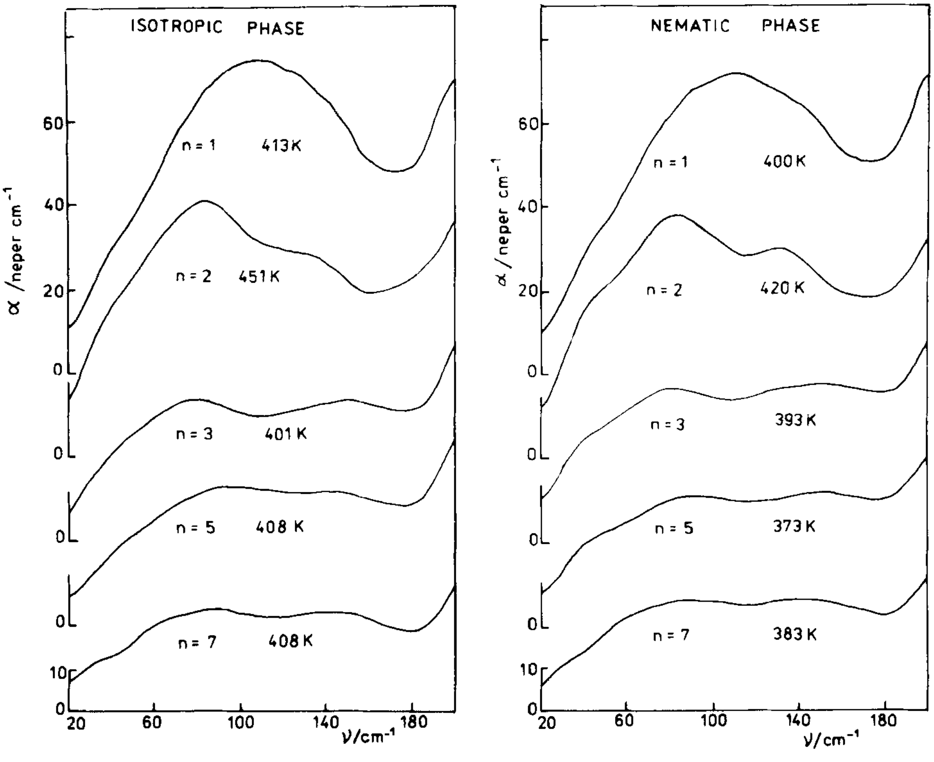

Figure 1. Absorption coefficients, $\alpha(\nu)$, for the isotropic and the nematic phase of the 4,4′-di-n-alkoxyazoxybenzenes with $n = 1, 2, 3, 5, 7$.

with those of solutions are shown in figure 2. The results of measurements for different deuteriated species are given in figures 4 and 5. An example of the temperature dependence of the spectra is shown in figure 3 for 4,4′-diethoxyazoxybenzene (PAP).

The spectra for PAA-d_0 (fully protonated) and PAA-d_8 (with deuteriated benzene rings) are very similar and consist of one broad maximum. In the spectrum of PAP-d_0 an additional broad band appears at a higher frequency. In the spectra of the samples with deuteriated terminal groups (PAA-d_6 and PAP-d_{10}) the higher frequency part of the absorption diminishes. It seems that it is shifted towards lower frequencies. We assume therefore that the higher frequency part is associated with the reorientation of the terminal groups. In order to estimate the torsional band frequency the relevant spectra were subtracted, i.e. PAA-d_0–PAA-d_6, and PAP-d_0–PAP-d_{10} for both the nematic and isotropic phases (cf. figure 6). In this way we estimate the torsional frequency to be equal to approximately $120\,\mathrm{cm}^{-1}$ and $135\,\mathrm{cm}^{-1}$ in the isotropic and nematic phases, respectively, for the two compounds. The higher frequency in the nematic phase and the fact that the torsional band in the isotropic phase is more smeared out than that in the nematic phase (for both compounds) is consistent with the fact that the liquid-crystalline ordering restricts, to a certain extent, the rotational freedom of the terminal groups [7]. The values of the two-fold barrier for the end group reorientation around the C–O bond are given in table 1. They were obtained from the simple Mathieu equation $\nu = nh\sqrt{(V/2I)}$, where I is the reduced moment of inertia of the end group for reorientation around the C–O bond (taken from [1]),

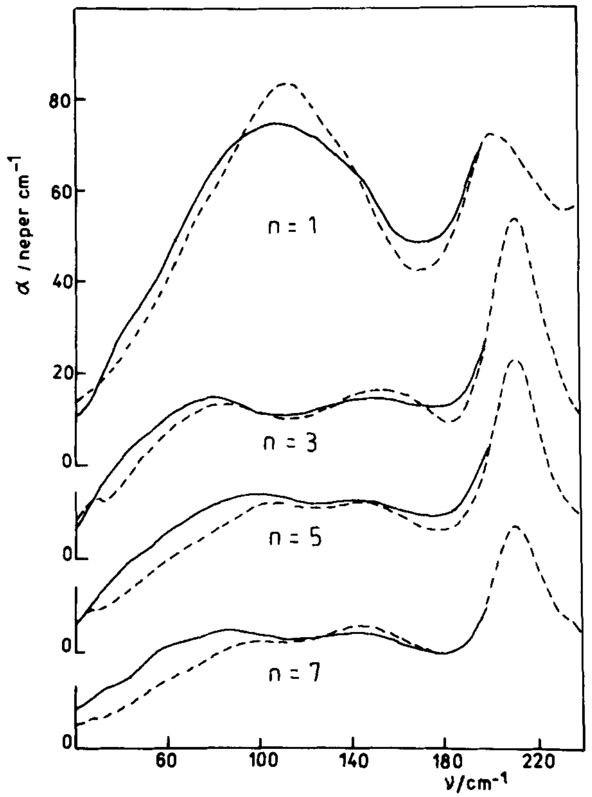

Figure 2. Far infrared spectra of 0·1 mole fraction benzene solutions for the 4,4′-di-*n*-alkoxyazoxybenzenes with $n = 1, 3, 5, 7$ (broken lines) compared with their isotropic phase spectra (solid lines). (The $\alpha(\nu)$ scale for the solution spectra is normalized to the same number of liquid crystal molecules per surface unit.)

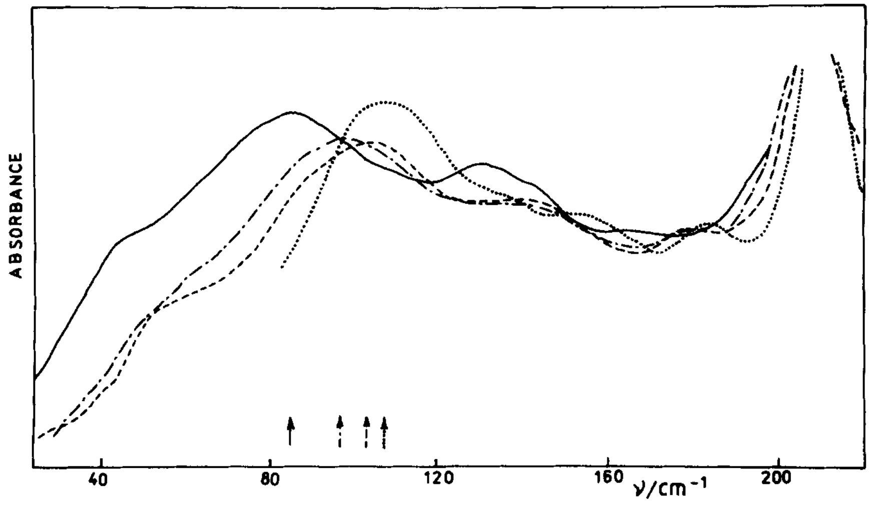

Figure 3. Temperature dependence of the PAP spectrum: ——, 420 K; –·–·–, 209 K; – – –, 198 K; ····, 83 K. The arrows mark the positions of the lower frequency band at the respective temperatures.

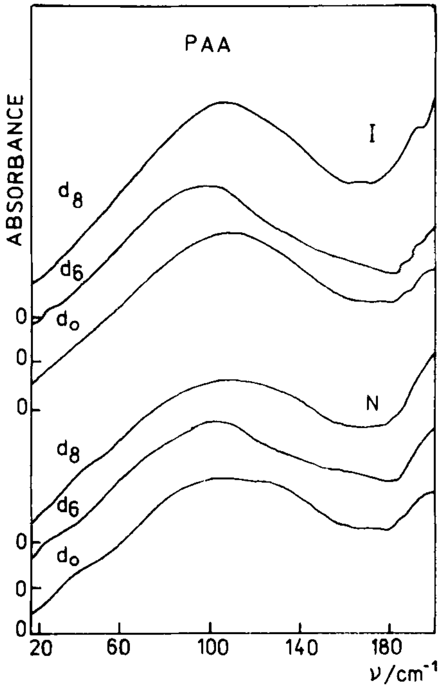

Figure 4. Far infrared spectra of the nematic and the isotropic phase of PAA-d_0, PAA-d_6 and PAA-d_8.

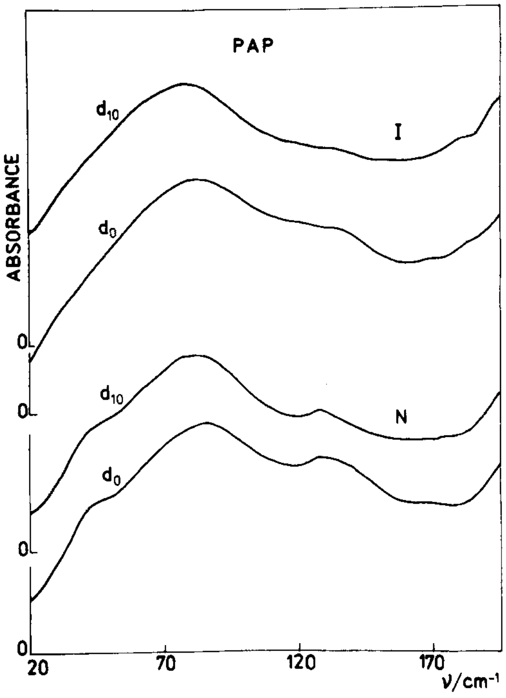

Figure 5. Far infrared spectra of the nematic and the isotropic phase of PAP-d_0 and PAP-d_{10}.

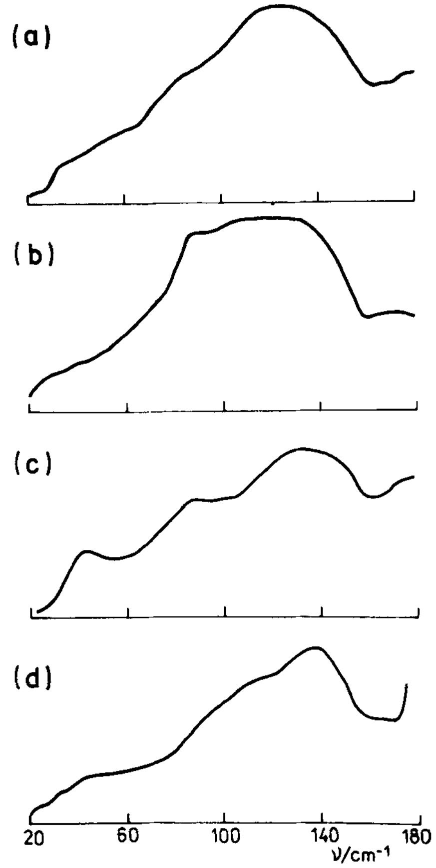

Figure 6. The differences between the far infrared spectra of: (*a*) PAA-d_0 and PAA-d_6 in the isotropic phase; (*b*) PAP-d_0 and PAP-d_{10} in the isotropic phase; (*c*) PAA-d_0 and PAA-d_6 in the nematic phase; (*d*) PAP-d_0 and PAP-d_{10} in the nematic phase.

Table 1. The frequencies of the torsional band and the barriers for reorientation of the alkoxy groups around the C–O bonds.

		ν cm^{-1}	V kJ mol^{-1}
PAA	I	122	59
	N	135	71
PAP	I	120	79
	N	138	105

ν is the torsional frequency, V is the barrier height and n is the multiplicity of the barrier. The high barrier values are consistent with the neutron data [8] which indicate (for PAA) that the OCH_3 groups are coupled to the rings and cannot reorient much faster relative to the ring. As in our previous paper [2] we interpret the lower frequency band as resulting mainly from librations of the molecules around their long axes (Poley absorption). For PAA, the torsional band and the Poley absorption band overlap fully giving apparently one band (at 105 cm^{-1}). The assignment of the Poley band is supported by the following observations:

(1) the position of this band tends to shift towards lower frequencies with increasing number of carbon atoms in the terminal groups (figure 1 and table 2) (*n* = 5 does not follow this pattern probably due to an exceptionally high packing coefficient for this nematogen [9]);
(2) the intensity of this band decreases with increasing moment of inertia (approximately proportional to I^{-1}) (cf. figures 1, 4 and 5 and table 2);
(3) in the solution spectra this band is changed, contrary to higher frequency modes (cf. figure 2), so that we can expect that the former band is connected with the external modes and the latter with internal modes;
(4) there is a strong temperature dependence of the position of this band (cf. figure 3).

Table 2. The absorption coefficients and the frequencies of the Poley absorption band in the nematic and isotropic phases of the 4,4′-di-*n*-alkoxyazoxybenzenes.

	Nematic phase			Isotropic phase		
n	Temperature/K	Poley max ν/cm^{-1}	$\alpha/\text{neper cm}^{-1}$	Temperature/K	Poley max ν/cm^{-1}	α/neper cm
1	400	105	62	413	105	74
2	420	85	59	451	82	61
3	398	78	35	401	78	34
5	373	92	33	408	98	33
7	383	88	26	408	85	24

The confined rotator model was used to determine quantitatively the parameters of the molecular motion [3]. This model has already been applied successfully to PAA and HOAB [2]. The model and the fitting procedure are described in detail elsewhere [2, 3] so that only a brief resumé is given here. In this model, a two-dimensional rotator librates in the potential cage formed by its neighbours and reflects elastically from the walls. The rectangular cage of width 2β exists for a time interval given by the Poisson distribution function with an average lifetime τ_l. Then the local configuration and angular momentum change instantaneously. This means that any other cage of the same size is formed, but with a different orientation. The motion of the cage is treated as rotational diffusion with a characteristic time τ_D. The model introduces three independent parameters namely β, τ_l and τ_D. τ_D can be determined from dielectric relaxation experiments, since it is natural to set it equal to the Debye relaxation time. The other two parameters, β and τ_l, are adjusted so that the best fit to the observed maximum of absorption $\alpha_{\max}$ and the frequency $\nu_{\max}$ is obtained. The results of such model fitting are presented in table 3 and figure 7. As we can see, the time τ_l of an unperturbed libration is close to the correlation time found from the quasi-elastic neutron scattering results. Taking into account the information about the low potential barriers for rotation of molecular moieties around the N-phenyl bond [10] it is probable that this internal reorientation may cause stochastic interruptions of the whole molecule libration. Such an interpretation is not inconsistent with the recent interpretation of the neutron scattering results.

Another outcome of the model fitting is the second possibility of the separation of the end chain torsional band, different from the deuteriation method described previously. In figure 7 we can see the results of subtraction of the model Poley band from the experimental spectra. The influence of the 210 cm^{-1} internal band was taken

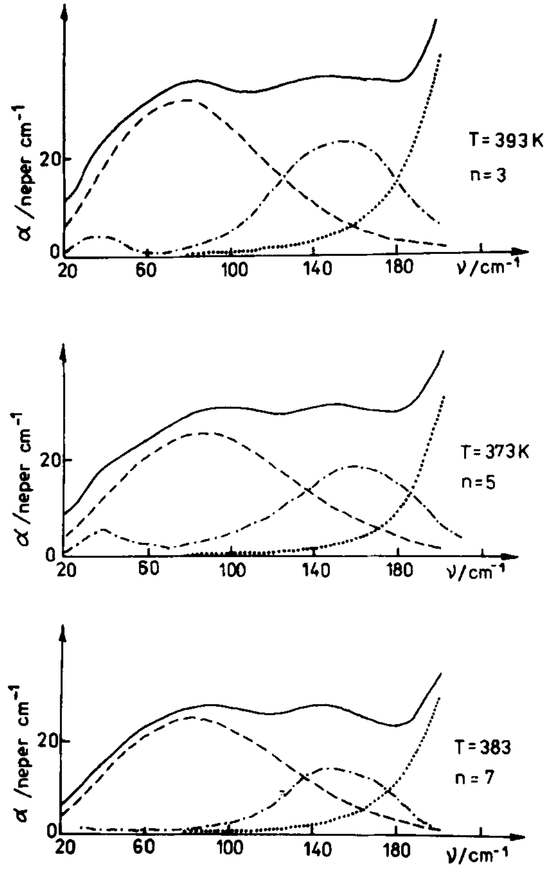

Table 7. Results of the confined rotator model fit for the 4,4′-di-*n*-alkoxyazoxybenzenes for $n = 3$, 5 and 7 in their nematic phases ——, experimental spectrum; ––––, model fitting; ····, part of the internal band fitted by a lorentzian line, –·–·–, result of subtraction of the fitted curves from the experimental result.

Table 3. The confined rotator model: experimental and fitting parameters compared with the correlation times derived from the quasi-elastic neutron scattering experiments.

Substance *n*	Temperature/K	β	τ_D/ps	τ_l/ps	τ_{QNS}/ps
1	400	0·13	22	2	4
2	420	0·14	29	4	5
3	393	0·15	49	4	9
5	373	0·12	104	8	5
7	383	0·12	110	10	12

into account. The frequencies of the torsional band separated in this way are higher than those obtained by analysis of the isotopic effects, but the differences can be explained by the inaccuracies of both methods.

It is worth noting that in our spectra for the nematic phase we observe a slight shoulder on the low frequency side of the Poley band. This might be connected with the libration of molecules around their short axes since such a process should be observed at low frequencies. In the Raman spectra for the crystal phases of the 4,4′-di-alkoxyazoxybenzenes Gruger *et al.* [11] observed a band which they interpreted as the librational phonon around the short axis in this frequency region. In addition it has been suggested that collective modes may also contribute to the absorption in this frequency region [12].

4. Conclusions

From the spectra presented here for some 4,4′-di-*n*-alkoxyazoxybenzenes together with the partly deuteriated compounds it is clear that the far infrared region consists of at least two broad bands. The band appearing at lower frequencies is due to Poley absorption and its frequency changes from one substance to another, whereas the other band can be attributed to torsional motions of terminal groups of the molecule around the O–C bonds.

In a confined rotator model taking the dielectric relaxation time as equal to the time of the reorientation of the potential cage, the average times of unperturbed libration are in good agreement with the correlation times derived from neutron scattering experiments.

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