

## Solvent shifts in the far i.r.

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**Abstract**—Solvent shifts in the far i.r. are rationalized in terms of a mean square torque parameter  $P(0)$ . Solvent viscosity is not an important factor, although the relative shapes and sizes of solute and solvent are important. To some extent, the polarity of the medium may give rise to a greater mean square torque by dielectric drag, especially in pure dipolar liquids.

### INTRODUCTION

This paper is an attempt at correlating solvent shifts observed in the far i.r. for a number of dipolar solutes, in an effort to bring out empirically the molecular factors responsible. The analytical techniques [1] at our disposal for describing 0-THz spectra are not yet at a stage of development where prediction can be made about spectral band-shapes given a form for the intermolecular potential. This is because such a description presupposes solution of the following intractable problems:

- (i) solving the equations of motion for a large number of bodies with electrical properties;
- (ii) that of knowing with enough precision what is being measured in 0-THz spectroscopy.

Infrared solvent shifts have been measured by many workers using frequencies above about 200–250  $\text{cm}^{-1}$ . The results have revealed a great deal about the nature of intermolecular interaction, its mechanism and the analytical form of the governing molecular potentials. Below 200  $\text{cm}^{-1}$ , far less is known about solvent shifts. It is known that the dominant spectral feature associated with molecular relaxation (the Poley absorption [2]) is solvent-dependent, more in some cases (supercooled liquids and glasses [3]) than in others, but until recently there has been no attempt at a systematic correlation. There have been many such studies in the frequency region below the far i.r. using the classical Debye theory [4–6]. These have clearly identified solvent shifts with changes in the Stokes law viscosity ( $\eta$ ). The Debye relaxation model gives  $\tau_0 = 4\pi\eta r^3/kT$  where  $r$  is the mean radius of the molecule. Such a relation for the Debye relaxation time results in values an order of magnitude larger than those observed except for very large molecules in small-molecule solvents (approximating best to true Brownian motion) [7]. Modifications to some advantage have involved [8] the replacement of  $r^3$  by the product of three half axes of the ellipsoid and more recently the replacement of  $\eta r^3$  with a function involving the geometries and mutual viscosity of solvent and solute molecules. If, alternatively, both the relaxation and the viscous drag are

treated as activation processes then a relation  $\tau_D \propto \eta^n$ , where  $n$  is some power less than unity, may be found to give more reasonable agreement with observation. Discrepancies from this rule are, however, frequent and some are exemplified here.

In an early paper by CHAN *et al.* [5] the relaxation of nitrobenzene was studied at 298 K in a series of nine solvents. Although the general trend was found linear with  $\eta$ , the relaxation in cyclohexane was faster than in  $\text{CCl}_4$  (9.3. compared to 14 ps), despite almost identical viscosities. These figures were in agreement with other determinations and further, the ease of rotation in  $\text{C}_6\text{H}_{12}$  was also observed for 1-nitronaphthalene. A similar result was found for pyridine by CROSSLEY and HASSELL [4] (3.1 and 5.0 ps in  $\text{C}_6\text{H}_{12}$  and  $\text{CCl}_4$ , respectively, at 298 K) which supports that obtained for chloroform, camphor and nitrobenzene by WHIFFEN [6]. A common finding is that of a “discrepancy” between benzene and *p*-xylene solvent systems (pure solvents again have near identical viscosities). Thus, MADAN [9] compares the values obtained by HASSELL and WALKER [10] for chlorobenzene, bromobenzene and nitrobenzene in *p*-xylene at 278 K (10.2, 14 and 13 ps) with his own in benzene solution at this temperature (9.7, 12.5 and 12 ps). In another paper by HASSELL and WALKER [11], data are quoted for the relaxation of pure toluene (7.4 ps) and for bromobenzene in benzene (11 ps). Because the two solutes toluene and bromobenzene have similar (van der Waals) volumes and the solvents toluene and benzene similar viscosities, the difference is unexplained. Another type of solvent effect occurs in the intensity of the processes [12]. This reflects the uncertainty of the effect of the dynamic internal field. Very little progress has been made using dielectric data in isolation of the far i.r., its high-frequency adjunct, where the detailed nature of the rotatory motions is exposed.

Typically [2], the peak far i.r. frequency ( $\bar{\nu}_{\text{max}}$ ) in the pure dipolar solute is higher than the solution value. In this paper the variation of  $\bar{\nu}_{\text{max}}$  with concentration in several solvents is studied and found to be linear. The difference  $\bar{\nu}_{\text{max}}(L) - \bar{\nu}_{\text{max}}(\infty)$ ,

between the liquid state  $\bar{\nu}_{\max}$  and the infinite dilution extrapolated peak position, is termed the "solvent shift" of a solvent. Alternatively, these far i.r. shifts may be considered in terms of the "mean square torque per unit volume of rotation" parameter  $P(0)$  introduced elsewhere [13].

### EXPERIMENTAL

Spectra have been measured [7] using a phase modulated Grubb Parson/N.P.L. Michelson interferometer with a solid state Golay detector and standard variable pathlength cell. All spectra presented are averages of two or more results on chemicals of AR grade or purer, and peak positions are estimated to be within  $\pm 2 \text{ cm}^{-1}$ .

### RESULTS AND DISCUSSION

Solvent effects are expected in the far i.r. region because of the variations of  $\epsilon''(\omega)$  observed dielectrically. In this paper, firstly, the spectra of 11 pure liquids are reported at 293 K ( $\pm 2$  K) to supplement data already measured for  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  liquids [2], and for some 40 solute/decalin systems [3, 13]. This allows determination of the solvent shift between pure solute and decalin solution. Some intermediate concentrations have also been studied to establish the linearity of this shift. Secondly, the spectra of 10 solutes at 10% v/v in  $\text{CCl}_4$  solvent (293 K) have been measured to obtain  $\bar{\nu}_{\max}$  values for comparison with both pure liquid and decalin solution values. It is established that solutes in  $\text{CCl}_4$  solution are hindered to a slightly greater extent than in decalin solution. Thirdly, for three solutes,  $\text{CH}_2\text{Cl}_2$ , chloroform and nitrobenzene, solution spectra have been obtained in diphenylmethane solvent. Negative solvent shifts are observed for the last two solutes.

The data are conveniently summarized in Fig. 1. where "blocks" on the wavenumber axes indicate a measurement, and connecting lines the shifts. Except for pyridine and chloroform which may be complexed in  $\text{CCl}_4$  solvent, dilution in non-dipolar  $\text{CCl}_4$  solvent lowers the  $\bar{\nu}_{\max}$  value while a further reduction occurs when  $\text{CCl}_4$  is replaced by decalin. Where the  $\text{CCl}_4$  solution has not been studied, the decalin blocks are tagged with dashed lines. For most of the pure liquids, the present  $\bar{\nu}_{\max}$  values are similar to the literature data where available.

As a measure of the effect of replacing solute molecules by solvent molecules for a given solute and solvent, one may determine the  $\bar{\nu}_{\max}$  values for the liquid and for the infinitely dilute solution, and calculate the difference. Alternatively, the shift may be quoted as a percentage  $\Delta\bar{\nu}_{\max}/\bar{\nu}_{\max}(L)$ . The solution values are obtained by linear extrapolation as illustrated in Fig. 2. For  $\text{CH}_2\text{Cl}_2$ , the published values [18] measured (at 298 K) for the pure liquid and for four number densities in  $\text{CCl}_4$  are given by open circles. Full circles on this line represent the present measurements taken at 10 and 50% v/v concentrations at 293 K while similar circles on the

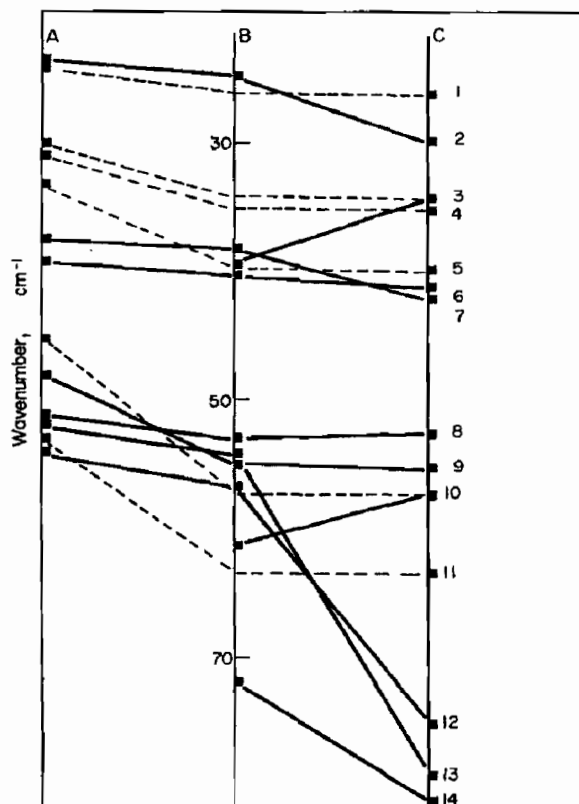


Fig. 1. Summary plot of solvent shifts in the far i.r. Solvents: A = decalin; B =  $\text{CCl}_4$ ; C = pure solute. (1) *t*-butylchloride [14, 15] ( $23 \text{ cm}^{-1}$ ); (2) bromobenzene [14, 15] ( $35.5 \pm 5 \text{ cm}^{-1}$ ); (3) chloroform [14, 16] ( $36 \text{ cm}^{-1}$ ); (4) pentafluorobenzene; (5) chlorobenzene [14] ( $36 \text{ cm}^{-1}$ ); (6) fluorobenzene [14] ( $35 \text{ cm}^{-1}$ ); (7) nitrobenzene [13] ( $43 \text{ cm}^{-1}$ ); (8) furan [17] ( $44 \text{ cm}^{-1}$ ); (9) benzonitrile [14] ( $57 \text{ cm}^{-1}$ ); (10) pyridine; (11) tetrahydrofuran; (12) dibromomethane; (13) dichloromethane; (14) acetonitrile ( $90 \text{ cm}^{-1}$ ). Literature values (for pure solute) are in parentheses. Ordinate peak wave number [ $\bar{\nu}_{\max}(\text{cm}^{-1})$ ].

dashed line are for decalin solution. Similar data are given for benzonitrile ( $\Delta$ ) and nitrobenzene ( $\square$ ). For chloroform, three of the solution spectra are illustrated in Fig. 3 and these and the pure liquid spectrum have  $\bar{\nu}_{\max}$  values represented by ( $\bullet$ ) in Fig. 2. A negative shift is recorded for  $\text{CCl}_4$  and for diphenyl methane solvent while *n*-pentane and decalin result in the more usual positive shifts. No intermediate concentrations have yet been studied so that linearity is assumed.

Using these and similar linear (or assumed linear) plots, the limiting dilution peak frequencies are found and tabulated later together with  $\Delta\bar{\nu}_{\max}$  for decalin and  $\text{CCl}_4$  solutions at 293 K.

Comparing the percentage decreases of  $\bar{\nu}_{\max}$  upon dilution with either non-dipolar solute it is seen that in all cases, the decrease is less for  $\text{CCl}_4$  solvent, with a ratio of decreases ( $\Delta\bar{\nu}_{\text{CCl}_4}/\Delta\bar{\nu}_d$ ) from 0.75 to 0.9 in most cases. The figure for benzonitrile/ $\text{CCl}_4$  may be in error or otherwise may indicate complex formation. For furan a small

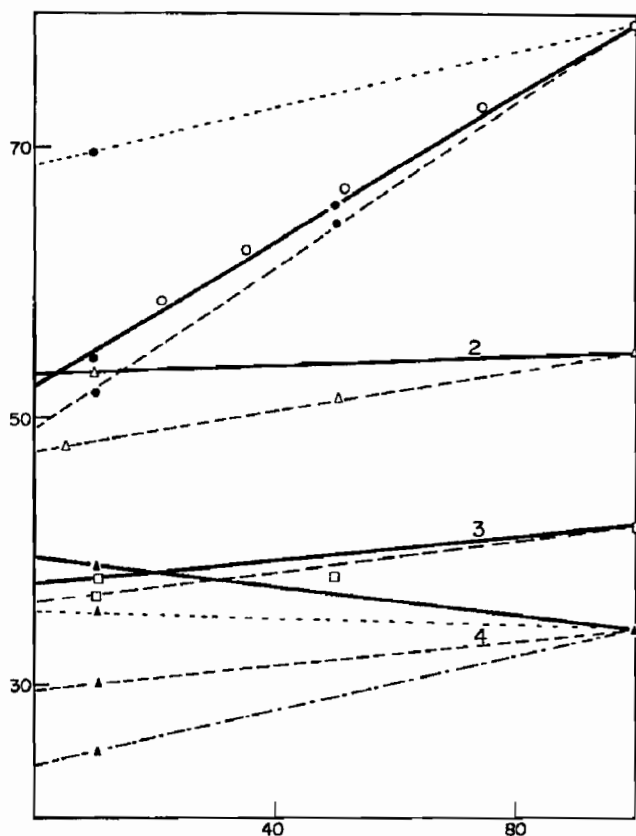


Fig. 2. Far i.r. peak shifts with solute concentration for several systems at 293 K. Ordinate:  $\bar{\nu}_{\max}$  ( $\text{cm}^{-1}$ ); abscissa: concentration (% v/v). (1) Methylene chloride; (2) benzonitrile; (3) nitrobenzene; (4) chloroform. —  $\text{CCl}_4$  solvent; ---- decalin solvent; ..... diphenylmethane solvent; - - - - - *n*-pentane solvent.

negative shift has occurred which is almost insignificant but does indicate the possibility of observing negative values (apart from those cases where complexing is presumed to occur).

The absolute values of the solvent shifts are arbitrary because they are based on pure liquid values. A better scheme for describing solvent shifts might be to choose one set of solvent data, e.g. the decalin series, as the zero level for each solute. In this scheme, the peak frequencies of  $\text{CCl}_4$  systems are on average 4.5% greater. This may be interpreted in terms of the mean square torque per unit volume parameter  $P(0)$  introduced and fully described elsewhere [13]. For decalin at 293 K, the value for  $P(0)$  was found [19] to be  $4.6 \times 10^{17} (\text{N m}^{-2})^2$ . This value is dependent on the choice of covalent radii and is larger than in reference [13]. As  $P(0)$  is proportional to the gradient of the line that best represents the data, it follows that a similar plot could be constructed for the  $\text{CCl}_4$  data with a gradient steeper by about 10%. This leads (on the basis of the limited number of systems studied) to a  $P(0)$  value for  $\text{CCl}_4$  systems at 293 K of  $5.02 \times 10^{17} (\text{N m}^{-2})^2$ . Thus,  $\text{CCl}_4$  may be described as a "high-torque solvent" in comparison with decalin.

The increased hindrance to rotation of  $\text{CCl}_4$  is not related to the difference of viscosity because decalin is the more viscous solvent ( $\eta_{\text{dec}} = 2.1 \text{ cP}$ ,  $\eta_{\text{CCl}_4} = 0.7 \text{ cP}$ ). However, the density of  $\text{CCl}_4$  is greater than for decalin ( $\rho_{\text{dec}} = 0.88 \text{ gm cm}^{-3}$ ;  $\rho_{\text{CCl}_4} = 1.595 \text{ gm cm}^{-3}$ ), so there is a closer-packed distribution of mass about the solute molecule. Alternatively, the difference may be due to the greater atomic polarizability of the chlorine environment compared with the hydrogen medium imposed by decalin. The size and mass distribution of the solvent molecule must play only a minor role otherwise the spherical  $\text{CCl}_4$  symmetry would allow the molecule to rotate more easily in the fluid and allow solute molecules to do likewise.

In diphenylmethane solvent, the dipolar solute molecule is probably trapped within cages of intermeshed phenyl rings. As a consequence, the far-i.r. peak librational frequency is higher than in decalin or  $\text{CCl}_4$  solvents (Fig. 3). For  $\text{CH}_2\text{Cl}_2$ ,  $\bar{\nu}_{\max}$  is midway between that of the  $\text{CCl}_4$  system and of the pure liquid while for chloroform and nitrobenzene negative solvent shifts are observed, i.e.  $\bar{\nu}_{\max}$  is greater

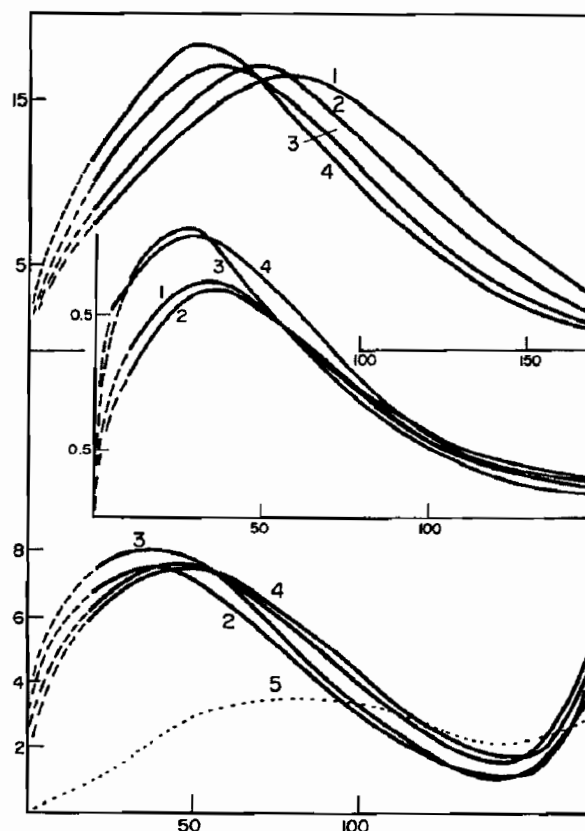


Fig. 3. Absorption spectra for  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_5\text{NO}_2$  in several environments (293 K). (a) Dichloromethane: (1) pure liquid (1/10th scale); (2) 10% v/v in diphenylmethane; (3) 10% v/v in  $\text{CCl}_4$ ; (4) 10% v/v in decalin. (b) Chloroform: (1) pure liquid (1/10th scale); (2) 10% v/v in diphenylmethane; (3) 10% v/v in *n*-pentane; (4) 10% v/v in decalin. (c) Nitrobenzene: (1) pure liquid (1/10th scale); (2) 10% v/v in decalin; (3) 10% v/v in  $\text{CCl}_4$ ; (4) 10% v/v in diphenylmethane; (5) diphenylmethane (1/2 scale). Ordinates:  $\alpha(\bar{\nu})$  (neper  $\text{cm}^{-1}$ ); abscissa  $\bar{\nu}$  ( $\text{cm}^{-1}$ ).

Table 1. Solvent shifts for decalin and CCl<sub>4</sub> solvents at 293 K

Solute	Decalin				CCl <sub>4</sub>		
	$\bar{\nu}_{\max}(L)$ (cm <sup>-1</sup> )	$\bar{\nu}_{\max}(\infty)$ (cm <sup>-1</sup> )	$\Delta\bar{\nu}_{\max}$ (cm <sup>-1</sup> )	$\frac{\Delta\bar{\nu}_{\max}}{\bar{\nu}_{\max}(L)}$ (%)	$\bar{\nu}_{\max}(\infty)$ (cm <sup>-1</sup> )	$\Delta\bar{\nu}_{\max}$ (cm <sup>-1</sup> )	$\frac{\Delta\bar{\nu}_{\max}}{\bar{\nu}_{\max}(L)}$ (%)
Pyridine	57	44	13	23	61 (complex)		
Fluorobenzene	43	39	4	9.3	40	3	7
Bromobenzene	30	23	7	23	24.5	5.5	18
Pentafluorobenzene	35	30	5	14			
Nitrobenzene	42	36.5	5.5	13	37.5	4.5	10.7
Benzonitrile	55	44	11	20	54	1	1.8
Furan	52.5	51	1.5	3	53	-0.5	-1
Tetrahydrofuran	63	52	11	17			
<i>t</i> -Butylchloride	26	24	2	7.7			
Chloroform	34	29.5	4.5	13	39 (complex)		
CH <sub>2</sub> Cl <sub>2</sub>	79	50	29	36.7	52.5	26.5	33
CH <sub>2</sub> Br <sub>2</sub>	75	52.5	22.5	30	55	20	26.6

in the diphenylmethane solvent than in the pure liquid. These frequency increases compared with the decalin systems are between 20% and 40%, which indicates that diphenylmethane is a "high-torque" solvent with a  $P(0)$  about 44–70% greater than for decalin at 298 K. This result is worth some further discussion as to the relative effects of electrostatics (multipole–multipole interactions) and hard van der Waals interactions in determining the position of  $\bar{\nu}_{\max}$ . In the weakly dipolar diphenylmethane, the latter result in a greater mean square torque than the strong dipole–dipole interactions of the pure chloroform and nitrobenzene solutes. In fact, it seems that in the chloroform/diphenylmethane system the harsh repulsive forces and van der Waals dispersions result in a greater rotational hindrance than the weak hydrogen-bonding of pure liquid chloroform.

In contrast, a single measurements made on a chloroform pentane system indicates that this solvent may be found to have a  $P(0)$  value lower than that for decalin.

The electrodynamic influence of the solvent may not be negligible, however. Thus, CCl<sub>4</sub>, although non-dipolar, does have a large absorption cross-section in the far i.r. compared with decalin, while the intensity of diphenylmethane is even larger (with a small dipole moment of 0.6 D). The maximum absorptions for the pure liquids are 0.5, 1.8 and 5.5 neper cm<sup>-1</sup> for decalin, CCl<sub>4</sub> and CH<sub>2</sub>Ph<sub>2</sub>, respectively. It seems, therefore, that solvent shifts occur when cross-correlations are reduced by dilution. If the solvent is dipolar, dilution is less effective and the resultant behaviour is more similar to that of the pure liquid solute than for a non-dipolar solvent. If the solvent absorption is appreciable compared with that of the solute, then strictly one should not attempt to extract the solute contribution by subtraction of an appropriate proportion

(90%) of the pure solvent spectrum. Such subtraction is necessary, however, as the theory is at present limited to systems consisting of one type of polar species in an environment whose detailed nature is not required [except that it exerts a Gaussian distribution of torques on the species in question, whose correlation is described by a memory equation containing an exponential memory  $K_1(t)$ ]. Thus, the band-shapes given for the chloroform–CH<sub>2</sub>(Ph)<sub>2</sub> and nitrobenzene–CH<sub>2</sub>(Ph)<sub>2</sub> systems (Fig. 3) represent the behaviour of these solutes under the assumption that the solutes do not affect the behaviour of the solvent. The total band-shapes in such cases may be re-obtained by adding 90% of the solvent absorption. To determine details of the torques for any particular system the solvent corrected band-shapes may be Fourier-transformed and analysed in a manner described in the literature [19]. For CH<sub>2</sub>Cl<sub>2</sub> systems (Fig. 3), the  $K_0$  (mean square torque) parameter of this analysis increases along the series decalin–CCl<sub>4</sub>–CH<sub>2</sub>Ph<sub>2</sub>–pure liquid. As the band-shapes are similar except for the frequency shifts, this is also the order of increasing Debye relaxation times. Experimentally, the loss peaks which fall between 70 GHz and 10 cm<sup>-1</sup> (300 GHz) cannot be directly observed with our present apparatus but it appears [19] that relaxation in the pure liquid is slower than for decalin solution where the loss peak is at about 180 GHz (100 GHz for pure liquid).

According to the Debye theory, the macroscopic relaxation time  $\tau_D$  is related to the inverse loss peak frequency  $\tau_{\text{exp}}$  by  $\tau_D = (\epsilon_\infty + 2)/(\epsilon_0 + 2)\tau_{\text{exp}}$  so although  $\tau_D = \tau_{\text{exp}}$  for the dilute solutions, the slower macroscopic relaxation in pure CH<sub>2</sub>Cl<sub>2</sub> ( $\epsilon_0 = 9.0$ ,  $\epsilon_\infty = 2.2$ ) in fact corresponds to a  $\tau_D$  of 0.6 ps which is smaller than that found for decalin solution (0.9 ps) in qualitative agreement with the viscosities. However, the peak shift in the far i.r.

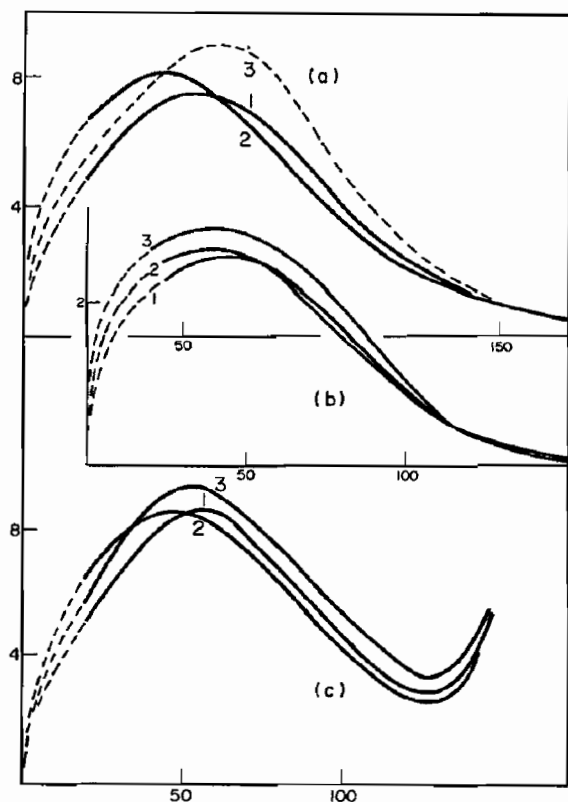


Fig. 4. Absorption spectra for pyridine, fluorobenzene and benzonitrile in pure liquid and in decalin and  $\text{CCl}_4$  solution states (293 K). (a) *Pyridine*: (1) pure liquid (one tenth); (2) 10% v/v in decalin; (3) 10% v/v in carbon tetrachloride, illustrating a complex formation. (b) *Fluorobenzene*: (1) pure liquid (one tenth); (2) 10% v/v in decalin; (3) 10% v/v in  $\text{CCl}_4$ . (c) *Benzonitrile*: (1) pure liquid (one tenth); (2) 5% v/v in decalin ( $\times 2$ ); (3) 10% v/v in  $\text{CCl}_4$ . Ordinates:  $\alpha(\bar{\nu})$  (neper  $\text{cm}^{-1}$ ); abscissa;  $\bar{\nu}(\text{cm}^{-1})$ .

implies [from the product  $K_0/(\gamma K_1)$  of best-fit parameters] that the microscopic rotation rate is faster for the more viscous decalin solution. Using the Cole internal-field factor  $3\epsilon_0/2\epsilon_0 + \epsilon_\infty$ , one obtains values of  $\tau_D = 1.2$  ps for the pure  $\text{CH}_2\text{Cl}_2$  and 0.9 ps for the viscous decalin solution, which are in better agreement with the far-i.r. predictions.

For the chloroform and nitrobenzene systems, the best-fit parameters indicate that the mean square torque decreases on replacing each pure liquid with decalin (or  $\text{CCl}_4$ ) but increases on replacement with diphenylmethane. This indicates that the "increasing polarity = increasing mean square torque" hypothesis is not totally correct because  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_5\text{NO}_2$  are both more dipolar than diphenylmethane. Therefore, in considering solvent shifts in the far i.r., it appears that both a polarity effect and a solvent rotational hindrance effect are contributory factors. The latter effect might depend on the ratio of sizes of solute and solvent molecules. Therefore, a system of small molecules, e.g.  $\text{CH}_2\text{Cl}_2$ , may rotate easily in decalin because the momentary cages of solvent molecules may have dimensions which remain large compared with the  $\text{CH}_2\text{Cl}_2$  molecule. To understand more

fully far i.r. solvent shifts, a variety of comparative studies would have to be made, with an accuracy sufficient to determine band centres to within  $1 \text{ cm}^{-1}$  as well as to obtain significant band-shapes. For a given solute in dilute solution of a variety of solvents, the percentage increases in  $\bar{\nu}_{\text{max}}$  should be compared with solute and solvent sizes. In addition, a series of increasingly polar solvents should be investigated.

In conclusion, viscosity is not an important factor in determining  $\bar{\nu}_{\text{max}}$ , although the relative shapes and sizes of solute and solvent might be. To some extent, the polarity of the medium may give rise to greater mean square torques by dielectric friction, especially for pure polar liquids. However, this is not always significant, as is illustrated by the following consideration. In benzene solution,  $\text{CH}_2\text{Cl}_2$  has a  $\bar{\nu}_{\text{max}}$  of  $58 \text{ cm}^{-1}$ . In toluene, this peak position is at  $60 \text{ cm}^{-1}$ , which is low compared with the diphenylmethane solution value of  $69 \text{ cm}^{-1}$  despite a similar polarity. The polarity of the toluene medium can be smoothly increased without change of  $\text{CH}_2\text{Cl}_2$  concentration by considering ternary systems of  $\text{CH}_2\text{Cl}_2$  in toluene/pyridine. For a solvent of 10/90 pyridine/toluene, the  $\bar{\nu}_{\text{max}}$  of the  $\text{CH}_2\text{Cl}_2$  contribution is hardly shifted despite a doubling of the solvent absorption in the far-i.r. region and an increase in  $(\epsilon_0 - \epsilon_\infty)$  of about five.

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