

INSTYTUT FIZYKI JĄDROWEJ  
INSTITUTE OF NUCLEAR PHYSICS  
ИНСТИТУТ ЯДЕРНОЙ ФИЗИКИ



KRAKÓW

R A P O R T No 1318/PS

INF.. 1318/PS

FAR INFRARED STUDY OF MOLECULAR  
REORIENTATIONS IN SOME  
ALKOXYAZOXYBENZENES

MAŁGORZATA GODLEWSKA, JERZY A. JANIK  
ANTONI KOCOT, XUAN P. NGUYEN  
JAN ŚCIESIŃSKI, WACŁAW WITKO

KRAKÓW 1986

FAR INFRARED STUDY OF MOLECULAR REORIENTATIONS IN SOME  
ALKOXYAZOXYBENZENES

BADANIE REORIENTACJI MOLEKULARNEJ W ALKOXYAZOXYBENZENACH  
METODĄ SPEKTROSKOPII W DALEKIEJ PODCZERWIENI (FIR)

ИССЛЕДОВАНИЕ МОЛЕКУЛЯРНОЙ РЕОРЕНТАЦИИ В АЛКОКСИАЗОКСИБЕНЗОЛАХ  
МЕТОДОМ ДАЛЕКОЙ ИНФРАКРАСНОЙ СПЕКТРОСКОПИИ

Małgorzata GODLEWSKA<sup>X</sup>, Jerzy A. JAWIK<sup>O</sup>, Antoni KOCOT<sup>+</sup>,  
Luan P. NGUYEN<sup>O</sup>, Jan ŚCIBIŃSKI<sup>O</sup>, Wacław WITKO<sup>O</sup>

<sup>X</sup>Institute of Physics, Jagiellonian University, 30-059 Kraków,  
Poland

<sup>O</sup>Institute of Nuclear Physics, 31-342 Kraków, Poland

<sup>+</sup>Institute of Physics, Silesian University, 40-007 Katowice,  
Poland

CRACOW

May, 1986

**NAKŁADEM INSTYTUTU FIZYKI JĄDROWEJ W KRAKOWIE  
UL. RADZIKOWSKIEGO 152**

*Kopię kserograficzną, druk i oprawę wykonano w IFJ Kraków*

---

*Wydanie 1*

*Zam. 160/86*

*Nakład 125 egz.*

Far infrared spectra in the frequency range  $20 - 200 \text{ cm}^{-1}$  for di-n-alkoxyazoxybenzene homologous series are presented for the isotropic and nematic phases and for 0.1 M solution in benzene. Additionally some partly deuterated samples were measured. The spectra generally consist of two broad bands. By comparison of the spectra for differently deuterated compounds it was 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 connect 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 happens to be in good agreement with the correlation times as derived from the quasielastic neutron scattering experiments (QNS).

W pracy przedstawiono widma w zakresie dalekiej podczerwieni  $20 - 200 \text{ cm}^{-1}$  dla fazy nematycznej i izotropowej kilku związków z szeregu homologicznego dwu-alkoksyoazybenzenów oraz ich 0.1 M roztworów w benzynie. Dodatkowo zmierzono widma kilku związków częściowo zdeuterowanych. W widmach występują, na ogół, dwa szerokie pasma. Przez porównanie widm dla różnie zdeuterowanych związków możliwym stało się przypisanie pasma o wyższej częstotliwości wewnętrzny drganiem torsyjnym grup końcowych. Pasma przy niższej częstotliwości związane jest z absorpcją Poley'a molekuł wykonujących ruchy libracyjne. Przeprowadzone dla tego pasma obliczenia z zastosowaniem modelu ograniczonego rotatora dla wszystkich badanych substancji dostarczają rotacyjne czasy korelacji, które okazują się być zgodne z czasami korelacji wynikającymi z eksperymentów kwazielastycznego rozpraszania neutronów (QNS).

... 200 см<sup>-1</sup> для некоторых d<sup>1</sup>-d-алкоксиазоксибензолов в изотропной и нематической фазе и для 0,1 М растворов в бензоле. Дополнительно измерены были некоторые соединения в которых часть водорода заменена была дейтерием. В спектрах обнаружено две широкие абсорбционные полосы. Сравнения спектров для разных дейтерации позволило отнести полосу при высокой частоте к внутренней вибрации периферийных групп. Полосу при низких частотах можно связать с эффектом абсорбции Поля для либрующих молекул. Для этой полосы сделаны были модельные расчеты для всех соединений используя модель ограниченного ротатора. Полученные времена ротационной корреляции совпадают хорошо с результатами экспериментов квазиупругого рассеяния дейтерием (QDS).

### 3. INTRODUCTION

The vibrational far-infrared spectroscopy is a suitable tool to study intermolecular vibrations of polar substances. Some intramolecular motions can be also observed in this region.

In the first systematic approach Venugopalan and Prasad presented for infrared spectra for the seven members of di-n-alkoxyazoxybenzene homologous series /1/. In the isotropic phase all these substances exhibit one very broad absorption band. Venugopalan and Prasad consider four factors contributing to the absorption in the FIR region: (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 in the case of molecules with shorter terminal groups (1 to 3 carbon atoms) the torsional motion dominates, whereas for longer terminal groups (4 - 7 carbon atoms) Poley absorption prevails /1/.

The present paper is the continuation of our earlier FIR study /2/ which was undertaken with the aim to derive absorption coefficients and not only qualitative spectra. Then, for the Poley absorption a model fitting leading to such molecular parameters as, for instance, characteristic times would be possible /3/. The characteristic times calculated in this way can be compared with correlation times resulting from other experiments e.g. the dielectric relaxation, the incoherent quasielastic neutron scattering (QNS) and the Raman scattering /4/. Preliminary results of such model fitting and comparison were already published by us for the two members of di-n-alkoxyazoxybenzenes homologous series; PAA (n=1) and HQAB (n=7) /2/.

Now we present a similar study for the next 3 members of the series i.e. n=2,3 and 5. Contrary to /1/ we observe in all compounds (except PAA) two broad bands. To elucidate the problem of assignment of these bands the measurements for partly deuterated

species and for benzene solutions were performed. Poley absorption band should be less sensitive to the deuteration 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 deuteration. On the contrary, the torsional band frequency should be distinctly sensitive to the deuteration of the terminal groups as it is inversely proportional to the square root of the reduced inertia moment of the end groups. In the spectra of solutions one can expect a change in external modes while the internal modes should remain the same. The absolute absorption coefficient values for the isotropic and nematic phases of the studied species is presented and discussed in terms of the confined rotator model.

## 2. EXPERIMENTAL

The far infrared (FIR) absorption measurements were performed in the range  $20 - 200 \text{ cm}^{-1}$  using a vacuum version of the Digilab PTS-14 Fourier Transform Spectrometer. The resolution of measurements was  $4 \text{ cm}^{-1}$ . Experimental conditions and preparations were the same as in /2/. The sample was placed between the  $n$ -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 a high refractive index of quartz, one window was ultrasonically shaped to obtain a non flat surface. Therefore measurements with different spacers were performed to derive correct absolute values of absorption coefficient.

The di- $n$ -alkoxyazoxybenzenes were synthesized in a cooperating organic laboratory /5/ and purified until the melting and clearing points according to literature /5/ were achieved. The same procedure was applied for the deuterated samples and the isotopic substitutions were checked additionally by the mass spectroscopy and NMR /6/.

The temperature of the sample was controlled by a thermocouple and the accuracy better than  $\pm 0.5^\circ$  was achieved in whole range of temperature in which the spectra were recorded.

Benzene solutions 0.1 MF (molar fraction) of  $n = 1, 3, 5, 7$  were prepared and their spectra were recorded in the 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 Fig. 1. The temperature in which the spectra were recorded are marked.

The comparison of the isotropic phase spectra with those of solutions are shown in Fig. 2. The results of measurements for differently deuterated species are presented in Figs 4 and 5. The example of temperature dependence of spectra is shown in Fig. 3 in case of PAP ( $n=2$ ).

The spectra for PAA- $d_0$  (fully protonated) and PAA- $d_8$  (with deuterated benzene rings) are very similar and consist of one broad maximum. In the spectrum of PAP- $d_0$  an additional broad band appears at higher frequency. In the spectra of the samples with deuterated terminal groups (PAA- $d_6$  and PAP- $d_{10}$ ) the higher frequency part of the absorption diminishes. It seems that it is shifted towards frequencies. We assume therefore that higher frequency part is connected 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 (see Fig. 6). In that way we roughly estimate the torsional frequency to be equal to ca.  $120 \text{ cm}^{-1}$  and ca.  $135 \text{ cm}^{-1}$  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 in the nematic phase (for both compounds) is consistent with the fact that a 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 I. They were obtained from the simple Mathieu equation  $\nu = nh\sqrt{\frac{V}{2I}}$ , where I is the reduced moment of inertia of the end group for the reorientation around the C-O bond (taken from /1/),  $\nu$  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<sub>3</sub> groups are coupled to the rings and cannot reorient much faster relatively to the ring. As in our previous paper /2/ we interpret the lower frequency band as resulting mainly from librations of the molecules around the long axis (Poley absorption).

Table I The frequencies of the torsional band and the barriers for reorientations of the Alkoxy Groups around the C-O bonds

		$\nu$ [cm <sup>-1</sup> ]	V [kcal/mole]
PAA	I	122	14
	II	135	17
PAP	I	120	19
	II	138	25

This assignment is supported by the following facts:

- 1) the position of this band is shifting towards lower frequencies with the increasing number of carbon atoms in the terminal groups (Fig. 1) (n=5 does not follow this pattern probably due to an exceptionally high packing coefficient of this substance /9/).
- 2) the intensity of this band is decreasing with increasing moment of inertia (roughly proportional to I<sup>-1</sup>) (Fig. 1,4,5, and Table II).

table II The absorption coefficients and the frequencies of Poley absorption band in the nematic and isotropic phases of di-n-alkoxyazoxybenzenes

n	nematic phase			isotropic phase		
	temp. [K]	Poley max $\nu$ [cm <sup>-1</sup> ]	$\epsilon$ [neper/cm]	temp. [K]	Poley max $\nu$ [cm <sup>-1</sup> ]	$\epsilon$ [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

3) in the spectra of solutions this band is changed, contrary to higher frequency (i.e. internal) modes (Fig. 2)

4) there is a strong temperature dependence of the position of this band (Fig. 3).

To determine quantitatively the parameters of the molecular motion the confined rotator model was used /3/. This model was already successfully applied to PAA and HOAB /2/. The model and the fitting procedure were described in details elsewhere /2,3/ so that only a brief resume is given here. In this model, a two-dimensional rotator librates (with a characteristic time  $\tau_1$ ) in the potential cage formed by its neighbours and it reflects elastically from the walls. The rectangular cage (of the width  $2\beta$ ) exists for a time interval  $\tau_D$  and then the configuration and angular momentum change instantaneously. This means that the other cage is formed with a different orientation. The model introduces three independent parameters -  $\beta$ ,  $\tau_1$  and  $\tau_D$ .  $\tau_D$  can be determined from dielectric relaxation experiments, since it is natural to put it as equal to the Debye relaxation time. The two other parameters  $\beta$  and  $\tau_1$  are adjusted so that the best fit to the observed maximum of absorption  $\epsilon_{max}$  and the frequency  $\nu_{max}$  is obtained. The results of such model fitting

are presented in Table III and Fig. 7. As it may be seen, the time  $\tau_1$  of an unperturbed libration is close to the correlation time from the QNS results. Taking into account the new existing information about low potential barriers for rotation of molecular moieties around the N-Phenyle bond /10/ it is probable that this internal reorientation may cause stochastic interruption of the whole molecule libration. Such interpretation is not contradictory to the recent interpretation of the QNS results.

Another outcome of the model fitting is the possibility of separation of the torsional band. In Fig. 7 one can see the results of subtraction of the model Poley band from the experimental spectra. The influence of the  $210 \text{ cm}^{-1}$  internal band was taken into account. The frequencies of the torsional band separated in this way are higher than those obtained by analysis of the isotopic effects described above, but the differences can be explained by the inaccuracies of both methods. The change of the intensity of this band with the increase of the terminal group length supports the assignment presented here.

It is worth noticing that in our spectra for the nematic phase we observe a slight shoulder on the low frequency side of the Poley band. One can suggest that it might be connected with the

Table III The confined rotator model; experimental and fitting parameters compared with the correlation times derived from the quasielastic neutron scattering (QNS) experiments

Substance n	Temp. [K]	$\beta$	$\tau_0$ [ps]	$\tau_1$ [ps]	$\tau_{\text{QNS}}$ [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

libration of molecules around their short axes since such process should be observed at low frequencies. In the Raman spectra for the crystal phases of di-alkoxyazoxybenzenes Gruger et al. /11/ observed a band which they interpreted as the librational phonon around short axis in this frequency region. There are also suggestions that collective modes may also contribute to the absorption in this frequency region /12/.

#### 4. CONCLUSIONS

1. From the spectra presented here for some di-n-alkoxyazoxybenzenes together with the partly deuterated compounds it is clear that the far IR 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 molecules around the O-C bond.
2. In a confined rotator model assuming the dielectric relaxation time as equal to the lifetime of the potential cage, the average times of unperturbed libration are in good agreement with the correlation times derived from neutron experiments.

#### ACKNOWLEDGEMENTS

The authors would like to thank Professor J.M. Janik for her interest and discussions. The work of Dr. A. Suszko-Purzycka, Dr. J. Chruściel and Mrs D. Chruściel of the Agro-Pedagogical School in Siedlce at the preparation of normal and deuterated compounds is highly appreciated.

LITERATURE

- /1/ Venugopalan S., Prasad S.N., 1979, J.Chem.Phys. 71, 5293.
- /2/ Janik J.A., Godlewska M., Grzechulski T., Kocot A., Scieszka E., Scieszinski J., Witke W., 1983, Mol.Cryst. and Liq.Cryst., 98, 67.
- /3/ Gajduk V.I., Kakmykov Y.P., 1981, J.Chem.Soc., Faraday Trans. 2, 77, 929.
- /4/ Janik J.A., 1982, Advances in Liquid Cryst., 5, 215.
- /5/ Demus D., Demus H., Zaschke H., 1974, Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, p. 166, 169.
- /6/ Chruściel J. - unpublished results.
- /7/ Wróbel S., 1985, Mol.Cryst.Liq.Cryst., 127, 67.
- /8/ Janik J.A., Janik J.M., Otnes K., 1980, Liq.Cryst., Proc. of the Intern.Conf. in Bangalore 1979, (Heyden) p. 391.
- /9/ Shivaprakash N.C., Rajalakshmi P.K., Shashidhara Prasad J., 1980, Liquid Crystals in One and Two Dimensional Order, edited by G. Heppke and W. Beltrich (Springer Verlag) p.72.
- /10/ Perrin H., Berges J., 1982, J.Phys.Lett., 43, 531.
- /11/ Gruger A., Romain F., Le Calvé M., 1984, Mol.Cryst.Liq. Cryst., 116, 57.
- /12/ Conrad H.M., Stiller H.H., Stockmayer R., 1975, Phys.Rev. Lett., 36, 264.

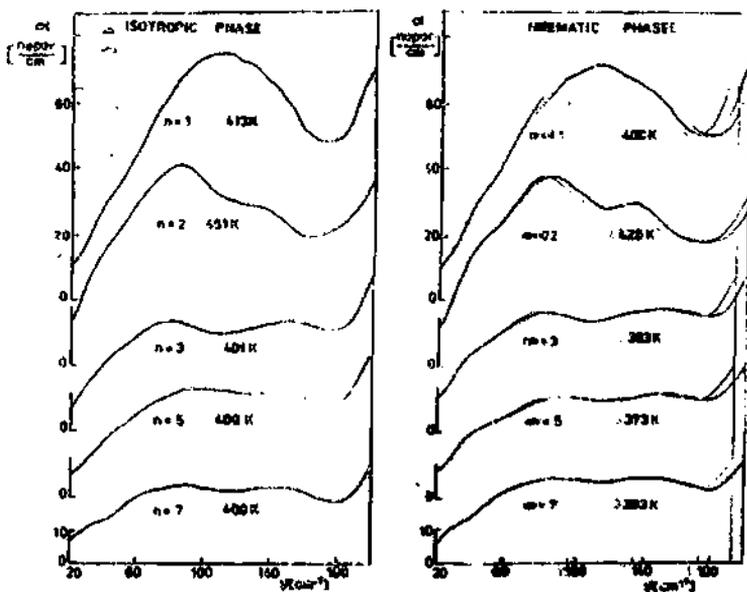


Fig. 1 Absorption coefficients  $\alpha(\lambda)$  for the isotropic and the nematic phase of di-n-alkoxyazobenzene with  $n = 1, 2, 3, 5, 7$ .

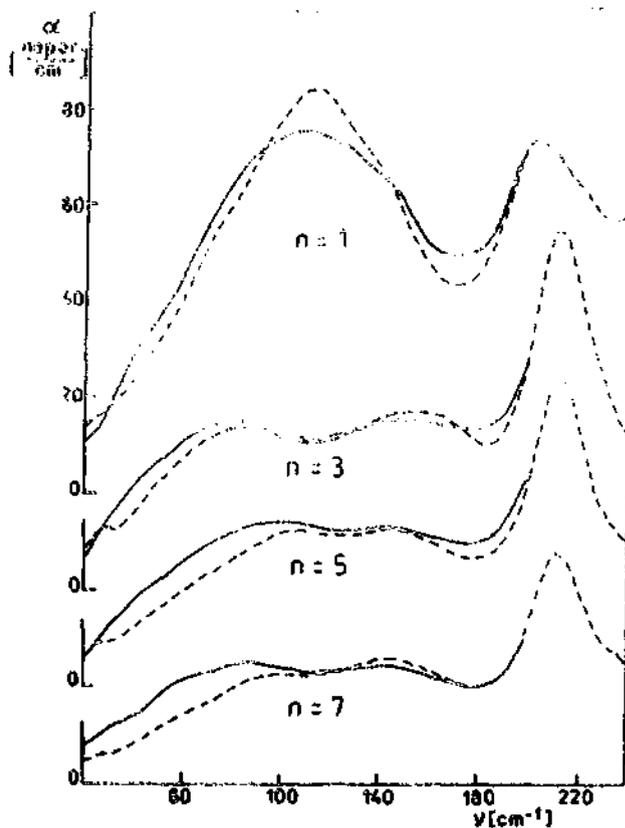


Fig. 2 Far IR spectra of 0.1 M benzene solutions for di-n-alkoxyazobenzene with  $n = 1, 3, 5, 7$  (broken lines) compared with their isotropic phase spectra (solid line). [  $\alpha(\nu)$  scale for spectra of the solutions is normalized to the same number of liquid crystal molecules per surface unit ].

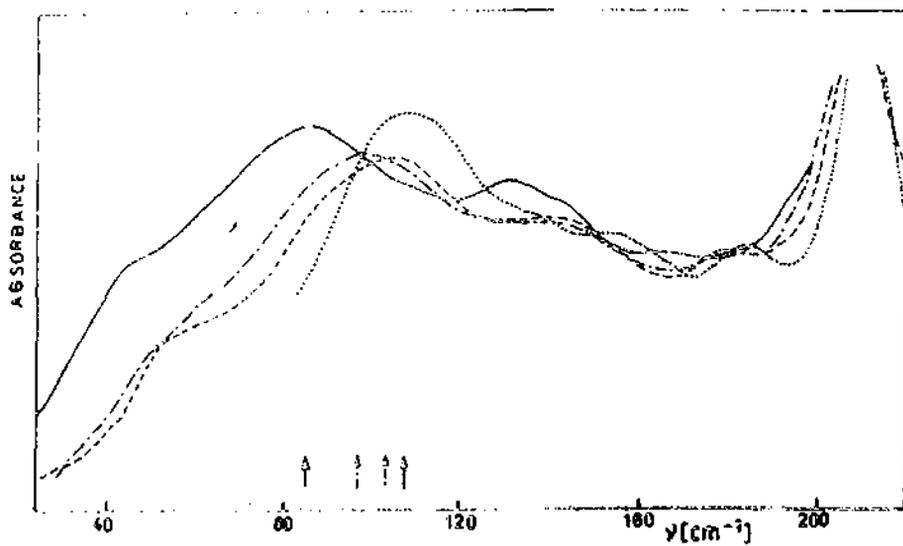


Fig. 3 Temperature dependence of PAP spectrum: — 420 K, - - - 209 K, - - - 198 K, ..... 83 K. The arrows mark the positions of the lower frequency band at the respective temperatures.

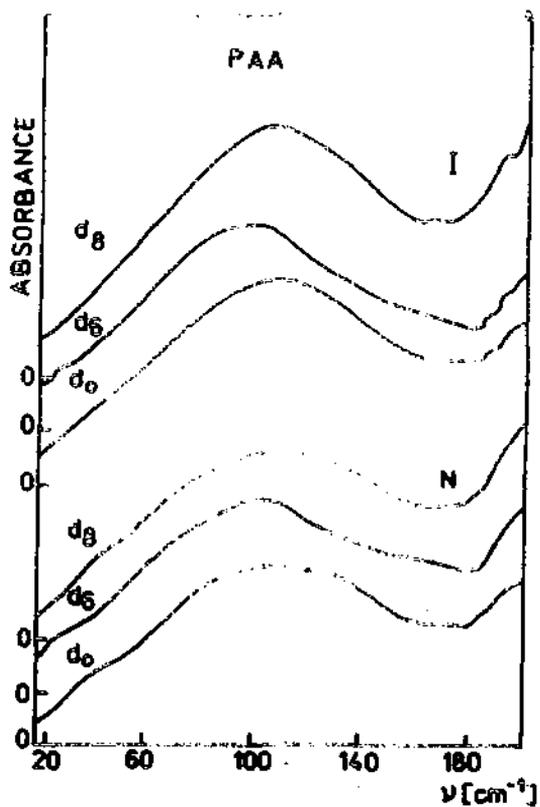


Fig. 4 Far infrared spectra of the nematic and the isotropic phase of PAA- $d_0$ , PAA- $d_6$ , PAA- $d_8$ .

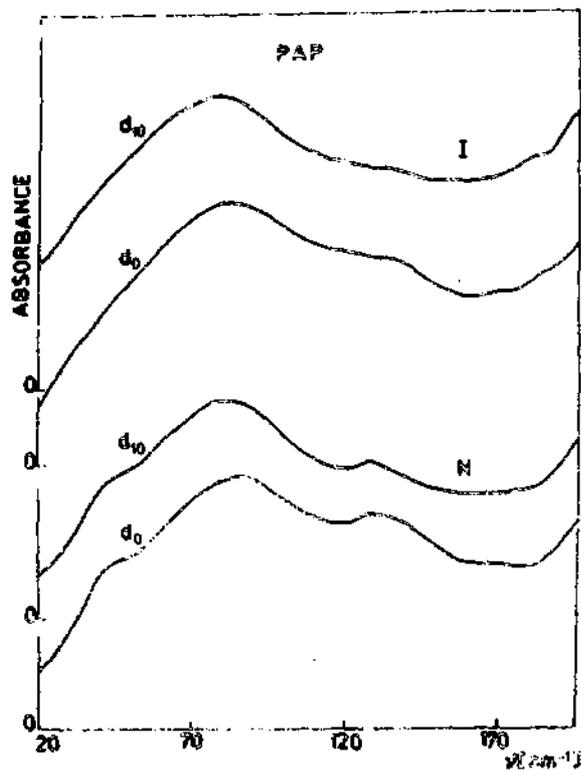


Fig. 5 Par infrared spectra of the nematic and the isotropic phase of PAP-d<sub>0</sub> and PAP-d<sub>10</sub>.

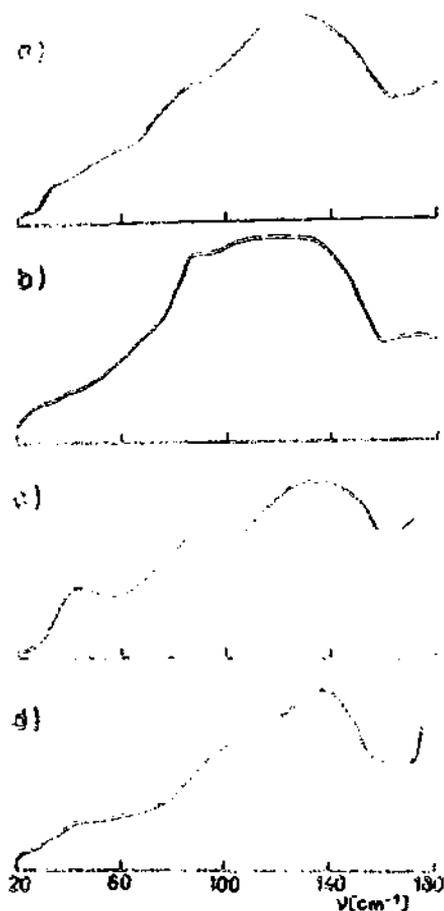


Fig. 8 The differences between the far infrared spectra of:  
 a) PAA-d<sub>0</sub> and PAA-d<sub>6</sub> in the isotropic phase,  
 b) PAP-d<sub>0</sub> and PAP-d<sub>10</sub> " " " "  
 c) PAA-d<sub>0</sub> and PAA-d<sub>6</sub> in the nematic phase  
 d) PAP-d<sub>0</sub> and PAP-d<sub>10</sub> " " " "

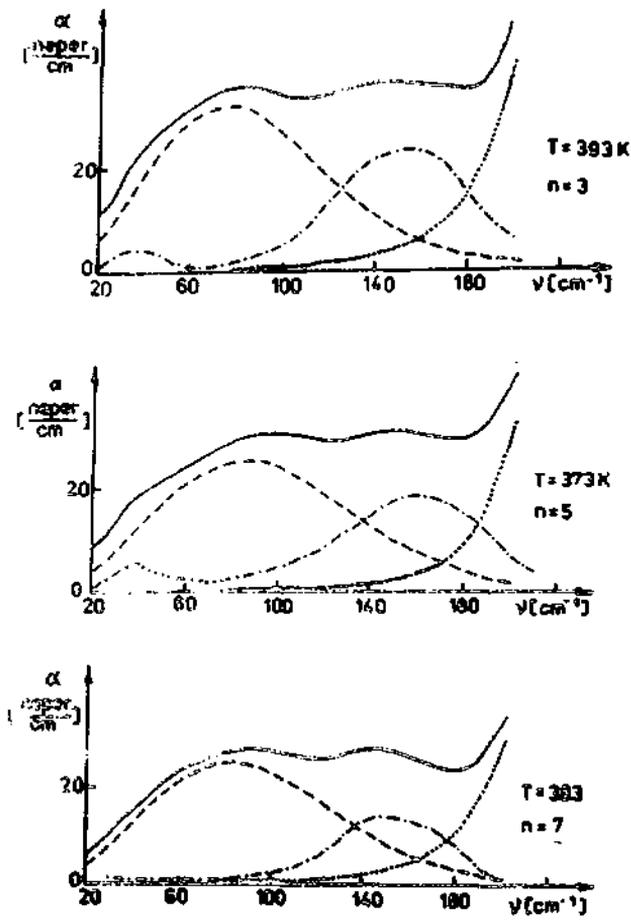


Fig. 7 Results of the confined rotator model fittings for di-n-alkoxyazoxybenzenes for  $n = 3, 5$  and  $7$  in their nematic phases ——— experimental spectrum, - - - - - model fitting, ..... - part of the internal band fitted by a Lorentz line, - · - · - result of subtraction of the fitted curves from the experimental one.