ALKOXY INTERNAL TORSION IN LIQUID DIMETHYL AND DIETHYL CARBONATES: AN EXTENDED MICROWAVE/FAR INFRARED ANALYSIS

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The absorption and dispersion spectra of pure dimethyl- and diethyl-carbonates are reported over frequencies ranging from static to ca. 360 cm^{-1} at room temperature. It is shown that the intensive modes centred respectively at 130 cm^{-1} for dimethylcarbonate and 110 cm^{-1} for diethylcarbonate cannot arise from the short time details of the whole molecule rotational diffusion but rather correspond to internal torsional oscillations of the alkoxy groups. A possible contribution of dielectrically active chemical relaxation processes associated with the hindered rotation of the alkoxy groups is also discussed.

1. Introduction

Recently the kinetics of the cis—trans isomerisms in p-dimethoxybenzene [1] and p-diacetylbenzene [2] dissolved in tetrachlorethylene have been studied using a novel combination of dielectric and ^{13}C NMR relaxation. The major conclusions were that only the methoxy group rotation is fast enough to significantly perturb the long time part of the dielectric relaxation process, whereas both the acetyl and methoxy group torsional oscillations strongly dominate the far

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infrared spectrum. A natural extension of this work is to molecules in which the two "tops" do not rotate about collinear axes and in this brief communication we report some preliminary results on two such molecules dimethyl and diethyl carbonate.

The non-collinearity of axes introduces an immediate further degree of complexity into the analysis of the internal motions since there are now more conformers to be considered in the chemical and orientational relaxation processes and a rigorous theoretical estimation of the corresponding torsional frequencies also become far more difficult. Additionally, for the present molecules, the elucidation of the dielectric

relaxation processes is made more complicated because no valuable information on the reorientation of the "rigid" carbonate frame O—CO—O can be gained from ^{13}C NMR relaxation measurements. A promising way to reach such information is via ^{17}O NMR quadrupolar relaxation studies of the carbonyl group [3] but this technique requires the non-trivial determination of the corresponding quadrupolar coupling constant. In this preliminary work we have therefore confined ourselves to an examination of the absorption/dispersion spectra over a range of frequencies from virtually zero up to 360 cm^{-1} and to an initial qualitative discussion of the results.

2. Experimental

The microwave measurements were carried out at discrete frequencies ranging from 9 to 112 GHz, using interferometric techniques developed at the University of Nancy I and described previously [1,2,4]. The various far infrared absorption/dispersion spectra have been obtained by Fourier transform spectroscopy. The absorption spectra were carried out with three separate Michelson interferometers at Aberystwyth,

at the Post Office Telecommunication H.Q., and at the National Physical Laboratory (N.P.L.). The region 2–30 cm^{-1}, where the power emitted from the conventional high pressure mercury source is low, was covered using a Rollin helium cooled In/Sb crystal detector producing very high signal to noise ratios (ca. 10^3:1). The versatile high-performance dispersive Fourier transform interferometer (DFTS) built at the N.P.L. featuring wire grid polarization beamsplitters and phase modulation [5] allowed us to measure simultaneously the absorption and dispersion spectra of these fairly absorbing systems.

The purification techniques used for the carbonates are described by Ménard and Chabanel [6], and the solvents used were spectroscopic grade dried over zeolite type 3A previously baked out at ca. 400°C.

3. Results

The results are presented in figs. 1 to 6. Internal consistency of these measurements can be judged from the very good match obtained between the far infrared absorption data and the microwave points as illustrated by fig. 2. Studies of dilute solutions showed
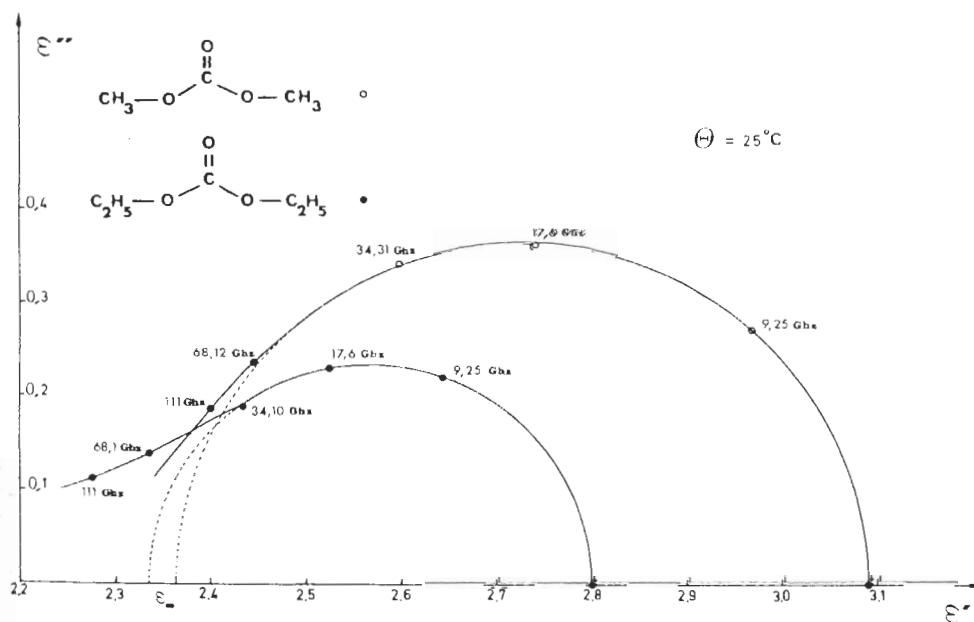

Fig. 1. Cole–Cole plots of pure dimethyl- and diethyl-carbonates at 298 K. The skewing becomes significant at millimetre wavelengths.
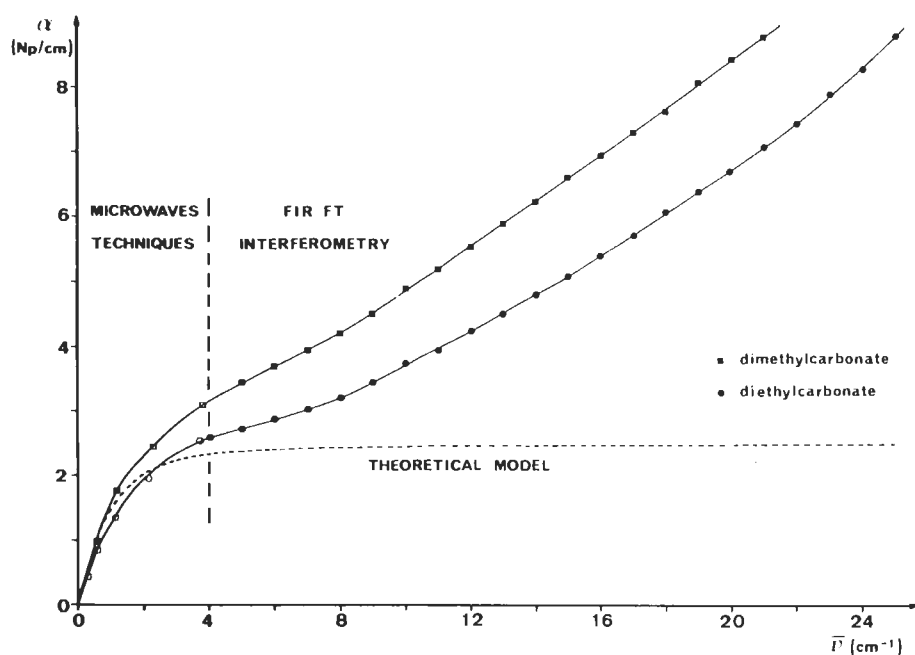
Fig. 2. Absorption spectra of pure dimethylcarbonate (■) and diethylcarbonate (●) in the overlapping very far infrared/microwave regions. The trace - - - is the simulated far IR absorption spectrum of a rigid dipole relaxing as pure dimethylcarbonate. The inertial decay to transparency of this simulated spectrum would occur for $\bar{\nu} \geqslant 50$ cm^{-1}.

that the very intense peaks centred at ca. 145 cm^{-1} and 250 cm^{-1} in pure dimethylcarbonate do not exhibit any apparent splitting, whereas the broad absorption observed in the far infrared region for di-

ethylcarbonate is more likely made up from the superposition of at least two broad lines peaking respectively at ca. 100 cm^{-1} and 160 cm^{-1}. A small shift (15 cm^{-1}) towards the low frequencies of the 145

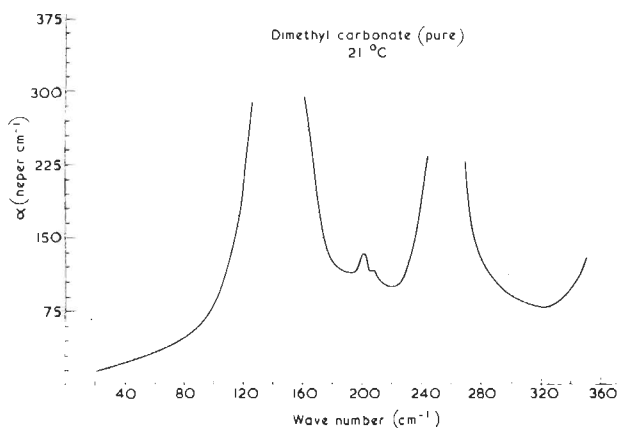
Fig. 3. Far infrared absorption of pure liquid dimethylcarbonate from 20 to 360 cm^{-1}, featuring the intense mode at ca. 140 cm^{-1} which is thought to be responsible for the skewing of the Cole–Cole plot at millimetre wavelengths (fig. 1).
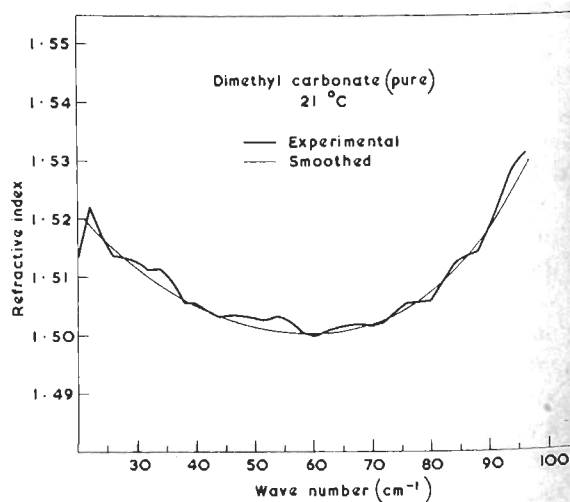

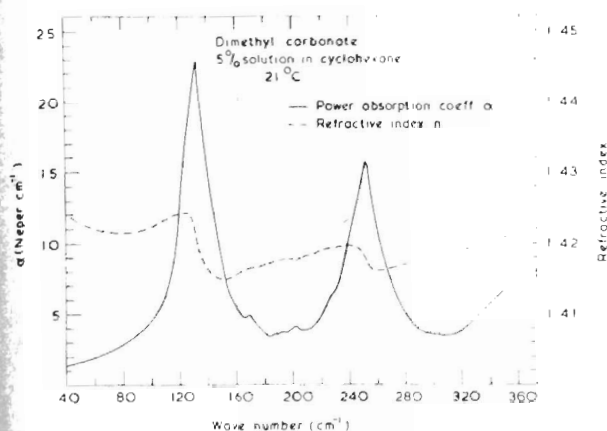Fig. 4. Refractive index of pure dimethylcarbonate at 294 K in the frequency range 20–100 cm^{-1}.

Fig. 5. Absorption coefficient and refractive index spectra of a dilute solution (5%, v/v) of dimethylcarbonate in cyclohexane at 294 K.

cm^{-1} line of pure dimethylcarbonate on dilution in cyclohexane is worth noting. As the far infrared absorption due to this very strong and broad line peaking at 145 cm^{-1} is already fairly intense in the range 2–30 cm^{-1}, it is not very surprising to observe at millimetre wavelengths at significant deviation from the semi-circular Cole/Cole plot defined by the low frequency microwave measurements (fig. 1). Obviously, attempts [7] to explain such a deviation in terms of another Debye process would be highly question-
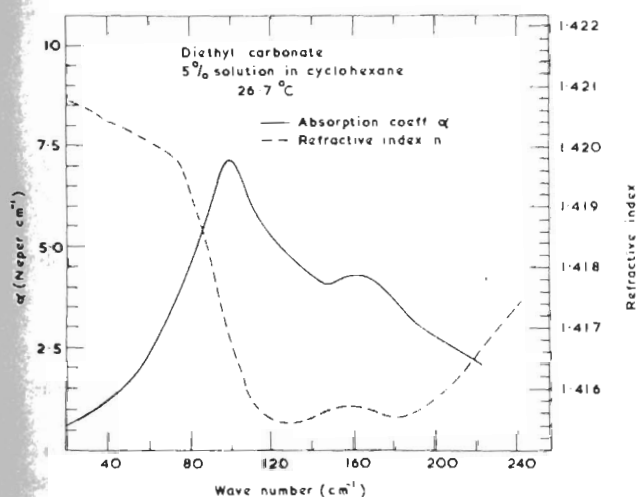
Fig. 6. Absorption coefficient and refractive index spectra of a dilute solution (5%, v/v) of diethylcarbonate in cyclohexane at 300 K.

able and should be abandoned. A semi-circular extrapolation of the microwave data led to ϵ_∞ values of 2.3_6 and 2.3_4 respectively for pure dimethyl- and diethyl-carbonate, but any physical meaning attaching to this parameter is inherently restricted to the analysis of the low frequency dipolar correlation function.

Due to the presence of the 145 cm^{-1} line, the dispersion spectrum of pure dimethylcarbonate exhibits a flat portion in the 40–80 cm^{-1} range before increasing again. The refractive index at the minimum is ca. 1.50 and is thus markedly smaller than $\epsilon_\infty^{1/2} = 1.53_6$. This is a consequence, of course, of the short time details of the dipolar correlation function.

4. Discussion

It is essential to realize that for the systems investigated here, both the internal rotation of the whole methoxy/ethoxy groups and the overall rotation of the whole molecule should contribute to the dielectric relaxation process.

A simple approach [1,2] for describing the long time phenomena consists in assuming a competition between a diffusive and nearly isotropic rotation of the whole molecule, and a more complex chemical relaxation process accounting for the various possible rotational isomerisms taking place between the three rotamers shown in fig. 7. There is experimental evi-
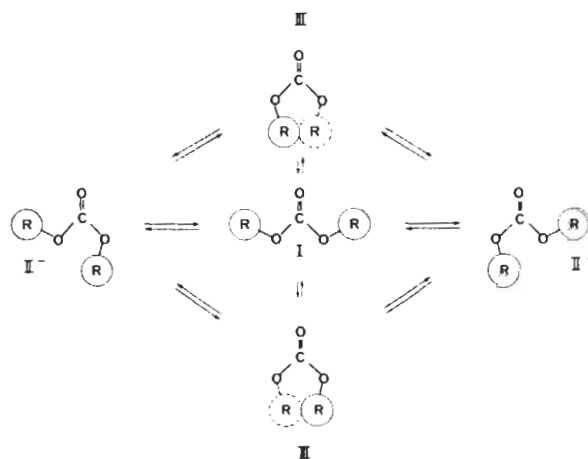
Fig. 7. Rotational isomerism in dimethyl- and diethyl-carbonates.

dence [8,9] supporting unambiguously the presence of the two planar conformers I and II, which have also been predicted to be stable from ab initio theoretical calculations [10] whereas the gauche structure III was merely suspected from accurate nonlinear dielectric experiments [11]. Obviously each one of the structures II and III exhibits a degeneracy corresponding to symmetric configurations of the rotating groups R and therefore a five site model shown in fig. 7 would be required for describing the overall kinetics of the internal motions.

If one further assumes no coupling between internal and overall rotation (a perhaps questionable assumption for anisotropic rotators such as diethylcarbonate), the dipolar correlation function may then be written:

$$C_\mu(t) = \Psi_\mu^{chem}(t) \exp(-t/\tau_{rot}),$$

where $\Psi_\mu^{chem}(t)$ can easily be calculated from group theory considerations [12,13] applied to the aforementioned five site model. Unfortunately no quantitative analysis of our data is yet possible, as no separate estimation of the overall rotation correlation time τ_{rot} is available. Work is still in progress for extracting such information from ^{17}O lineshape measurements [3].

As the microwave data relative to dimethylcarbonate fall satisfactorily onto a semi-circular Cole/Cole plot, the long time behavior of $C_\mu(t)$ might be reasonably approximated by an exponential decay. Therefore if Ψ^{chem} gives rise to any substantial contribution to the relaxation process, then it should be dominated by a single exponential decay and should not exhibit a broad distribution of relaxation times. From a direct comparison of the apparent relaxation times of pure dimethylcarbonate (DMC) and pure dimethoxymethame (DMM) [14]:

$$\tau_{app}(DMC) \approx 7.0_4 \text{ ps}, \quad \tau_{app}(DMM) \approx 1.8 \text{ ps},$$

it becomes apparent that the fast dynamics of the internal rotations might well constitute the main relaxation process of dimethoxymethane but that the methoxy group rotations are quite sensitively hindered in the case of dimethylcarbonate, as a consequence of the partial delocalization of the π-electrons in the carbonate group. However one should keep in mind

that even hindered rotations have been found to contribute significantly to the dielectric relaxation in the case of paradimethoxybenzene solutions [1].

The same analysis holds certainly for diethylcarbonate (τ_{app} = 11 ps) but additional difficulties might arise from the more anisotropic character of this molecule, and from the non-rigidity of the ethyl group thus resulting in a possibly non-exponential decay of the dipolar correlation function. These effects would obviously contribute together with the far IR resonant phenomena to give a skewed shape to the Cole/Cole plot in the millimetre wave region.

The next problem with which we are concerned is to interpret qualitatively the presence of strong absorption bands peaking in the far infrared. According to the Mori–Kubo version of the fluctuation dissipation theory [15], there should be associated with every low frequency relaxation process, a far infrared active resonant phenomenon (libration or torsion) which reflects the short time behavior of the dipole correlation function [16]. In the case of the rotation of a rigid molecule, a number of authors [17–20] have recently related the functional form of this librational far IR peak to the autocorrelation function of the derivative $\dot\Gamma$ of the random couple Γ acting on the molecule. It is pertinent to note here that choosing an exponential form for $\langle\Gamma(0)\Gamma(t)\rangle$ is the basis for the widely used M and J diffusion models [21] which have been shown to be invalid from the computer experiments of O'Dell and Berne [22] and from the work of Larkin et al. [23].

The equation of Quentrec and Bezot [18] was used for generating the simulated far IR absorption spectrum of a rigid dipole relaxing as pure dimethylcarbonate (fig. 2). The inertial decay to transparency of the absorption coefficient would then occur for $50 \leqslant \bar\nu \leqslant 100$ cm^{-1}. Thus it is obvious that the intense peak at 120 cm^{-1} cannot be due to whole molecule torsional oscillation, neither can the 110 cm^{-1} peak in diethylcarbonate. It is therefore highly probable that these are the methoxy and ethoxy internal librational modes associated with the chemical relaxation process. A theoretical study of these modes for such completely asymmetric molecules featuring two non-collinear rotation axes is a fairly complex exercise [1], which is still in progress.

Acknowledgement

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