# Intense quasielastic neutron scattering of 4,4'-diethyoxyazoxybenzene and its connection with the inelastic neutron scattering spectrum

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# Intense quasielastic neutron scattering of 4,4'-diethyoxyazoxybenzene and its connection with the inelastic neutron scattering spectrum

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This is a continuation of a previous study of the odd–even effect for compounds of the series of 4,4'-di-n-alkyloxyazoxybenzenes. The reduction of the elastic component of the neutron scattering spectra (the elasticity depression), studied earlier at constant $\Delta T$ from the clearing point, has now been studied at constant temperature. The ethyoxy member of the series shows an exceptionally large elasticity depression; this is interpreted as evidence of a small steric hindrance for molecular motions due to the high nematic order parameter. This statement has been corroborated by the inelastic neutron scattering measurements for solid compounds of the series.

## 1. Introduction

This paper concerns the molecular motion in compounds belonging to the 4,4'-di-n-alkyloxyazoxybenzene homologous series; the structural formula of these substances, (n-OAOB) is: $H_{2n+1}C_nO\phi N_2O\phi OC_nH_{2n+1}$, where $\phi$ stands for the benzene ring. In papers [1] and [2] we discussed two effects connected with neutron scattering by these compounds in the nematic phase. First, the intensities of the quasielastic scattering components were significantly greater than expected from the predictions of models based upon the assumption of rigid alkyl chains. Secondly, this enhancement of the quasielastic intensity (registered as a relative depression of the elastic intensity) showed the odd–even effect for several early members of the series. The first effect may be explained by the occurrence of an additional quasielastic scattering caused by segmental reorientations in the chains. As was suggested in [2] the second effect is dominated by the second member of the series (i.e. by 2-OAOB), which exhibits an anomalously large enhancement of the quasielastic component.

This paper is a result of a more critical approach to the computing procedure of the model fittings applied so far and we intend to find out whether the anomalous depression of the elastic component observed for 2-OAOB does or does not exceed the normal temperature effect.

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## 2. Remarks concerning verification of the computer procedure

In the model fittings (as explained in [1, 2]) we seek to determine two parameters: the correlation time $\tau_1$ for molecular fragment reorientation and the relative depression $p$ of the elastic scattering component. Our old data [1, 2] were processed on the CDC-CYBER. Recently we have written a completely new fitting program for an IBM personal computer. A comparison of the treatment of the data by the new computer program with that by the previous one is presented in the figures in this paper.

## 3. Remarks concerning temperature effects

In [1, 2] we decided to relate the measured elasticity depressions to constant $\Delta T$ from the clearing points. Because of the odd–even behaviour of the clearing points, there exists a possibility that the odd–even behaviour of the elasticity depression indirectly reflects this behaviour. This is plausible, especially for 2-OAOB, since this substance has a relatively high nematic–isotropic transition temperature as compared to the neighbouring members of the series. We decided, therefore, to relate the measured elasticity depressions not at a constant $\Delta T$ from the clearing points but at a constant temperature of 120°C. It is true that this was impossible for 2-OAOB, since its melting point is 136·6°C but we decided to extrapolate the results obtained at higher temperatures to 120°C.

## 4. QNS elasticity depression results for nematic *n*-OAOBs

Since molecules in liquid crystals undergo many types of motion, it is necessary to measure the quasielastic scattering over a wide energy transfer. It is generally believed that such measurements must be made for a wide scattering vector range and with a very good energy transfer resolution. As for a wide scattering vector range, its exploitation is no doubt useful and even necessary for simpler reorienting molecular units such as $CH_3$, $NH_3$ or $NH_4$ groups. For liquid crystal molecules the advantage of exploitation of a wide scattering vector range is almost always non-existent, since the molecules are flexible and undergo many types of internal motions, which leads to a multi-component quasielastic spectrum with too many parameters to be fitted. As far as the necessity of measurements with a very good energy transfer resolution is concerned the situation appears to be as follows. We are inclined to avoid the terms good energy transfer resolution or poor energy transfer resolution, when we deal with the quasielastic neutron scattering method, since the energy resolution should be properly chosen according to the correlation time window which we plan to study. If we chose, for instance, the resolution of the order of $100\,\mu eV$, we adjust our time window for the *c.* 10 ps region, i.e. we observe only the fastest motions in our experiment. If we chose, for instance, the resolution of the order of $1\,\mu eV$, we observe only the slowest motions (i.e. translational diffusion). Therefore, in this study, we accept the following standpoint. We chose the energy resolution being *c.* $140\,\mu eV$, which is well-suited to observe the fastest motions, in the picosecond range. Such a resolution cuts off the whole spectrum of slower motions, including (probably) the spinning of the whole molecule, as well as the translational diffusion. The motions which remain within the observation window are then the internal ones, still too many to be resolved (spinning of the rings, conformation changes in the chains, etc.). Hence we have decided to take them into consideration in a rough approximation only, i.e. by looking at a deviation of the quasielastic spectra from a relatively simple reorientational (internal) model. In order to do that we introduce (as explained in [1]) the notion of the elasticity

depression. We do that in the following way. We first assume that the (too) simple reorientational model we start from is a reorientation of molecular fragments consisting of rigid chains coupled with benzene rings around the CN bonds. Instead of the usual model scattering function

$$S(\mathbf{Q}, \omega) = f_0(\mathbf{Q})\delta(\omega) + \frac{2}{\pi} \sum_{k=1}^{\infty} f_k(\mathbf{Q}) \frac{\Gamma_k}{\Gamma_k^2 + (\hbar\omega)^2},$$

we introduce a function

$$F(\mathbf{Q}, \omega) = p\delta(\omega) + (1-p)S(\mathbf{Q}, \omega).$$

In these equations $\hbar\omega$ and $\hbar\mathbf{Q}$ are the neutron energy and momentum transfers, respectively, $\Gamma_k = (\hbar^2 k^2/\tau_1)$; $\tau_1$ is the correlation time connected with the reorientational motion, and $f_0$ and $f_k$ are form factors which can be calculated for a given model. The new parameter $p$ is usually negative and so we call it the elasticity depression. Its negative value tells us that there are other motions present than suggested by the model. We suppose that these other motions are: spinning of the benzene rings, conformational changes in (various) chain segments and the terminal $CH_3$ rotations. To resolve them is (we think) quite impossible even by performing a detailed $\mathbf{Q}$ analysis. Two remarks have to be made here: first, we should remember that the elasticity depression parameter is not a molecular property, hence it must be considered for a particular scattering angle, or rather a particular scattering vector, $\mathbf{Q}$. Secondly, the correlation times $\tau_1$ obtained by fitting, have to be considered as average times for all motions in the picosecond range, i.e. as those which correspond to the time window as determined by the energy resolution.

Figure 1 presents the elasticity depression results obtained by applying the model of rotational diffusion of the alkyloxy chains (together with benzene rings) around the CN bonds. Figure 1 (*a*) presents the data from [2], obtained not at constant temperature but at $\Delta T$ of $-2°$. For each substance there are two points corresponding to the two computation procedures, as explained in § 2. There is agreement between the results of these procedures. Similar agreement was obtained for the correlation times in the ps range.

Figure 1 (*b*) presents the results at 120°C, obtained from the experimental material which was the basis of [1]. The extrapolation procedure for 2-OAOB was as follows. We first calculated the elasticity depressions for 140°C and 167·5°C. These depressions happened to be equal, hence the depression value for 120°C was not different. This corresponds to the lower point on the plot in figure 1 (*b*). Then we decided to apply (to the 2-OAOB depression data) the maximal temperature coefficient observed for other substances of the series. In this case the extrapolation procedure gave us the higher point for the plot of figure 1 (*b*). We may see that the anomalous depression for 2-OAOB still exists, which means that it is not the result of a temperature effect only but that there must be more factors causing it. We believe (as stated in [1,2]) that those additional factors are connected with the high nematic order parameter $S$ for 2-OAOB, which reduces the steric constraints for molecular motions and in consequence enhances the quasielastic component of neutron scattering.

The experimental material used in this work was that described in [1,2] obtained at the Institut for Energiteknikk, Kjeller, Norway, during our studies of particular members of the series. The relevant references are listed in [1]; also the relevant formulas may be found in [1].
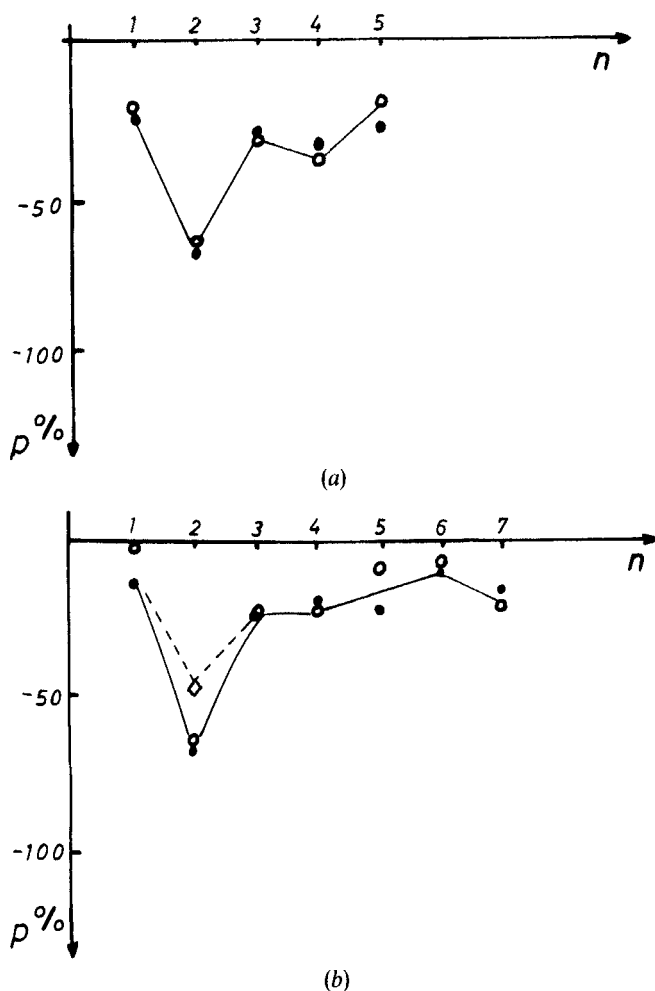
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Figure 1. Elasticity depression results for members of the 4,4'-di-*n*-alkyloxyazoxybenzene series in the nematic phase. Neutron scattering angle 30°. (*a*) For compounds $n = 1$–5 at temperatures $T_{NI} - 2°$. ●, old computing procedure (CYBER); ○, new computing procedure (IBM). (*b*) For compounds $n = 1$–7 at 120°C ● and ○ have the same meaning as in (*a*). Lower points for $n = 2$ correspond to 140°C. Upper points for $n = 2$ correspond to the extrapolation to 120° when a maximally strong temperature dependence is assumed.

## 5. INS results for solid *n*-OAOBs

In addition to measurements with the nematic phases of the series we decided to perform the inelastic neutron scattering measurements for the solids as well ($n = 1$–6). It is know that an approximately parallel arrangement of molecules is maintained after the substances have been frozen [3–8]. The inelastic neutron scattering measurements were made on the neutron spectrometer KD SOG-M installed at the IBR-2 pulsed reactor of the Joint Institute for Nuclear Research at Dubna, USSR [9], at 120 K. The results in the form of the scattered neutron intensity distribution versus the neutron wavelength and also in the form of the excited states density versus the frequency are
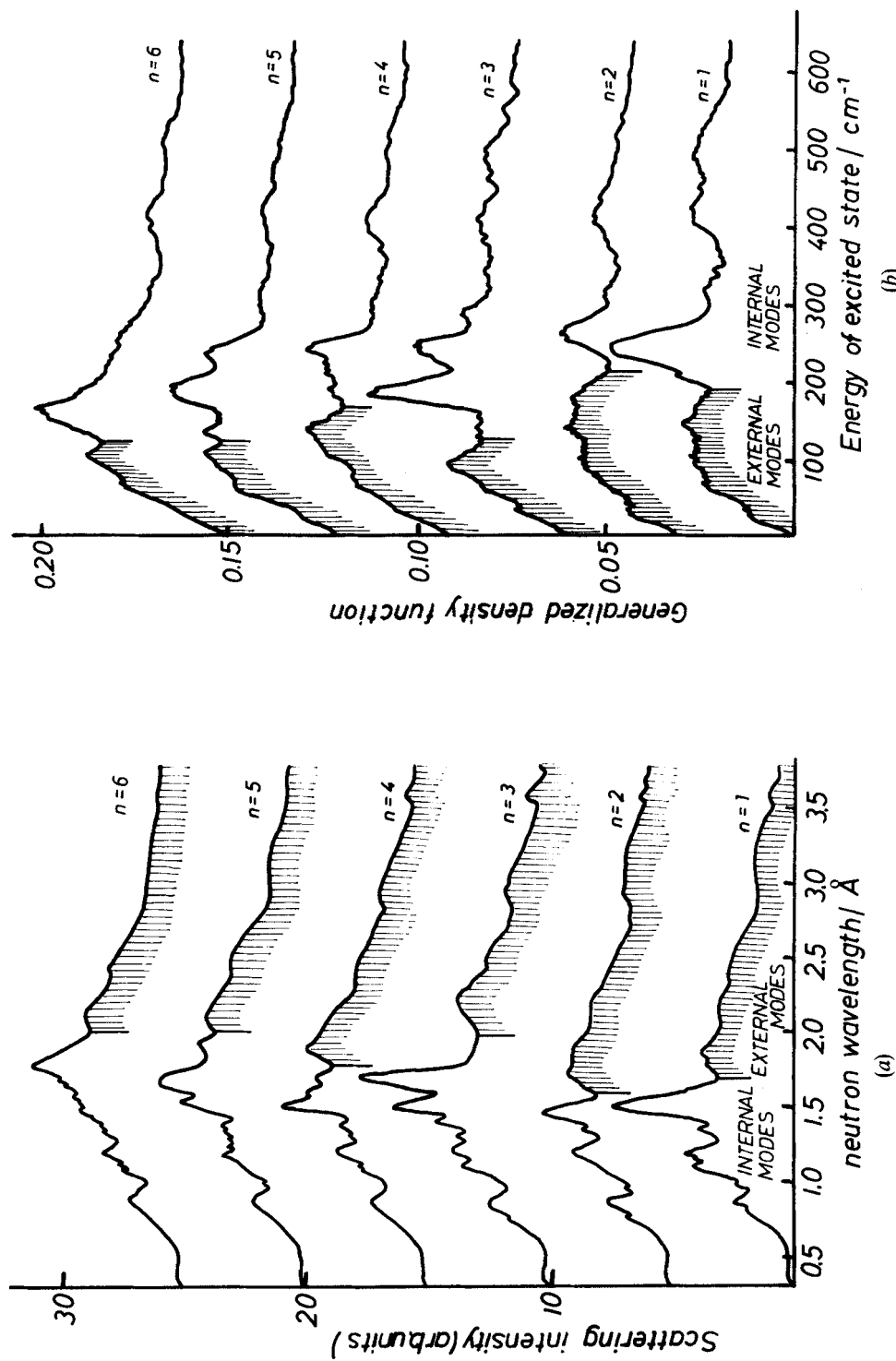
Figure 2.   (*a*) Inelastic neutron scattering spectrum versus neutron wavelength for polycrystalline *n*-OAOBs (*n* = 1–6) at 120 K. (*b*) Density of excited state versus their energy obtained from the results in (*a*).

shown in figure 2. We believe that the intense maximum observed for 1-OAOB (i.e. for PAA) at $\sim 245\,cm^{-1}$ corresponds to torsional vibrations of the terminal $CH_3$ groups. This vibration was observed previously and so interpreted [10]. We think that the same interpretation applies to the $\sim 266\,cm^{-1}$ peak for 2-OAOB, the $\sim 247\,cm^{-1}$ peak for 3-OAOB, the $\sim 245\,cm^{-1}$ peak for 4-OAOB and the $\sim 240\,cm^{-1}$ peak for 5-OAOB. The decreasing peak intensity corresponds to the decrease with increasing $n$ of the relative contribution of hydrogens belonging to the $CH_3$ groups. We are inclined to believe that other vibrational peaks (at lower frequencies) correspond to other segmental torsions. However, a detailed interpretation of the inelastic neutron scattering spectra by ascribing the peaks to particular internal vibrations was not the aim of this work.

However, let us note that for all polycrystalline substances under study, we may distinguish two regions in the inelastic neutron scattering spectra. One a nearly continuous region of lattice motions and the other a region corresponding to internal normal vibrations and composed of well-developed peaks at higher frequencies. We can see that the two regions are well separated and that the border frequency shows an odd–even alternation. Indeed, this border lies at $\sim 191\,cm^{-1}$ for 1-OAOB, $\sim 218\,cm^{-1}$ for 2-OAOB, $\sim 130\,cm^{-1}$ for 3-OAOB, $\sim 171\,cm^{-1}$ for 4-OAOB, $\sim 125\,cm^{-1}$ for 5-OAOB and $\sim 126\,cm^{-1}$ for 6-OAOB. Thus, it is evident that 2-OAOB possesses a maximally developed region of lattice motions. This seems to corroborate the quasielastic neutron scattering results described in section 4, since the lattice motions transform after melting into stochastic ones which influences such spectra.

## 6. Conclusions

The following conclusions may be derived from our results:

(i) The computerized fitting procedure is phenomenologically correct, this was checked on two computers, using two fitting programs.

(ii) The enhancement of the quasielastic neutron scattering component (observed as the elasticity depression) is largest for 2-OAOB, which indicates the existence of richer and more intense stochastic motions appearing in the ps range for this substance in the nematic phase.

(iii) The inelastic neutron scattering spectra obtained for the polycrystalline substances corroborate this statement since the lattice motion spectrum for 2-OAOB occupies the largest region of the low frequency part of the spectra.

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