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Re-investigation of the methyl and methoxy group hindered rotations in *p*-dimethoxybenzene, by comparison of dielectric and far infra-red spectra with ^{13}C N.M.R. relaxation data

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Dielectric relaxation measurements and for infra-red spectra relative to the same *para*-dimethoxybenzene/tetrachloroethylene solution have been concomitantly analysed with ^{13}C N.M.R. (T_1 and N.O.E.) relaxation data, in order to study the intramolecular dynamics of the methoxy and methyl group internal motions. From a direct comparison between the microscopic dipolar (τ_μ) and N.M.R. (τ_C^{NMR}) correlation times, it can be shown that the methoxy group internal rotation significantly contributes to the dielectric relaxation process. A quantitative analysis in terms of a ' Chemical Relaxation Process ' permitted an estimation of both the kinetic constant $k_{cis \to trans}$ of the dielectrically ' active ' cis/trans isomerism of the *para*-dimethoxybenzene molecule, and of the jumping rate of the methyl group from any of its three equivalent positions. The methoxy-torsional modes for the deuterated *para*-$(CD_3O)_2\phi$ and normal species have been assigned to features respectively observed at 82 and 92 cm^{-1} in the far infra-red spectra of these compounds. Also a speculative assignment of the methyl torsions has been investigated. The coherence of the different results has been carefully discussed.

1. INTRODUCTION

A number of dielectric studies has been made in the pure liquid phase or in dilute solution, on compounds having one or more methoxy groups [1–10]. In these previous investigations, the only practicable way of *qualitatively* estimating the contribution of the group rotation to the overall dielectric relaxation was by comparison within a homologous series of compounds having roughly the same molecular shape. Such analyses may have been hazardous because of inevitable changes in the dipole moment (magnitude or orientation in the molecular frame), local field, microscopic viscosity, and very often, in the barrier height, to internal rotation itself (for instance, in the case of electron donating or withdrawing aromatic substituents).

The present paper will report how three complementary techniques: dielectric relaxation, far infra-red spectroscopy, and ^{13}C N.M.R. Relaxation measurements have been used to extract directly more complete and *quantitative* information on the different internal motions. New improvements in microwave [11] and far infra-red instrumentation [12] now allow the experimentalist to obtain excellent agreement between the low (2 MHz–120 GHz) and high (3 cm^{-1}–200 cm^{-1}) frequency parts of the spectra, and so to give a better description of the short-time behaviour of the dipolar correlation functions. On the other hand, recent developments in ^{13}C pulsed Fourier transform–N.M.R. spectroscopy now offer a great deal of additional local information since simultaneous measurements of the longitudinal relaxation time (T_1) and of the N.O.E. (Nuclear Overhauser Enhancement) factor (η) are possible for each individual line of the ^{13}C spectrum.

The particular system which we have chosen, for experimental convenience, is a solution of *p*-dimethoxybenzene (*p*-D.M.B.) in tetrachlorethylene ($4{\cdot}17_6$ mole *p*-D.M.B. dm^{-3}). The interpretation of the dielectric measurements is expected to be simplified by the fact that the solvent is non-polar, and that there is in the solute only one internal rotation axis (figure 1), and along this, due to the molecular symmetry, there is no component of the electric dipole. Specials reference will be made to our partial results on *para* $(CD_3O–)_2C_6H_4$ at the same concentration in the same solvent.

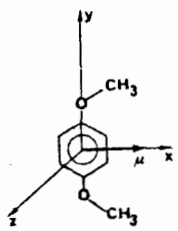


Figure 1. *p*-Dimethoxy benzene molecule in the cis position; μ represents the direction of the resultant dipole.

2. Experimental

The microwave measurements below 112 GHz were made at the University of Nancy I (France). In the millimetre wave range the measurements of the complex permittivity of the liquid were carried out at fixed frequencies produced by klystrons. These were coupled to a broad-band Michelson interferometer featuring oversized waveguides [14]. The values of the real (ϵ') and imaginary (ϵ'') parts of the complex permittivity were computed from the entire interferogram using a least squares optimization method [15]. In the centimetre wave range the same method was used to process the interferogram produced by another interferometer built with a standard waveguide.

Submillimetre wave measurements [16] were carried out at the Post Office Research Department and at the University College of Wales, Aberystwyth. At Aberystwyth a commercial Grubb Parsons/N.P.L. [17] interferometer, employing amplitude modulation (A.M.), was used to cover the spectral range 20 to 200 cm^{-1}. At the Post Office Research Station two commercially available interferometers were modified to cover the spectral ranges (i) 2 to 31 cm^{-1},

(ii) 20 to 400 cm^{-1}. In both cases the air-cooled lamp housing was replaced by a more efficient water-cooled unit and phase modulation (P.M.) was incorporated [18, 19]. During the period when the experimental observations were being made the apparatus was left permanently switched on to ensure maximum stability. These measures improved the quality of the results. Over the range 20 to 400 cm^{-1}, where quartz and diamond Golay detectors were used, signal-to-noise ratios (as defined by Chamberlain [18] as great as 1000 were obtained [20]. Resolution in this region was 4 cm^{-1}.

For the range 2 to 31 cm^{-1} a Rollin-InSb, liquid helium-cooled detector [21] was employed together with a 4 mm black-polyethylene filter. Signal-to-noise ratios as great as 10 000 were obtained, whilst the reproducibility of three consecutive runs was estimated to be of the order of 0·1 per cent. The resolution was 2 cm^{-1}.

A variable-path cell VC–01 was used, made by Beckmann–R.I.I.C. and fitted with polypropylene windows. The cell was placed in a converging beam of radiation following a lens of focal length 12 cm. No correction was made for convergence [22] but as very small path lengths of liquid were used these effects were estimated to be small. Because of the size of the cell it could not be placed in the usual sample-holder of the interferometer ; it was placed in a compartment attached to the evacuated interferometer and was flushed with dry oxygen-free nitrogen.

The spectrum of the detected power was computed for a number of interferograms for two thicknesses of the given liquid and the power absorption coefficient was calculated from the ratio of the two averages. Surface and internal reflection effects were eliminated [23].

Proton noise decoupled ^{13}C N.M.R. spectra were recorded at 22·6 MHz in the Fourier transform mode, with the Bruker HX90 instrument of the University of Nancy, interfaced with a Nicolet 1080 computer. The deuterium lock signal was provided by a capillary containing C_6D_6, in order to avoid any interaction with the sample. Determination of T_1 for various nuclei can be readily accomplished by the usual 180°, τ, 90° pulse sequence, with Fourier transformation of the free induction signal following each 90° pulse. In this way spectra were obtained in which the nuclei were partially relaxed. The duration of each 90° pulse was 15 μs. The method was slightly modified in order to increase the rapidity of the measurements [24]. A spectral range of 1200 Hz was chosen in each case. Interferograms were stored in a 16 K array. The accuracy of the T_1 values is believed to be *ca.* 5 per cent. N.O.E. measurements were carried out by the so-called ' gated decoupling ' technique [25]. A special device allowing such experiments has been built at the Nancy I University. The uncertainty of one determination is of the order of $\pm$ 10 per cent but this has been decreased by repeating the experiment more than five times.

The solution was prepared by weight to $\pm$ 0·1 mg, the solute (obtained from Fluka-A.G., purum grade) being recrystallized from benzene. The solvent (Fluka or B.D.H., spectroscopic grade) was dried with freshly baked type 3A zeolite. The deuterated compound (*para*$(CD_3O)_2C_6H_4$) was synthesized at the Laboratoire de Chimie Théorique, Université de Nancy I, by action of deuterated dimethyl sulphate on hydroquinone. The purity of the deuterated final compound was such that no methyl proton signal could be seen by ^1H N.M.R. spectroscopy when recording the aromatic signals in standard conditions.

3. Results

The measured complex permittivities of the solution in the frequency range 2 MHz–111 GHz are reported at three temperatures (298 K, 323 K, and 348 K) in table 1. The ϵ' and ϵ'' values quoted are each believed to have uncertainties less than 1 per cent. The Cole–Cole plots at these three temperatures are shown in figure 2. Far infra-red absorption spectra obtained at 298 K for both the normal and the deuterated compounds are shown in figures 3 and 4. The overlap between the microwave interferometric measurements and the results obtained by Michelson free-space interferometry in the region 3–28 cm^{-1} is very satisfactory as illustrated by figure 4. Thus, we have for the first time a complete set of absorption data from virtually zero frequency up to 200 cm^{-1}.

	298 K		323 K		348 K	
F/GHz	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
2×10^{-3}	$3{\cdot}47_4$	0	$3{\cdot}29_6$	0	$3{\cdot}15_7$	0
$9{\cdot}25_2$	$3{\cdot}12_5$	$0{\cdot}44_6$	$3{\cdot}13_4$	$0{\cdot}32_2$	$3{\cdot}07_0$	$0{\cdot}24_2$
$17{\cdot}59_7$	$2{\cdot}85_0$	$0{\cdot}45_2$	$2{\cdot}91_7$	$0{\cdot}42_5$	$2{\cdot}92_2$	$0{\cdot}35_0$
$34{\cdot}30_9$	$2{\cdot}65_0$	$0{\cdot}35_3$	$2{\cdot}67_5$	$0{\cdot}36_7$	$2{\cdot}72_0$	$0{\cdot}37_6$
$68{\cdot}1_2$	$2{\cdot}54_3$	$0{\cdot}22_6$	$2{\cdot}53_0$	$0{\cdot}26_0$	$2{\cdot}53_2$	$0{\cdot}28_3$
$111{\cdot}1_8$	$2{\cdot}50_0$	$0{\cdot}17_0$	$2{\cdot}48_0$	$0{\cdot}20_0$	$2{\cdot}45_5$	$0{\cdot}22_8$
ϵ_∞ (extrapolated)	$2{\cdot}47_5$	0	$2{\cdot}43_2$	0	$2{\cdot}40_1$	0

Table 1.

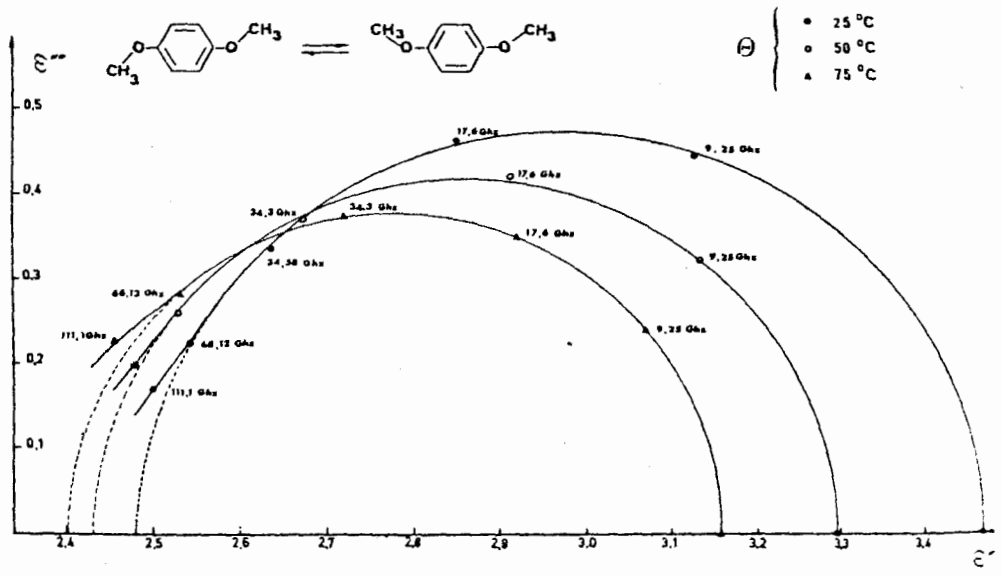


Figure 2. Cole–Cole plots for a solution of a $4{\cdot}17_6$ mole dm^{-3} *p*-dimethoxybenzene in C_2Cl_4 at 298, 323 and 348 K. The frequencies of the (ϵ'', ϵ') measurements are indicated on each plot. The dotted lines correspond to a semi-circular extrapolation, leading to the determinations of the three values of ϵ_∞.

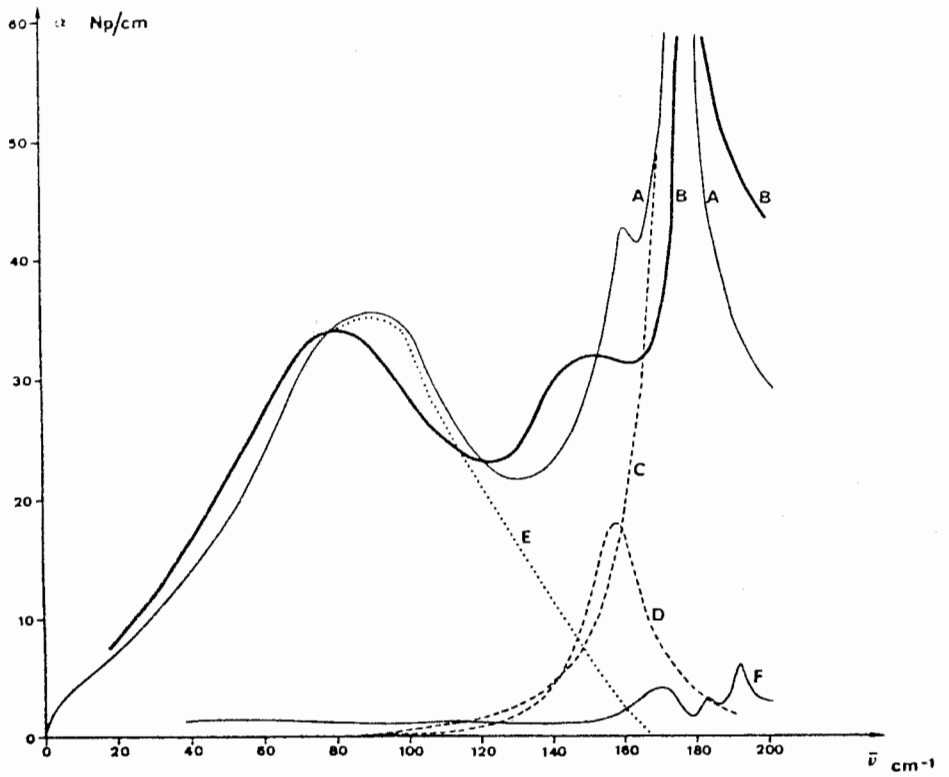


Figure 3. — (A) The far infra-red absorption of *p*-dimethoxybenzene/C_2Cl_4 ($4{\cdot}17_6$ mole dm^{-3}) at room temperature. ▬ (B) The deuterated compound absorption at the same concentration. – – – – (C) and (D), idealized lineshapes for some of the higher frequency absorptions (see text). . . . . (E) unresolved low frequency band extracted from (A). — (F), solvent absorption.

T	298 K		323 K		348 K	
^{13}C N.M.R. relaxation	C_{ortho}	C_{CH_3}	C_{ortho}	C_{CH_3}	C_{ortho}	C_{CH_3}
η	$1{\cdot}6_5$	$1{\cdot}7_5$	$1{\cdot}7_6$	$1{\cdot}8_0$	$1{\cdot}7_7$	$1{\cdot}8_7$
T_1/s	$5{\cdot}5_4$	$5{\cdot}1_2$	7·8	$6{\cdot}9_5$	10·1	$9{\cdot}6_5$
$\frac{\eta}{T_1}$/s	$0{\cdot}29_8$	$0{\cdot}34_2$	$0{\cdot}22_6$	$0{\cdot}25_9$	$0{\cdot}17_5$	$0{\cdot}19_4$
$\tau_C^{N.M.R.}$/ps	$7{\cdot}7_5$	$2{\cdot}7_3$	$5{\cdot}1_3$	$2{\cdot}0_7$	$3{\cdot}9_8$	$1{\cdot}5_5$
Dielectric relaxation	τ_μ^H	$\tau_\mu^{P.G.}$	τ_μ^H	$\tau_\mu^{P.G.}$	τ_μ^H	$\tau_\mu^{P.G.}$
τ_μ/ps	12·2	11·1	$7{\cdot}8_8$	$7{\cdot}1_9$	$5{\cdot}5_3$	$5{\cdot}0_8$
$\frac{\tau_\mu}{\tau_{C\,ortho}^{N.M.R.}}$	$1{\cdot}8_2$	$1{\cdot}6_5$	$1{\cdot}5_3$	$1{\cdot}4_1$	$1{\cdot}3_8$	$1{\cdot}2_7$

Table 2.

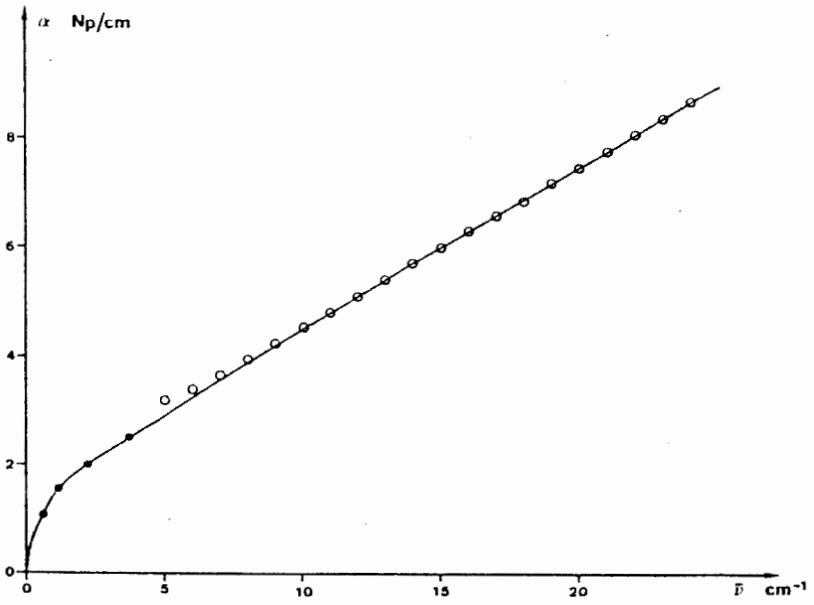


Figure 4. Detail of the low frequency absorption spectrum of *p*-dimethoxybenzene/C_2Cl_4 at room temperature. ● : Microwave interferometry with klystron sources. ○ : Michelson interferometry with a He(1) Rollin detector.

N.M.R. relaxation measurements have been separately carried out on the signal relative to the four equivalent ortho aromatic carbons, and on the line due to the methyl carbons. The solvent peak and those of the C_6D_6 reference are well separated from those of the solute, so that no interference might affect the results. The T_1 and N.O.E. enhancement factor η_{CH} of the various carbons studied are reported in table 2 for the three temperatures mentioned above.

4. Preliminary analysis of the experimental data of each technique

4.1. *Dielectric relaxation*

The microwave results seem to fit a semicircle to a very good approximation, except for the frequencies above 68 GHz : the deviation at higher frequencies can be explained by the existence of a very strong and broad far infra-red band peaking at $92{\cdot}0 \pm 2$ cm^{-1}. This confirms the prediction of Klages and Kraus [1]. Thus our results support quite well the existence of only one ' resultant ' relaxation time accounting for the low frequency part of the dielectric process : this is linked to the fact that the vectorial dipolar correlation function is nearly exponential except at times shorter than 2 ps as will be shown from the far infra-red measurements.

The semicircular approximation, for the Cole–Cole plots, allows us to extrapolate to ϵ_∞ values (table 1), and to calculate apparent relaxation times τ_C^{Diel} the values of which are reported in table 2. The calculation of the microscopic relaxation time τ_μ, from the macroscopic one τ_C^{Diel}, involves the assumption of a specific model, in order to evaluate the internal field correction. This problem has been discussed by many authors in the past [26–31] but a recent

study [32] leads to the conclusion that such an involved correction might be often overestimated in importance. Therefore, we will restrict our discussion to the expressions given respectively by Hill [33] and by Powles–Glarum [33]:

$$\tau_\mu^{\mathrm{H}} = \tau_{\mathrm{C}}^{\mathrm{Diel}}, \tag{1 a}$$

$$\tau_\mu^{\mathrm{PG}} = \frac{2\epsilon_0 + \epsilon_\infty}{3\epsilon_0}\,\tau_{\mathrm{C}}^{\mathrm{Diel}}; \tag{1 b}$$

we also will not take into account any influence of the anisotropy of the Onsager-type cavity surrounding the central molecule [34].

4.2. *Far infra-red spectra*

The far infra-red absorption spectrum of the *p*-dimethoxybenzene–C_2Cl_4 solution consists of a broad band centred at 92 cm^{-1} ($\alpha_{max} = 35{\cdot}0 \pm 1{\cdot}0$ neper cm^{-1}, half width ~ 75 cm^{-1}) together with a sharper, more intense and overlapping peak at 178 ± 1 cm^{-1} ($\alpha_{max} \sim 80$ neper cm^{-1}, half width 15 cm^{-1}). This band at 178 cm^{-1} appears to show a shoulder at 160 cm^{-1}. In order to confirm this observation and to interpolate the contribution of this 160 cm^{-1} band, the Brot lineshape expression has been applied to the feature peaking at 178 cm^{-1}. The Brot [35] expression is

$$\alpha(\tilde{\nu}) = \frac{A}{2}\left\{\frac{\tilde{\nu}^2/\tau_i}{c^2\pi^2(\tilde{\nu}^2 - \tilde{\nu}_{\max}{}^2)^2 + \tilde{\nu}^2/\tau_i{}^2}\right\}, \tag{2}$$

where A is related to the transition dipole and τ_i to the time between collisions: these are treated as adjustable parameters. The value of τ_i was selected as 0·5 ps and is similar to that calculated by Haffmans and Larkin [36] for liquids of similar number density. From this analysis the spectrum is clearly shown to consist of three discrete features centred at 92, ~ 160, and 180 cm^{-1} respectively. For the deuterated compound these three features are much better resolved and found to be situated at 82 cm^{-1}, ~ 145 cm^{-1}, and 207 cm^{-1} respectively.

Our discussion will be concerned with the two lower frequency bands. The broad 92 cm^{-1} (or 82 cm^{-1} for the deuterated compound) feature could be first analysed in terms of a libration [35] of a permanent dipole in a cage defined by the nearest surrounding molecules: this mechanism is believed to cause all dipolar molecules to absorb in this region: i.e. the Poley absorption [37]. *para*-Dimethoxybenzene molecules having the two methoxy groups in the cis, polar configuration, might be regarded as rigid dipoles and would give rise to such an absorption. However, the 'excess' absorption is *very* considerable when compared with other molecules of similar dipole moment [38–40]. From the analysis of the experimental integrated intensity of the 92 cm^{-1} band, using the expression derived from Gordon's sum rules [41],

$$\frac{9n_x}{(n_x{}^2+2)^2}\int_{\mathrm{Band}}\frac{\alpha(\tilde{\nu})\,d\tilde{\nu}}{N} = \frac{\pi\mu_z{}^2}{3c^2}\left\{\frac{1}{I_z}+\frac{1}{I_y}\right\}, \tag{3}$$

where $9n_x/(n_x{}^2+2)^2$ is the Polo–Wilson correction factor for internal field [42], an estimate can be made of the dipole moment perpendicular to

the main molecular axis. The values used in the computation are as follows :

$$I_x = 1351 \times 10^{-40} \text{ g cm}^2, \qquad n_\infty = \sqrt{\epsilon_\infty} = 1{\cdot}5_8,$$
$$I_y = 213 \times 10^{-40} \text{ g cm}^2, \qquad N = 1{\cdot}60 \times 10^{21} \text{ mol ml}^{-1},$$
$$I_z = 1148 \times 10^{-40} \text{ g cm}^2, \qquad \int_0^\infty \alpha(\nu)\, d\tilde{\nu} = (2956 \pm 150) \text{ cm}^{-2}.$$

The resultant value of $\mu_z = 4{\cdot}5 \pm 0{\cdot}4$ D is much larger than the apparent dipole moment obtained by dielectric measurements : $1{\cdot}5_4$ D at 25°C, and leads us to believe that the main contribution to this band has another origin†. In contrast the shift of the centre of the band on deuteration of the methoxy groups supports quantitatively the hypothesis of torsional modes of the methoxy groups. Also a recent study [43] on anisole and two deuterated species, in both the gas and the liquid phases, confirms this assignment.

An alternative way of representing the result is to Fourier transform the low frequency absorption band, to give a ' pseudo ' rotational velocity correlation function (R.V.C.F.) of the unit vector along the transition dipole axis using the relation given by Brot [44] :

$$\langle \dot{u}(0) \cdot \sum_i \dot{u}_i(t) \rangle = \frac{2}{\pi} \frac{3kTV}{4\pi N\mu^2} 9c \int_0^\infty \frac{n \cdot \alpha \cos \omega t \, d\omega}{(\epsilon' + 2)^2 + \epsilon''^2}. \tag{4}$$

Due to the lack of far infra-red experimental dispersion data, only a more or less approximate short-time behaviour can be obtained from the latter expression,

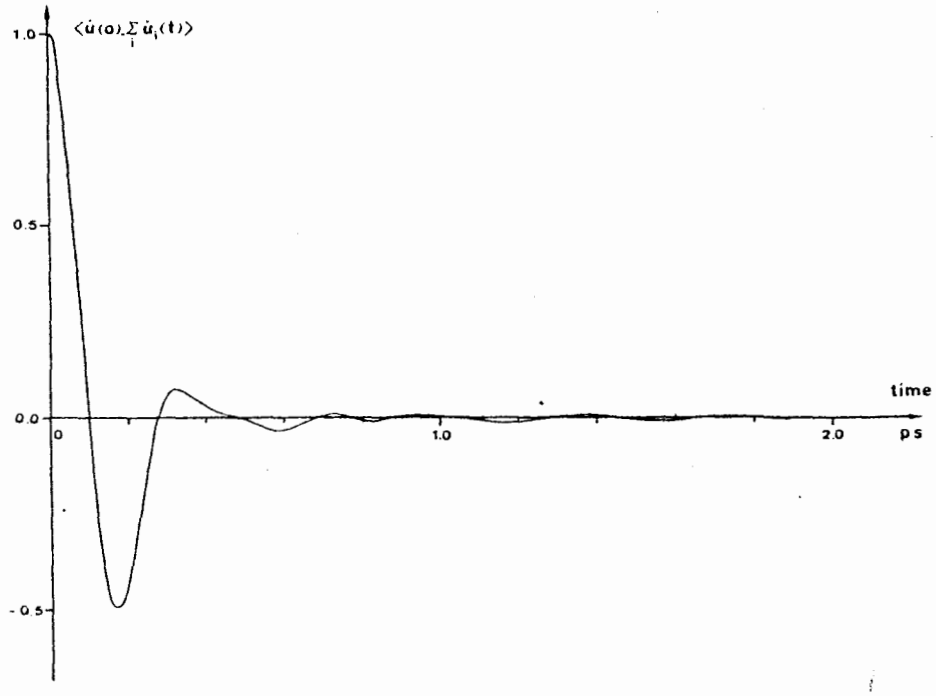


Figure 5. Fourier transform of the experimental $z(\tilde{\nu})$ curve (see figure 3) of the broad band absorption in *p*-dimethoxybenzene/C_2Cl_4.

† $D \approx 3{\cdot}335\,640 \times 10^{-30}$ C m.

:cepts the usual simplification $\epsilon' \sim \epsilon_x \gg \epsilon''$. The computed 'pseudo' . normalized to unity at time $t=0$ is shown in figure 5. The damped ns reflect both the librational motions of the whole cis conformers, nternal torsional motion of the methoxy groups, but occur at too short < 2 ps) to affect the exponential behaviour of the vectorial dipolar ɔn function (D.V.C.F.) at the time scale of the microwave measure-

4.3. ^{13}C *N.M.R. relaxation experiments*

ıatic ortho carbons

experimental data might be interpreted in the first approximation using wing equation derived from the work of Kuhlmann *et al.* [45] :

$$\frac{\eta_{CH}}{T_1} = \frac{\gamma_H{}^3 \cdot \gamma_C \cdot \hbar^2}{2} \frac{\tau_{C\ ortho}{}^{N.M.R.}}{[r_{CH}{}^{Arom}]^6}. \tag{5}$$

values of the ratio η_{CH}/T_1 for the present measurements and those of are listed in table 2. The great advantage of formula (5) is that it ɔne to extract the dipole–dipole contribution to the magnetic relaxation without any further approximation. It is also worth noting that the $_1/T_1$ is now independent of the sample : this fact allowed us to check lity of the experimental procedures using standard C_6H_6 results [46].

ne accepts the hypothesis of an *isotropic* and *diffusional* reorientation of the whole molecule, the (isotropic) diffusion constant D_0 is related .R. by

$$6D_0 = (\tau_C{}^{N.M.R.})^{-1}. \tag{6}$$

he case of an anisotropic diffusion, $\tau_C{}^{N.M.R.}$ of equation (5) has to be l by a more complicated expression of the three diffusion coefficients D_z (see figure 1) : $F(D_x, D_y, D_z)$.

; function has been given analytically by Huntress [47] for the general t reduces to the following for a planar molecule :

$$_x, D_y, D_z) = \frac{3}{4D_r} \left\{ (D_x + D_s)\cos^2\phi + (D_y + D_s)\sin^2\phi - \frac{(D_y - D_x)^2}{D_z + D_s} \sin^2\phi \cos^2\phi \right\}, \tag{7}$$

ϕ (in this case : 30°) defines the orientation of the inter-nuclear vector he molecular frame, D_r and D_s being given by the following symmetric ions :

$$D_r = 3[D_xD_y + D_yD_z + D_zD_x],$$

$$D_s = \tfrac{1}{3}[D_x + D_y + D_z].$$

ystematic determination of the three diffusion coefficients would need dependent sets of data. In the present paper we will restrict ourselves ing the consequences of the neglect of such an anisotropic character of

the diffusion. For the system considered two hypotheses have to be examined :

(*a*) First (in our opinion the most probable case) $D_z \geqslant D_x, D_y$:

Letting $D_x = D(1-\eta)$, $D_y = D(1-\xi)$, $D_z = D$, then it follows that ($\phi = 30°$)

$$F^{-1} = 2D\left\{3 - \frac{9\xi+3\eta}{8} - \left(\frac{9\eta+27\xi}{24}\right)\left(\frac{13\eta+7\xi}{24}\right) + \xi\eta + \tfrac{9}{64}(\eta-\xi)^2 + \ldots\right\}. \quad (8)$$

(*b*) Secondly : $D_y \geqslant D_x, D_z$

Letting now : $D_x = D(1-\epsilon)$, $D_y = D$, $D_z = D(1-\delta)$, then

$$F^{-1} = 2D\left\{3 - \frac{9\epsilon+36\delta}{24} - \left(\frac{9\epsilon+36\delta}{24}\right)\left(\frac{13\epsilon+4\delta}{24}\right) + \epsilon\delta + \tfrac{9}{64}\epsilon^2 + \ldots\right\}. \quad (8')$$

These expressions will have to be compared with the corresponding ones appearing in the analysis of an anisotropic dipolar diffusion in dielectric relaxation :

$$(a')\ D_y + D_z = 2D\left[1 - \frac{\xi}{2}\right],$$

$$(b')\ D_y + D_z = 2D\left[1 - \frac{\delta}{2}\right].$$

Then, it can be easily verified that for reasonable values of either (η, ξ) or (δ, ϵ), the second-order correction terms in (8) or (8') lead to a maximum difference of less than -10 per cent and -15 per cent in the well-known ratio $\rho = 3$ which is usually expected between the dielectric and N.M.R. correlation times. This finding will be of some importance in our final discussion.

Selective deuteration in the aromatic ring might perhaps afford additional information concerning the rotational anisotropy of the motion, not using conventional ^{2}D quadrupolar relaxation but rather by ^{13}C relaxation time measurements. However, no experiment of this type has been so far reported.

(2) *Methyl carbon relaxation*

Analysis of the experimental results has been carried out in the same way using

$$\frac{\eta_{CH}}{T_1} = \frac{\gamma_H{}^3\gamma_C\hbar^2}{2}\sum_{3H}\frac{\tau_{CH_3}{}^{N.M.R.}}{[r_{CH}{}^{methyl}]^6}. \quad (9)$$

Corresponding values of $\tau_{CH_3}{}^{N.M.R.}$ are listed in table 2. The problem of methyl group rotation about a fixed but arbitrary axis in the molecular frame has been previously studied by different authors : Woessner [49] and more recently Versmold [50, 51]. Using Woessner's notation, $\tau_{CH_3}{}^{N.M.R.}$ can be related to the jumping rate $2R/3$ of the methyl group from any of its three equivalent positions by

$$\tau_{CH_3}^{N.M.R.} = \frac{1}{2D_\perp}\left\{\frac{A_1}{6} + \frac{A_2+A_3}{6+R/D_\perp} + \frac{B_1}{5+\sigma} + \frac{B_2+B_3}{5+\sigma+R/D_\perp} + \frac{C_1}{4\sigma+2} + \frac{C_2+C_3}{4\sigma+2+R/D_\perp}\right\} \quad (10)$$

with

$$\sigma = \frac{D_\parallel}{D_\perp},$$

where $D_\parallel$ and $D_\perp$ are the diffusion coefficients of a symmetric ellipsoidal rotator, A_i, B_j, C_k being specific constants defined in reference [49]. If the molecule is assumed to undergo isotropic reorientation, the latter formula reduces to

$$\tau_{CH_3}^{N.M.R.} = \frac{1}{2D_0} \cdot \left\{\frac{1}{3+R/2D_0}\right\}, \quad (11)$$

to which we shall restrict our analysis for lack of knowledge of the anisotropic diffusion coefficients $D_\perp$ and $D_\parallel$. It is interesting to note that the movement of the methyl protons will be affected by (i) the methyl group internal rotations, (ii) the methoxy group reorientations, and finally (iii) by the rotational diffusion process of the whole molecule : the formula (11), therefore, will have to be extended to account simultaneously for (ii) and (iii), if one is interested in obtaining any estimation of R.

5. Hindered methoxy group rotations

5.1. *Comparison between dielectric and N.M.R. results*

The microscopic correlation times τ_μ^{Diel} are not short enough to give from themselves any evidence of a notable contribution from the methoxy group rotations to the dielectric relaxation. However, the measured ratio

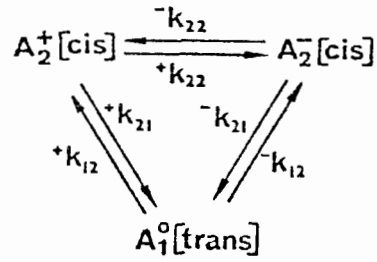
$$\rho_{app} = \frac{\tau_\mu^{Diel}}{\tau_C^{N.M.R.}}$$

is considerably less than 3 (see table 2), leading to a discussion of three different interpretations.

(1) Substantial contribution from internal methoxy group rotation to the dielectric relaxation phenomenon.
(2) Breakdown of the Debye-Perrin rotational diffusion model, i.e. reorientation of the whole molecule by large angle jumps [52].
(3) Strongly anisotropic rotational motion of the whole molecule [48].

From previous experimental studies concerning rigid or quasi-rigid molecules of intermediate size [38, 44, 53], one might guess that the two latter interpretations (still to be discussed further in the text), are not the most probable ones. In contrast, the first explanation may be quantitatively supported using the model of dielectrically active ' Chemical Relaxation Processes ' as previously discussed by Williams and Cook [54] and Goulon [55].

If one assumes that the *p*-dimethoxybenzene molecule exists in the two planar cis (polar) and trans (non-polar) configurations, the rotation of the methoxy groups gives rise to both cis/trans isomerism and cis/cis inversion mechanisms. We can therefore summarize the internal motions using a triangular kinetic scheme :



with respect to the symmetry of the system, the dipolar correlation function is found to have the following time dependence :

$$\langle \mu(0) \cdot \mu(t) \rangle = \tfrac{1}{2} \langle \mu(0) \cdot \mu(0) \rangle \{ \exp(-t/\tau_2) + \exp(-t/\tau_1) \} \cdot \exp(-t/\tau_0), \qquad (12)$$

where τ_0 characterizes the reorientational process of the whole cis conformer, considered as a rigid molecule, and τ_1, τ_2 are given by

$$\frac{1}{\tau_1} = k_{21} + 2k_{12} = k_{21} \cdot [1 + K_{eq}], \qquad (13\,a)$$

$$\frac{1}{\tau_2} = k_{21} + 2k_{22} = k_{21} \cdot [1 + K'] \qquad (13\,b)$$

According to the ' Curie principle ' stated by Prigogine and Mazur†, this form of the dipolar correlation function assumes a total statistical independence between the internal (chemical) process, and the external (diffusional) process.

From non-linear high-field static dielectric measurements [56] it can be shown that the equilibrium constant $K_{eq} = A_2 \pm / A_1^0$ remains nearly constant and equal to unity $[1{\cdot}0_0 \pm 0{\cdot}0_3]$ over the whole temperature range considered, the energy difference between the cis and trans conformers being less than 0·1 kcal/mole. Unfortunately, no direct experimental information is available concerning the parameter K' : dielectric and far infra-red measurements do not allow a reasonable resolution and calculation of the two relaxation times arising from the coupled internal motions. Only a mean dipolar correlation time τ_μ may be considered in our interpretation :

$$\tau_\mu = \tfrac{1}{2}\tau_0 \cdot \left[\frac{\tau_1}{\tau_1 + \tau_0} + \frac{\tau_2}{\tau_2 + \tau_0} \right]. \qquad (14)$$

Using a more symmetric form of the latter expression :

$$\frac{1}{1 + (1 + K_{eq})x} + \frac{1}{1 + (1 + K')x} = 2R_r, \qquad (15)$$

† I. Prigogine and P. Mazur, *Physica*, **19**, 241, 1953.

where

$$x = k_{21} \cdot \tau_0 \quad \text{and} \quad R_\tau = \frac{\tau_\mu}{\tau_0} \leqslant 1 ;$$

the N.M.R. relaxation data concerning the aromatic ^{13}C nuclei can now be very simply injected via the direct identification: $\tau_0 = \rho \cdot \tau_{C\ ortho}{}^{N.M.R.}$ where deviations from the standard value $\rho_{th} = 3$ could account for a non-diffusional or and anisotropic reorientation of the whole molecule.

Two limiting cases: (I) $K' \simeq K_{eq} \simeq 1$ and (II) $K' \ll K_{eq}$ have been investigated for different but arbitrary choices of the ratio $\rho = 3{\cdot}0$; $2{\cdot}75$; $2{\cdot}5$; $2{\cdot}25$; $2{\cdot}0$. The corresponding values of k_{21} are listed in table 3.

Logarithmic plots versus (temperature)$^{-1}$, of the inverse of the two correlation times $\tau_0 = 3\tau_{C\ ortho}{}^{N.M.R.}$ and τ_μ are linear and allow us to calculate the apparent activation enthalpies:

$$^{\neq}\Delta G_0 = 2{\cdot}2_6 \text{ kcal/mole} \quad ^{\neq}\Delta G_\mu = 3{\cdot}3_4 \text{ kcal/mole.}$$

The difference between the two values, may be an additional indication that the N.M.R. and dielectric relaxation processes are of a different nature, the former being insensitive to any group rotation. The corresponding pre-exponential factor are

$$A_0 \simeq 0{\cdot}02_{(1)} \times 10^{12}\ s^{-1} \quad \text{and} \quad A_\mu \simeq 0{\cdot}2_2 \times 10^{12}\ s^{-1}.$$

In one assumes $K' \sim 0$, logarithmic plots of k_{21}, versus T^{-1} can also be fitted by a simple Arrhenius law only for $\rho \geqslant 2{\cdot}5$. Although this result might have a dubious significance (e.g. due to experimental uncertainties, and lack of knowledge of the temperature dependence of ρ for complex reorientational processes), we take it as an experimental support for the hypothesis of a diffusional nature of the motion of the whole molecule. The calculated activation energies $^{\neq}\Delta G_{21}$ are slightly affected (table 4) by the Powles–Glarum local field correction relative to τ_μ. Small deviations from the standard value $\rho_{th} = 3$ increase the calculated height of the barrier to internal rotation of the methoxy groups.

In the limiting case $K' \simeq K_{eq}$, the values of $^{\neq}\Delta G_{21}$ (table 4) remain of the same order of magnitude only for $\tau_\mu \simeq \tau_\mu{}^{H}$. It is worth noting that the Powles–Glarum correction leads to non-linear plots of k_{21} versus T^{-1}, and the lower mean values of $^{\neq}\Delta G_{21}$. The latter results therefore arouse suspicion about the validity of the assumptions $K' \sim K_{eq}$, $\tau_\mu \simeq \tau_\mu{}^{P.G.}$. The following analysis of the far infra-red data will also lead to the same conclusion.

The activation enthalpies obtained are rather high for a fast motion and consequently the corresponding pre-exponential factors A_{21} (listed in table 4) are also very large†.

3.2. *Analysis of the far infra-red active torsion of the methoxy groups*

Far infra-red spectroscopy has been widely applied to determine, in the gas and solid phases, apparent barriers to internal rotation. However, most of this work has been confined to systems in which the inertial tensor of the whole molecule is 'quasi'-*independent* of the relative orientation top/frame about the axis of internal rotation. Actually, the theoretical analysis of the torsion in

† This observation is due to one of the referees.

	τ_μ	τ_μ^{H}				$\tau_\mu^{P.G.}$		
	K' \ ρ	3·0	$2{\cdot}7_5$	2·5	$2{\cdot}2_5$	3·0	$2{\cdot}7_5$	2·5
$^{t}\Delta G_{21}$/(kcal mol^{-1})	$K'\sim 0$	$4{\cdot}7_5$	5·0	5·3	6·1	$4{\cdot}3_5$	4·4	4·7
$A_{21}\times 10^{-12}$/s^{-1}	$K'\sim 0$	2(6)·	3(3)·	5(5)·	17(0)·	$4{\cdot}_{(0)}$	$4{\cdot}_{(5)}$	$5{\cdot}_{(6)}$
$^{v}\Delta G_{21}$/(kcal mol^{-1})	$K'\sim 1$	4·5	4·7	5·2	5·8	3·6	3·8	4·0
$A_{21}\times 10^{-12}$/s^{-1}	$K'\sim 1$	$3{\cdot}_{(2)}$	3·(7)	$6{\cdot}_{(0)}$	$14{\cdot}_{(0)}$	$0{\cdot}_{(9)}$	1·	$1{\cdot}_{(3)}$

Table 4.

		298 K					323 K					348 K		
$K' \simeq 0$ (ρ / τ_μ)		3·0	2·7$_5$	2·5	2·2$_5$	2·0	3·0	2·7$_5$	2·5	2·2$_5$	2·0	3·0	2·7$_5$	2·5
τ_0/ps		20·2$_5$	18·5$_6$	16·9	15·2	13·5	15·4	14·1	12·8	11·5	10·2$_5$	11·9	10·9	9·9$_4$
$10^{-10}k_{21}$/s^{-1}	τ_μ^{H}	2·2$_5$	1·9$_3$	1·5$_4$	1·0$_8$	0·4$_1$	4·3$_7$	3·9$_3$	3·4$_0$	2·7$_8$	1·9$_3$	6·8$_9$	6·3$_2$	5·6$_4$
$\tau_2 = 2\tau_1$/ps	τ_μ^{H}	44·3	51·8	64·7	92·5	242·0	22·8	25·4	29·3	35·9	51·7	14·5	15·8	17·7
$10^{-10}k_{21}$/s^{-1}	$\tau_\mu^{P.G.}$	2·8$_6$	2·5$_3$	2·1$_4$	1·6$_7$	1·0$_1$	5·2$_6$	4·8$_1$	4·2$_8$	3·6$_5$	2·8$_8$	8·0$_5$	7·4$_7$	6·7$_8$
$\tau_2 = 2\tau_1$/ps	$\tau_\mu^{P.G.}$	34·9	39·5	46·7	59·9$_7$	91·8	19·0	20·8	23·3	27·4	34·7	12·4	13·4	14·7
$K' \simeq K_{eq} \simeq 1$ (ρ / τ_μ)		3·0$_0$	2·7$_5$	2·5	2·2$_5$	2·0	3·0	2·7$_5$	2·5	2·2$_5$	2·0	3·0	2·7$_5$	2·5
τ_0/ps		20·2$_5$	18·5$_6$	16·9	15·2	13·5	15·4	14·1	12·8	11·5	10·2$_5$	11·9	10·9	9·9$_4$
$10^{-10}k_{21}$/s^{-1}	τ_μ^{H}	1·6$_2$	1·3$_9$	1·1$_2$	0·7$_9$	0·3$_8$	3·0$_9$	2·8	2·4$_4$	2·0$_1$	1·4$_7$	4·8$_6$	4·4$_7$	4·0$_2$
$\tau_2 = \tau_1$/ps	τ_μ^{H}	30·9	35·9	44·5	63·0	131·0	16·1	17·8	20·4	24·8	34·0	10·3	11·2	12·4
$10^{-10}k_{21}$/s^{-1}	$\tau_\mu^{P.G.}$	2·0$_3$	1·8$_1$	1·5$_4$	1·2$_1$	0·8	3·7	3·4	3·0$_5$	2·6$_2$	2·0$_9$	5·6$_4$	5·2$_8$	4·8$_0$
$\tau_2 = \tau_1$/ps	$\tau_\mu^{P.G.}$	24·5	27·6	32·4	41·2	62·4	13·5	14·7	16·4	19·0	23·9	8·8$_6$	9·5$_0$	10·4

Table 3.

completely asymetric molecules remains a very complex exercise. One of the most useful approaches to this problem has been given by Quade *et al.* [57, 58] and other groups [59] in the case of molecules having one single degree of internal freedom. In a previous study [60] we have extended this method to systems which exhibit a bi-dimensional rotation (α_1, α_2) of two light tops ($-CH_3$) about a common molecular axis (O_1O_2) (figure 1), the para substituted aromatic ring being designated as the rigid, ' heavy ' frame.

The torsional part of the hamiltonian can be written [60]

$$H = \tfrac{1}{2}\{\mathbf{p}_u^2 \cdot F_{uu}(\alpha_u, \alpha_v) + F_{uu} \cdot \mathbf{p}_u^2 + 2\mathbf{p}_u \cdot F_{uu} \cdot \mathbf{p}_u + 2\mathbf{p}_u \cdot F_{uv}(\alpha_u, \alpha_v) \cdot \mathbf{p}_v + \mathbf{p}_v^2 \cdot F_{vv}(\alpha_u, \alpha_v) + F_{vv}\mathbf{p}_v^2 + 2\mathbf{p}_v F_{vv}\mathbf{p}_v + 2\mathbf{p}_v \cdot F_{vu}(\alpha_u, \alpha_v) \cdot \mathbf{p}_u\} + V(\alpha_u, \alpha_v) + f(\alpha_u, \alpha_v), \quad (16)$$

where

$$\alpha_u = \alpha_1 + \alpha_2, \quad \alpha_v = \alpha_1 - \alpha_2$$

are the usual coordinates of symmetry, and $\mathbf{p}_u$, $\mathbf{p}_v$ the corresponding operators :

$$\mathbf{p}_u = -i\hbar \frac{\partial}{\partial \alpha_u}, \quad \mathbf{p}_v = -i\hbar \frac{\partial}{\partial \alpha_v}.$$

The present expression of the torsional kinetic energy leads to a ' pseudo ' potential term $f(\alpha_u, \alpha_v)$, which may be considered as a small perturbation of the potential hindering the torsion. Actually, a major difficulty arises from the α_u, α_v dependence of the effective inverse moments of inertia F_{uu}, F_{vv}. Expanding the two functions $F_{uu}(\alpha_u, \alpha_v)$, $F_{vv}(\alpha_u, \alpha_v)$ respectively as

$$F(\alpha_u, \alpha_v) = F^0 + F^{(1)} \cdot \sin^2 \alpha_u + F^{(2)} \cdot \sin^2 \alpha_v + F^{(3)} \cdot \sin^2 \alpha_u \sin^2 \alpha_v + \ldots$$

$$+ F_{uv}(\alpha_u, \alpha_v) = (F_{uv}{}^0) + F_{uv}{}^{(1)} \sin \alpha_u \sin \alpha_v + \ldots \quad (17)$$

analytical expressions have been derived which allow us to calculate the coefficients F^0, $F^{(1)}$ ... up to $F^{(5)}$, provided that the structural parameters of the molecule can be reasonably estimated. However, we prefer to restrict the present analysis to the usual, but rather unsatisfactory approximation

$$F_{uu} \simeq F_{uu}{}^0, \quad F_{vv} \simeq F_{vv}{}^0, \quad F_{uv} \simeq F_{uv}{}^0 = 0,$$

although preliminary results indicate that the α_u, α_v dependent terms would turn out to slightly affect the (over) estimated barrier height of the hindering potential. The effective moments of inertia $F_{uu}{}^{-1}$ and $F_{vv}{}^{-1}$ calculated for the deuterated or normal compound in both cis and trans configurations, are listed in table 5.

para D.M.B.	Cis conformer	(C_{2v})	Trans conformer	(C_{2h})
$(F_{uu}{}^H)^{-1}$	$45{\cdot}4_1 \times 10^{-40}$ g cm^2	(B_2)	$33{\cdot}2_7 \times 10^{-40}$ g cm^2	(B_g)
$(F_{vv}{}^H)^{-1}$	$42{\cdot}9_5 \times 10^{-40}$ g cm^2	(A_2)	$65{\cdot}5_8 \times 10^{-40}$ g cm^2	(A_u)
$(F_{uu}{}^D)^{-1}$	$54{\cdot}4_4 \times 10^{-40}$ g cm^2	(B_2)	$40{\cdot}8_8 \times 10^{-40}$ g cm^2	(B_g)
$(F_{vv}{}^D)^{-1}$	$56{\cdot}5_2 \times 10^{-40}$ g cm^2	(A_2)	$86{\cdot}2_3 \times 10^{-40}$ g cm^2	(A_u)

Table 5.

the C_{2v} symmetry of the cis conformer, one may expect the torsional
$_2$) to be active in the far infra-red, and the torsional mode $\alpha_r(A_2)$ to
aman active. An opposite situation may also be predicted for the
onformer : the torsional modes $\alpha_u(B_g)$ and $\alpha_r(A_u)$ being respectively
l infra-red active.

cis and trans conformers correspond to the same energy (as sug-
he temperature independence of the equilibrium constant K_{eq}), the
: order of magnitude of F_{B_2} and F_{A_u} allows us to consider that the
ad feature peaking at 92 cm^{-1} in the far infra-red spectrum of the
) *p*-dimethoxybenzene solution (shifted to 82 cm^{-1} for the deuterated
s), might arise from contributions of both the B_2 (cis conformer)
rans conformer) torsional modes. Assuming still that these two
of comparable intensity, one may define an apparent mean moment
s

$$F_{app}^{-1} = [F_{B_2} \cdot F_{A_u}]^{-1/2}$$

n the numerical values

$$[F_{app}^{D}]^{-1} = 68{\cdot}_{51} \times 10^{-40} \text{ g cm}^2 \quad [F_{app}^{H}]^{-1} = 54{\cdot}_{57} \times 10^{-40} \text{ g cm}^2.$$

he band shift on deuteration can be quantitatively predicted from

$$\frac{\tilde{\nu}_H}{\tilde{\nu}_D} = \left[\frac{F_{app}^{D}}{F_{app}^{H}}\right]^{-1/2} = 1{\cdot}12_8.$$

he centre of the band observed for the deuterated compound is taken
cm^{-1}, one would expect this band to be shifted to $\tilde{\nu}_H = 91{\cdot}_{88}$ cm^{-1}
mal species : this gives excellent agreement with experimental results.
dual frequencies of each contributing mode may also be computed :

3 cm^{-1}, $\tilde{\nu}_{B_2}^{D} = 92$ cm^{-1} and $\tilde{\nu}_{A_u}^{H} = 84$ cm^{-1}, $\tilde{\nu}_{B_2}^{H} = 101$ cm^{-1}.

ing also the harmonic oscillator representation as valid, the height of
hindering a methoxy group torsion may be evaluated from

$$V_2 = \tfrac{1}{2}\left[\frac{\tilde{\nu}^2}{4F_{app}}\right] \simeq 5{\cdot}_{88} \text{ kcal/mole (2058 cm}^{-1}\text{)}.$$

alue is to be directly compared with previous results obtained in a
y by Owen *et al.* [61, 73] on pure anisole and substituted compounds :
$\simeq 6{\cdot}0_5$ kcal/mole. The small difference appearing between anisole
dimethoxybenzene barrier heights, if significant, might be due to a
coupling of the two methoxy groups.

5.3. *Discussion*

the aforementioned experimental results, there is little doubt that the
up internal rotation is fast enough to significantly contribute to the
xation. But there is also strong evidence that this internal motion
by a potential barrier which might be reasonably estimated at

$\sim 5{\cdot}3 \pm 0{\cdot}6$ kcal/mole. This rather high value, inferred from two independent analyses, might be coherent with a partial hybridization of the oxygen and ring p orbitals, leading to the expected predominance of the planar configurations. However, it has to be recalled that in the liquid state, inter- and intra-molecular contributions to torsional barriers are often of the same order [43], possibly due to some short-range correlation ordering of the phenyl groups of neighbouring molecules.

In order to explain the small variation between $^{*}\Delta G_{21}$ and V_2, we would like to review the assumptions or approximations used in each method of estimating the barrier height. In the comparison between the dielectric and the ^{13}C N.M.R. correlation times :

(i) the controversial local field corrections to τ_μ (including any mode of collective interaction of the molecular dipoles with the electric field) [32, 52],

(ii) the speculative estimation of the parameter ρ, on the basis of a more or less anisotropic, diffusional reorientation of the whole molecule [52],

(iii) the lack of information on the specific inversion process via the characteristic parameter K',

are the main sources of uncertainties. Due to the dilution of the *para*-dimethoxybenzene/C_2Cl_4 solutions and to the favourable condition, $\epsilon_s - \epsilon_\infty < 1$, one may expect (i) to only slightly perturb the final result. Assuming a diffusional reorientation of the whole molecule it has been shown in a previous section that a moderate anisotropy of this motion gives rise to only small deviations from $\rho_{th} = 3$, and might occasionally compensate the influence of (i). One has also to remember that our ' quasi ' semicircular Cole–Cole plot could as well be coherent with a large jump reorientational process of the whole molecule [52]. Actually, following Kivelson and Keyes [62], one may guess the present system to lie in the so-called ' slor-sail ' limit, where also small deviations form $\rho_{th} = 3$ are predicted. An experimental support to the validity of such a speculative assumption might be found in the perfect coherence of the dipolar and ^{13}C N.M.R. correlation times similarly obtained for a *para*-diacetylbenzene/C_2Cl_4 solution, the acetyl group rotations being too slow to significantly contribute to the dielectric relaxation process.

The main objection to the analysis of the far infra-red active methoxy groups torsional modes might be the rather complex nature of the broad bands peaking at $\tilde{\nu}_{II} = 92$ cm^{-1} and $\tilde{\nu}_{I} = 82$ cm^{-1}. Although they cannot be experimentally resolved, two distinct modes ($\tilde{\nu}_{A_u}$ for the trans conformer and $\tilde{\nu}_{B_1}$ for the cis conformer) which are, on a rather speculative basis, assumed to have about the same intensity, are clearly involved in our interpretation. The additional but much smaller contribution of the Poley absorption due to the cis conformer should slightly affect the shape of the band, but, in regard to the rough assignment of the torsional frequency of each mode, this perturbation has been neglected. Besides, one has to remember the aforementioned approximation inherent to the truncated series expansion of the various functions $F_{uu}(\alpha_u, \alpha_r)$, F_{rr}, F_{ur}. In spite of all the insufficiencies of the present analysis, it is worth noting that our results are consistent with previous works on anisole [61, 43]. Our study does not suggest any strong mixing between the methoxy torsions and the low frequency out-of-plane ring vibration, but this remains actually an open question.

6. Internal rotation of the methyl groups

6.1. *Analysis and discussion of the N.M.R. dielectric data*

The ^{13}C N.M.R. correlation times $\tau_{CH_3}^{N.M.R.}$ might also give interesting information on the movement of the methyl protons provided that the contributions of both the methoxy group internal rotation and the diffusional process of the whole molecule can be subtracted. In order to take into account the additional motion of the methoxy group, an extended form of the relationship [11] has been derived assuming for each methoxy group a chemical relaxation (or jump) process between two equivalent sites :

$$\tau_{CH_3}^{N.M.R.} = \frac{1}{[6D_0 + k_{21} \cdot (1 + K_{eq}) + R]} \tag{18}$$

or

$$\frac{\tau_0}{\tau_{CH_3}^{N.M.R.}} = \rho + [1 + K_{eq}] \cdot x + R \cdot \tau_0, \tag{19}$$

where $\tau_0 = \rho \tau_{C\ ortho}^{N.M.R.}$, $x = k_{21}\tau_0$, K_{eq} have been defined in the preceding section. With regard to the uncertainties in the evaluations of ρ and consequentially x, successive determinations of the jumping rate $2R/3$ of the methyl from any of its three equivalent configurations have been carried out assuming various values of ρ and x (table 6). Logarithmic plots of R versus T^{-1} are nearly linear and allow us to calculate an apparent activation energy for the methyl rotation :

$$^{*}\Delta G_{CH_3} = 1{\cdot}_8 \pm 0{\cdot}_3 \text{ kcal/mole.}$$

It is obvious that all the limitations which have been reviewed in the last section concerning any direct comparison of dielectric and N.M.R. relaxation data, hold again in the present determination of R. It is also worth noting that if our results confirm the readily acceptable idea that the methyl rotation is somewhat faster than the methoxy group rotation of the methyl group, our evaluation of the height of the barrier hindering the methyl internal rotation (~2 kcal/mole) might suggest an appreciable coupling of both the methyl and methoxy group internal motions. This conclusion seems to be consistent with recent N.M.R. and gas/phase microwave studies on comparable systems [63, 64].

6.2. *Far infra-red spectroscopic data*

The far infra-red spectra of the normal and deuterated *para*-dimethoxybenzene crystals do not allow of a firm assignment of the methyl torsion. Actually the spectrum of the deuterated species shows near 145 cm^{-1} the presence of an almost completely resolved band. Besides, one may also discern in the spectrum of the normal compound a badly resolved shoulder near 160 cm^{-1} which has been clearly confirmed by the lineshape analysis of the strong absorption peaking at 178 and by an apparent move of the latter band from 178 to 207 cm^{-1} on deuteration of the methyl groups. If now one assumes that these remarkable bands near 145 cm^{-1} and ~160 cm^{-1} have the same origin, it can be quantitatively shown that the apparent shift on deuteration (15 cm^{-1}) is much too small to be consistent with a rather speculative assignment of these bands to the τ-CH_3 torsional modes.

	T	298 K			323 K			348 K		
$K' \simeq 0$	ρ / τ_μ	3·0	$2{\cdot}7_5$	$2{\cdot}5_0$	$3{\cdot}0_0$	$2{\cdot}7_5$	$2{\cdot}5_0$	$3{\cdot}0_0$	$2{\cdot}7_5$	$2{\cdot}5_0$
$10^{-10} \times \frac{2R}{3}/s^{-1}$	τ_μ^{H}	11·5	12·0	12·5	13·4	14·0	14·7	17·1	17·9	18·8
R^{-1}/ps	τ_μ^{H}	5·8	$5{\cdot}5_6$	$5{\cdot}3_3$	$4{\cdot}9_7$	$4{\cdot}7_6$	$4{\cdot}5_3$	$3{\cdot}8_9$	$3{\cdot}7_2$	$3{\cdot}5_4$
$10^{-10} \times \frac{2R}{3}/s^{-1}$	$\tau_\mu^{P.G.}$	10·7	11·2	11·7	12·2	12·8	13·5	15·6	16·3	17·2
R^{-1}/ps	$\tau_\mu^{P.G.}$	6·2	$5{\cdot}9_6$	$5{\cdot}6_9$	$5{\cdot}4_5$	$5{\cdot}1_9$	$4{\cdot}9_2$	$4{\cdot}2_7$	$4{\cdot}0_7$	$3{\cdot}8_5$
$K' \simeq K_{eq} \simeq 1$	ρ / τ_μ	$3{\cdot}0_0$	$2{\cdot}7_5$	$2{\cdot}5_0$	$3{\cdot}0_0$	$2{\cdot}7_5$	$2{\cdot}5_0$	$3{\cdot}0_0$	$2{\cdot}7_5$	$2{\cdot}5_0$
$10^{-10} \times \frac{2R}{3}/s^{-1}$	τ_μ^{H}	12·4	12·7	13·0	15·1	15·5	16·0	19·8	20·4	21·0
R^{-1}/ps	τ_μ^{H}	$5{\cdot}3_7$	$5{\cdot}2_5$	$5{\cdot}1_0$	$4{\cdot}4_1$	$4{\cdot}3_0$	$4{\cdot}1_7$	$3{\cdot}3_6$	$3{\cdot}2_7$	$3{\cdot}1_8$
$10^{-10} \times \frac{2R}{3}/s^{-1}$	$\tau_\mu^{P.G.}$	11·8	12·1	12·5	14·3	14·7	15·2	18·8	19·3	19·9
R^{-1}/ps	$\tau_\mu^{P.G.}$	$5{\cdot}6_3$	$5{\cdot}4_9$	$5{\cdot}3_3$	$4{\cdot}6_6$	$4{\cdot}5_3$	$4{\cdot}3_9$	$3{\cdot}5_4$	$3{\cdot}4_5$	$3{\cdot}3_4$

Table 6.

In the case of the cis configuration of the *para*-dimethoxybenzene molecule, the hamiltonian relative to the torsion of the two methyl group has a very simple form due to the C_{2v} symmetry of the molecule [65, 66] :

$$H=(F+F')\mathsf{p}_+^2+M\alpha_+^2+(F-F')\mathsf{p}_-^2+N\alpha_-^2. \qquad (20)$$

In contrast to the problem of the torsion of the asymmetric methoxy groups, it is worth noting that the present effective inverse moments of inertia $F+F'$, $F-F'$ are strictly independent of α_+, α_- and may be easily calculated for both the normal (H) and the deuterated compound (D) [65, 66] :

$$F_H\simeq 0{\cdot}636\ (\text{u Å}^2)^{-1}\dagger, \quad F_H'\simeq 0{\cdot}002\ (\text{u Å}^2)^{-1},$$
$$F_D\simeq 0{\cdot}320\ (\text{u Å}^2)^{-1}, \quad F_D'\simeq 0{\cdot}001_9\ (\text{u Å}^2)^{-1}.$$

Very close estimations of the inverse effective moment of inertia for the methyl torsions have also been calculated for the C_{2h} trans conformation, using appropriate expressions [67].

Assuming that the feature observed at 145 cm^{-1} in the spectrum of the deuterated species is to be assigned to a pure $-CD_3$ torsion, one should expect from the latter evaluations of the effective inverse moments of inertia the $-CH_3$ torsion to be centred at about 203 cm^{-1}. Besides, the same assignment would lead to the following estimation of the barrier hindering the $-CD_3$ torsion :

$$V_3\simeq\frac{4}{9\hbar^2}\frac{\tilde{\nu}_D^2}{F_D}\simeq 2{\cdot}84\ \text{kcal/mole}.$$

Provided that our assignment is correct, the poor agreement of the predicted $-CH_3$ torsion with the experimental far infra-red spectrum of the normal compound, and also the considerable discrepancy between $^*\Delta G_{CH_3}$ and V_3 might suggest a strong mixing of the methyl torsions with other vibrations (e.g. methoxy groups torsional modes, and/or out-of-plane bending modes of the methoxy groups).

7. Conclusions

This first attempt to investigate the dynamics of internal motions by comparison of dielectric/^{13}C N.M.R. relaxation and far infra-red spectroscopic data seems to be quite encouraging. Let us emphasize again the main deductions of the present study : the internal rotation of the methoxy groups has been shown to contribute significantly to the dielectric relaxation process, and quantitative estimations of the kinetic parameters and activation energies for both methyl- and methoxy internal motions have been achieved. Further work is proceeding to improve the quality of the experimental ^{13}C N.M.R. measurements and the theoretical analysis of the dielectric and far infra-red data.

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† Å = 10^{-10} m ; u = unified atomic mass unit ≈ kg/6·022 05 × 10^{26}.

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