Far Infrared Solution Spectra

Volume of Rotation and Effective Torque

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Far infrared absorption bands have been measured for about thirty-five dipolar solutes in liquid and glassy decalin. The results are interpreted in terms of a general relation between the volume of molecular rotation and mean square torque. The band frequency maxima ($\bar{v}_{max}$) are dependent at constant temperature only on the root mean square torque divided by the reduced moment of inertia (I_r) so that the data are conveniently classified in terms of the "torque product" $T_q = 10^{36} I_r \bar{v}_{max}^2$. Denoting by V the volume swept out on molecular rotation the rule $T_q \propto V^2$ is obeyed generally both in the liquid and in the glass with a proportionality constant $P = 1.38 \times 10^{19}$ N m^{-2}, the mean force per unit normal area of the rotating molecule. Although $P(0)$ is independent of the temperature it is solvent dependent. For molecules such as C_6H_5Cl, C_6H_5Br, $C_6H_5NO_2$, α-chloro- and α-bromo-naphthalene there are indications that the librational relaxation is strongly coupled to the translation of the centres of mass.

The theory of the dielectric and far infrared absorption and dispersion observed in dipolar fluids is still in a primitive condition but with the rapid developments of generalised statistical mechanics and mode–mode coupling mechanics it is expected that a variety of new concepts will soon be available.[1] The process of evolution will inevitably be associated, at least initially, with a formidable mathematical abstraction and complexity which will hinder the emergence of a unified, tenable hypothesis useful to all those seeking a clear-cut theory of the liquid state of matter. The description of the Rytov splitting[2] of the depolarised Rayleigh band, for example, still involves a degree of intuition in deciding what modes are likely to be most effective in association with the multi-particle second-rank orientational density, which determines the basic bandshape. Since the zero-THz absorption bandshape of dipolar liquids is determined by the first-rank orientation density, such methods of mode–mode coupling, in terms merely of a single particle orientational autocorrelation function, will gradually become obsolete since the first-rank orientational density will couple to the velocity field, *i.e.*, the theoretical description will be rototranslational involving rototranslational memory tensors, the so-called time-dependent " friction coefficients ".

The purpose of this paper is to achieve a complementary viewpoint to such developments by making a simple, empirical comparison between zero-THz absorptions of molecules of widely different geometries in dilute decalin solution. Such a study is basic to any development of ideas as to the relative importance of molecular rotation and/or translation in determining the observed absorption bandshape. The mode–mode theory will have to be developed eventually to the point where the trends observed empirically may be explained in terms of molecular rototranslation and individual molecular symmetry types. (For some of the highest symmetries it is known already that certain aspects of the rotation/translation mixing are unobservable spectroscopically,[3] but of course may be simulated with a computer.[4])

Dilute solutions in an " inert " solvent were chosen for study in accord with the usual hypothesis that such dilution of polar species reduces the ever-present electrodynamic (dipole–dipole) effects and allows a single-molecular treatment.   *Cis*-decalin is particularly suitable as it has a small absorption cross-section in the far infrared and also because its ability to supercool to form a glassy matrix allows us to compare in this paper liquid solution results with similar systems at low temperatures.[5]

In the glass,[5] the relative importance of translation and rotation will be drastically different from that in the room temperature solution, but must be amenable to one and the same overall theoretical description.

The empirical correlation developed in this paper centres on a comparison of the far infrared peak frequencies ($\bar{\nu}_{max}$) which are here related to molecular volumes of rotation *via* a single particle orientational Mori approximant completely decoupled from translation, as is currently the practice.[6]   Within this viewpoint we derive a general relation which is predictive in the sense that $\bar{\nu}_{max}$ may be estimated knowing only the molecular geometry.   The accuracy of this empirical statement is then a measure of (among other things) the sensitivity of the zero-THz spectrum to rototranslation, as opposed to the merely rotational aspects embodied in the empirical derivation.

We stress the importance of the far infrared region in what follows because *any* type of model of the complicated dynamics and interactions can be accepted only if tested over an adequate range of frequency.

Absorption and dispersion measurements over the whole range of frequencies up to the far infrared (THz) are particularly useful in this respect since information is available in terms of $\alpha(\bar{\nu})$, the power absorption coefficient, $n(\bar{\nu})$, the refractive index, and $\varepsilon^*(\bar{\nu})$, the complex permittivity over up to ten decades of frequency.   The short time process giving rise to THz absorption is observable in a degree of detail unobtainable with any other associated spectral method, including depolarised light scattering, for which paradoxically the mode–mode theory is much more fully developed.   Classical dielectric spectroscopy [of $\varepsilon^*(\bar{\nu})$ alone] is much less effective in distinguishing between subtle modelling techniques since inertial and memory effects are almost unobservable.[7]   In effect, therefore, almost every model of $\varepsilon^*(\bar{\nu})$ tends to produce an identical Debye-type complex permittivity, except, of course, in the f.i.r.

In deriving our empirical correlation we use original data from about thirty-five solutes in decalin at 293 ± 2 K.   These are grouped into sets according to their structure, *i.e.*, aromatic or flexible, six-or five-membered heterocyclics, spherical and " butterfly " molecules of high and low molecular weights, flexible halogenoalkanes *etc.*

EXPERIMENTAL

The spectra were obtained using the standard technique of submillimetre interferometry fully described elsewhere.[8]   Solutions were made up by volume and carefully dried.   For solutions made up in this way the extent of concentrations will be different for different solutes (and for the same solute in different solvents).   To measure the dependence of rotation/translation coupling on concentration, number density comparison should be made. Results were supplemented where necessary with spot frequency klystron measurements in the GHz region.   Spectra recorded under slightly different conditions of optical or electronic alignment often differ quite significantly in shape.   In order to estimate maximum uncertainty bounds the results for this paper have been collected over a period of twelve months, mostly with triplicate repetition.   The extremes of bandshape observed are plotted in fig. 1-5. The dual curves act as bounds for the systematic errors that arise due to imperfect collimation, ageing of the beam divider or source, humidity changes in the electronics, absorption of impurities by windows *etc.*   The random errors (electronic noise) are minimised by averaging two or more interferograms as also are multiple reflection effects, so that the actual computed

output is as smooth as the curves drawn in these figures.   All curves are for 10 % v/v sol-utions except for thiophene (20 %) and benzonitrile (5 %) and all are corrected for solvent absorption.   Peak positions can generally be quoted to ± 2 cm^{-1} except for those spectra where the peak occurs below 30 cm^{-1}.

RESULTS

SOLVENT ABSORPTION

The decalin (B.D.H.) used as solvent was an isomeric mixture of *cis* and *trans* forms, of density $\rho = 0.886$ gm cm^{-3}.   From literature values of *cis* and *trans* decalin densities, a 70/30 *cis/trans* ratio is estimated.   The far infrared absorption of this solvent at 293 K (fig. 1) exhibits a broad shoulder of induced absorption around 70 cm^{-1}, headed by a proper mode at 150 cm^{-1}.   The spectrum is more intense than the literature curve [9] for pure *trans*-decalin, possibly due to a greater flexibility of *cis* isomer and hence a greater polarisability and induced absorption.

SOLUTE ABSORPTIONS

The results are summarised in tables 1 and 2 and grouped in accordance with a classification scheme to be developed below.   The peak positions listed in these
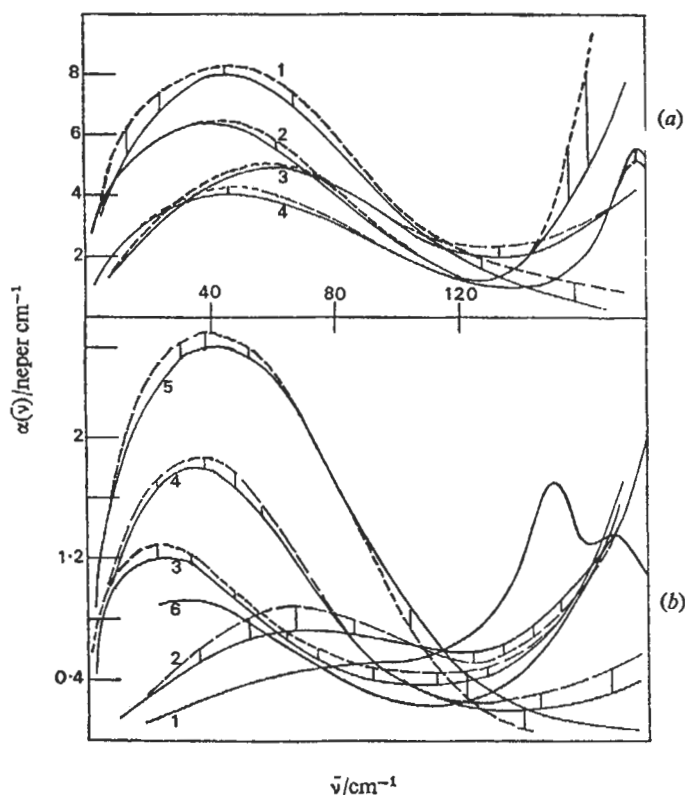

FIG. 1.—Far infrared power absorption coefficient at 293 K for 10 % v/v solutions in decalin, corrected for solvent absorption.   The bars measure the greatest observed difference between separate averages of successive runs (see text).   (*a*) (1) Pyridine ; (2) nitrobenzene ; (3) 2-methylpyridine ; (4) benzonitrile (5 % v/v) ;   (*b*) (1) decalin ; (2) toluene ; (3) bromobenzene ; (4) chlorobenzene ; (5) fluorobenzene ; (6) pentafluorobenzene.

tables are dependent at constant temperature only on the root of the mean square torque divided by the reduced inertia, so the experimental parameter to be used [5] in this classification is $I_r \bar{v}_{max}^2$ or, more conveniently, the " torque product " $T_q = 10^{38} I_r \bar{v}_{max}^2$.

Such attempts at classification are not new; Hindle *et al.*[10] studied twenty-one pure liquids classifiable as either (geometrically) spherical (*e.g.*, $CHCl_3$) or planar (*e.g.*, $C_6H_5NO_2$) and found that the product $AI\mu^{-2}$ was approximately a constant for molecules of the same class. (A is the integrated absorption per molecule, I the average

TABLE 1.—CLASSIFICATION SCHEME (BASED ON T_q VALUES) FOR CYCLIC MOLECULES IN DECALIN AT 293 K

group	specimen	μ_a/D	$I_a/10^{-38}$ g cm^2	$I_b/10^{-38}$ g cm^2	$I_c/10^{-38}$ g cm^2	$I_r/10^{-38}$ g cm^2	$\bar{v}_{max}$ /cm^{-1}	T_q/g
A_1	pyridine	2.19	1.4	1.45	2.86	0.96	44 ± 2	1858 ± 9 %
A_2	fluorobenzene	1.4	1.47	3.25	4.72	1.92	39 ± 2	2923 ± 10 %
	chlorobenzene	1.58	1.47	5.30	6.77	2.97	33 ± 2	3433 ± 12 %
	bromobenzene	1.56	1.47	8.20	9.67	4.43	24 ± 3	2551 ± 25 %
	pentafluorobenzene	—	8.32	6.29	14.60	4.40	30 ± 4	3960 ± 26 %
A_3	toluene	0.36	1.52	3.25	4.77	1.92	62 ± 5	7380 ± 16 %
	oxylene	0.64	2.56	3.67	6.20	2.30	65 ± 5	9717 ± 16 %
	nitrobenzene	3.97	2.08	6.90	9.00	3.90	39 ± 2	5935 ± 9 %
	benzonitrile	4.03	1.47	5.50	6.97	3.07	47 ± 2	6781 ± 8 %
	2-methyl- pyridine	$\mu_a=0.74$ $\mu_b=1.90$	1.52	3.25	4.77	1.22	59 ± 2	4304 ± 7 %
B	1-chloro- naphthalene	$\mu_a=1.0$ $\mu_b=1.21$	5.5	8.5	14	4.43	46 ± 2	9374 ± 8 %
	1-bromo- naphthalene	$\mu_a=1.48$ $\mu_b=0.54$	5.97	13.2	19.2	5.17	37 ± 3	7077 ± 16 %
C_1	furan	0.67	0.88	0.91	1.79	0.6	51 ± 2	1560 ± 8 %
	thiophene	0.53	1.04	1.54	2.58	0.96	46 ± 3	2031 ± 13 %
	thiazole	$\mu_a=\mu_b$ $=1.26$	1.04	1.54	2.58	0.83	45 ± 3	1686 ± 13 %
D_1	piperidine	0.8	1.87	1.91	3.3	1.04	55	3130
	tetrahydropyran	1.53	1.77	1.82	3.18	1.15	44 ± 3	2226 ± 14 %
	thioxane	1.5	1.68	1.9	3.2	1.15	57 ± 5	3736 ± 20 %
D_2	2,3-dihydropyran	—	1.5	1.69	2.9	1.04	50 ± 2	2600 ± 8 %
E_1	tetrahydrofuran	1.65	1.05	1.31	2.23	0.825	45 ± 5	1670
	pyrolidine	1.58	1.33	1.36	2.38	0.85	52 ± 5	2298
E_2	2-methyl- tetrahydrofuran					1.5	46 ± 5	3174

inertia and μ the dipole moment.) This apparently novel result is a restatement of the Gordon sum rule, which is not sensitive to the position ($\bar{v}_{max}$) of the far infrared band, but the molecular shape dependency of the proportionality constant particularly illustrates that use of I and not I_r in this second term coefficient of the time expansion of $C_\mu(t)$ is incorrect. The use of $I_r \bar{v}_{max}^2$ (or T_q) as an empirical parameter (shown presently to be proportional to the $t = 0$ value of $\langle \Gamma(t).\Gamma(0) \rangle$, *i.e.*, the mean square torque and hence to the volume swept out on rotation) has a far greater predictive power and applicability, the extent of which is currently being investigated.

GROUP A1 AND A2. BENZENE ANALOGUES (A1) AND HALOGENO-DERIVATIVES (A2)

Benzene is included in this group as the parent structure. It is non-dipolar but strongly quadrupolar, with an intense far infrared induced band in its pure liquid

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TABLE 2.—CLASSIFICATION SCHEME FOR ACYCLIC SOLUTES IN DECALIN AT 293 K

group	solute or liquid	μ_a /D	μ_b /D	μ_c /D	$I_a/10^{-38}$ g cm²	$I_b/10^{-38}$ g cm²	$I_c/10^{-38}$ g cm²	$I_r/10^{-38}$ g cm²	$\bar{\nu}_{max}$ /cm⁻¹	T_q/gm
F₁	2-chloro-2-nitro-propane	1.56	3.35	—	3.06	4.41	4.97	1.96	33±2	2134
	t-butyl-chloride	2.15	—	—	1.91	2.86	2.86	1.43	23±2	756
	chloroform	—	—	1.1	2.52	2.52	5.0	1.26	31±2	1210
F₂	CH_2Cl_2				0.26	2.57	2.80	0.24	52±2	649
	CH_2Br_2				0.32	6.79	6.79	0.30	54±2	875
	SCl_2				0.26	3.82	4.39	0.24	50	600
	SO_2				0.13	0.78	0.91	0.11	50	275
F₃	acetone[15]				0.86	0.74	1.6	0.51	53	1342
	acetonitrile	3.39			—	0.875	0.875	0.44	72	2280
	$SOCl_2$[14]				3.53	1.37	4.1	1.07	34	1237
	propyne	2.07				0.98	0.98	0.49	72	2540
F₄	HCl[16]							0.0135	122	200
	H₂O[17]				0.0123	0.0183	0.03	0.011	150	247
	NH₃[18]				0.028	0.028	0.044	0.014	138	266
	HBr[19]							0.024	108	280
G	1-bromo-pentane	0.857	0.515	(e)	0.32	13.4	13.7	1.06	58	3633
		0.50	0.866	(f)	1.05	5.91	6.9	1.11		
e ≡ elongated ;	1-bromo-2-methylbutane	0.1	0.42	(e)	0.2	8.1	8.1	0.9	60	3330
f ≡ folded		0.42	0.91	(f)	1.0	4.46	5.3	0.95		
	diphenylamine	0.31	0	0.95	18.63	3.57	13.4	2.98	60	10728

state.[9] A similar degree of induced absorption may well be expected for the pure halogenobenzenes, but this is minimised by dilution. The value of I_r is computed using, where possible, the principal moments of inertia I_a, I_b and I_c about axes which intersect at the centre of mass, obtained from gas phase microwave studies, or otherwise from structural data, in the general formulae

$$\mu^2 I_r^{-1} = (\mu_b^2 + \mu_c^2)I_a^{-1} + (\mu_c^2 + \mu_a^2)I_b^{-1} + (\mu_a^2 + \mu_b^2)I_c^{-1}$$

where μ_i are the dipole vector components in the molecular frame. The factor T_q then generally lies between 1800 g for pyridine, the only A1 class molecule studied, and 4000 g for pentafluorobenzene of A2 class. Similar T_q values to pyridine are expected for pyrimidine, pyridazine and thiopyran, also of A1 class, which will be studied in future. Confirmation of such values will increase the indication, already apparent in this group, of increasing torque with increasing substituent size. Note also the low frequency and intensity of the bromobenzene spectrum compared with the spectra of the lighter halogenobenzenes shown in fig. 1(a). The low value of T_q (less than that for chlorobenzene) may be due in part to the larger errors of measurement in this system but may also be interpreted as a consequence of rotation–translation coupling to be discussed shortly. The low intensity is in accord with Hindle's rule above (both PhCl and PhBr having similar μ values).

GROUP A3. SIX-MEMBERED AROMATIC RINGS WITH BULKY SUBSTITUENTS

The —CH₃ group substituent is interesting in comparison with the —Br substituent as, although it presents a rotating radius similar to that of the bromine atom (≈ 1.2 Å), its mass is over five times less. The CH₃ and other substituents in this group sweep out a large volume of rotation and will experience a high torque.

The other molecules in this group have been chosen to overcome the lack of far infrared intensity associated with toluene (fig. 1). The factor T_q lies between 6400 and 7400 g with the exception of 2-methylpyridine (4400 g) where relaxation can occur by rotation around the long axis. The apparent mean square torques (T_q values) are thus significantly higher than those in groups A1 and A2. We pursue this correlation between the value of T_q found for a given solute molecule and its speculated volume of rotation by extending this study to both larger and smaller aromatic rings.

GROUP B. THE HALOGENONAPHTHALENES

The values of T_q for these double rings are almost three times the value for the corresponding halogenobenzenes, indicating that they are rotationally hindered to a correspondingly greater extent. We observe again [fig. 2(a)] an apparent reversal of order of the T_q values between chloro and bromo compounds ($\doteqdot 10\,000$ g for $C_{10}H_7Cl$ and 7000 g for $C_{10}H_7Br$) but the correct order of intensities, corresponding to the known dipole strength. In part, the variations are due to different orientations of the dipole vector with respect to the principal inertial axes. [For both $C_{10}H_7Cl$ and $C_{10}H_7Br$ the dipole was taken as being along the C—X bond, presumed to be parallel to C_9—C_{10} and the axis of least inertia (a) was then computed to be at 45 and 18° to the dipole vector, respectively.] However, again we may suppose that mode–mode coupling is not negligible and that a greater translational contribution occurs for
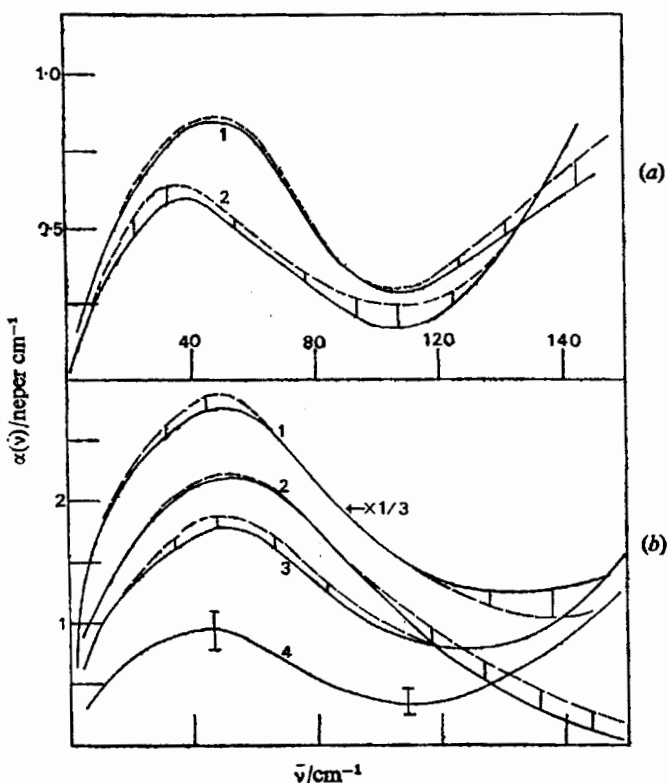

FIG. 2.—As for fig. 1; (a) (1) 1-chloronaphthalene; (2) 1-bromonaphthalene at 293 K; (b) (1) thiazole: (2) furan; (3) thiophene (20 %); (4) thiophene, (10 %.)

$C_{10}H_7Br$, so giving a lower T_q value relative to that of $C_{10}H_7Cl$. It will be interesting in future to compare data for 2-halogenonaphthalenes and also the fluoronaphthalenes.

GROUP C1. FIVE-MEMBERED HETEROCYCLICS

Three solutes, furan, thiophene and thiazole, were studied [fig. 2(b)] to typify this group. Within the uncertainties quoted, variation of T_q within this class is occurring as the ring size becomes larger, T_q values ranging from 1500 to 2000 g. These are smaller than or comparable with the six-membered pyridine T_q value. The lower T_q value of thiazole as compared with thiophene is presumably due to the possibility of relaxation of the former about the a axis which, not involving motion of the S atom, is less hindered. The structure of thiazole is presumed to be identical to that of thiophene (i.e., undistorted by replacement of CH with N as found for pyridine), as accurate data were unavailable. We intend to supplement data in this group C1 with those from pyrrole and oxazole in decalin systems and also to characterise group C2 (derivatives) by studying 2-chlorofuran or N-methylpyrrole, the former to compare with the halogenobenzenes and the latter with toluene (without the problem of low intensity).

GROUP D1 AND D2. NON-AROMATIC SIX-MEMBERED RINGS AND DERIVATIVES

These exist in structural conformations for which several microwave and n.m.r. studies are conveniently available. Moments of inertia were estimated from these data. The T_q values range between 1600 and 2800 g [fig. 3(a)] being generally lower than expected from ring-size comparison with the six-membered aromatic compounds (2000-35000) g. A possible explanation is that the former are almost spherical although inertiawise they are almost oblate symmetric tops. Cyclohexane, for instance, forms a low density rotator phase solid in which X-ray study [11] shows a f.c.c. structure typical of many other spherical rotator phase molecules. Within this group there is a wide variation in T_q for seemingly identically shaped molecules. Although I_r and $\bar{v}_{max}$ may be uncertain to the extent of ± 10 %, the following correlations can be pointed out. The lowest value obtained (2000 g) for 1,3-dioxane reflects a slight contraction of the ring due to shorter C—O bonds (1.41 Å) compared with the C—C bonds (1.53 Å). However, across the series tetrahydropyran and piperidine the T_q values increase with the heteronuclear bond length. In thioxane the long C—S bond requires a larger volume in which to rotate, hence a high value of 3700 g is obtained.

An intermediate case between the dynamics of aromatic and saturated rings appears for 2,3-dihydropyran, a semi-saturated ring. The factor T_q is 2667 g, a value higher than that of tetrahydropyran but smaller than for the halogenobenzenes. This is presumably due to its shape being intermediate between disc and sphere.

GROUP E1. FIVE-MEMBERED SATURATED RINGS AND THEIR DERIVATIVES (E2)

In these cases the far infrared absorption due to pseudo-rotation is well known.[12] The intensity of this absorption in tetrahydrofuran was estimated by scaling the gas phase absorptions up to the liquid density of 8.3×10^{20} molecule cm^{-3} (10 % v/v solution). It is assumed therefore that the intramolecular pseudorotatory states remain unaffected for molecules in decalin solution although the whole molecule
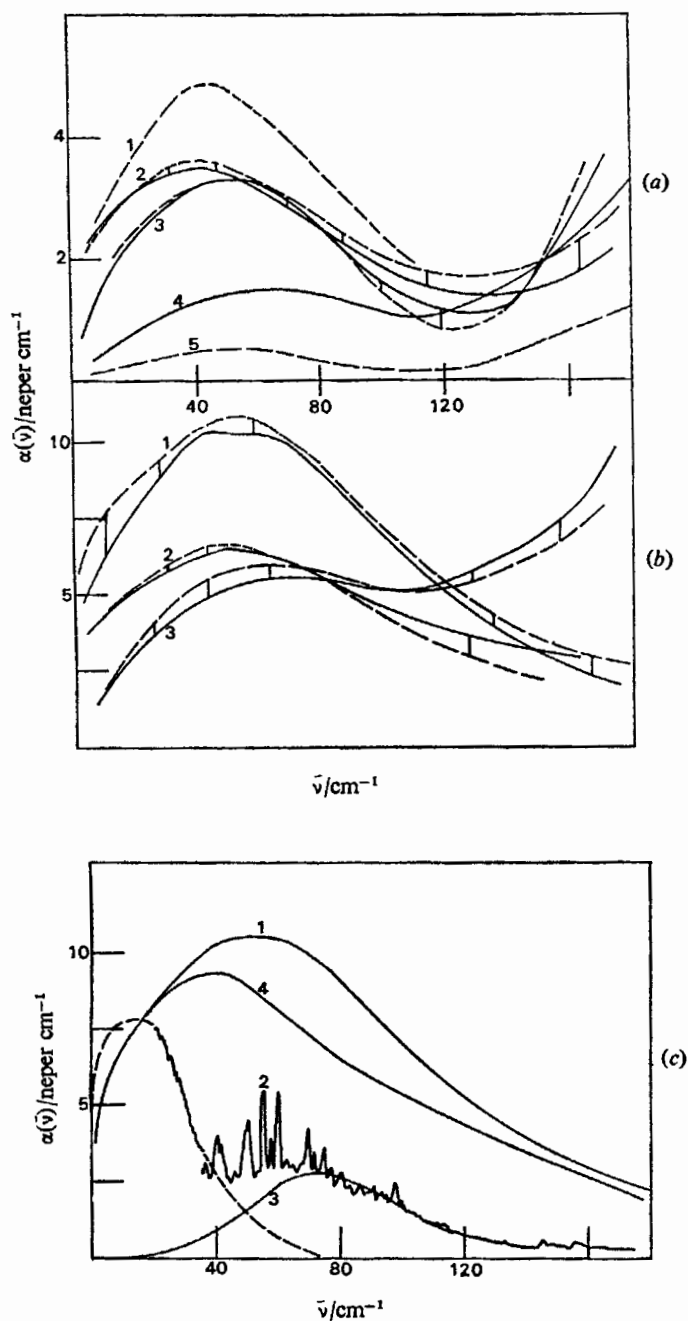
FIG. 3.—(a) (1) 1,3-dioxane; (2) tetrahydropyran; (3) 2,3-dihydropyran; (4) thioxane; (5) piperidine; (b) (1) tetrahydrofuran; (2) 2-methyl-tetrahydrofuran; (3) pyrrolidine; (c) (1) measured spectrum of liquid tetrahydrofuran; (2) measured vapour spectrum;[12, 18] (3) pseudo rotator spectrum; (4) corrected liquid spectrum (see text).

rotational peaks will evolve into a libration band in the usual way. The far infrared spectrum of tetrahydrofuran (10 % v/v) in decalin is shown in fig. 3(b) and (c). Also shown is the literature gas spectrum [12] with intensity scaled to match the solution as above. The gas spectrum below ≈ 30 cm^{-1} is mainly the gas phase pure rotational envelope. Subtraction of this leaves a broad pseudo-rotation complex peaking at 70 cm^{-1}. As is common with most low frequency vibrations, this band will probably be less intense and very much broadened in the liquid state, but even so, the apparent librational peak position of 50 cm^{-1} might be lower by 10 cm^{-1} or more because of the pseudorotatory vibration. The relative intensity of proper mode and librational mode is also reflected in the ratio of the instantaneous dipole over the mean, ≈ 20 %. By reference to molecules in groups A to C one might expect a value for T_q in the range 1560-2000 g. The value obtained when vibrational effects are neglected is 2230 g ($\bar{v}_{max} = 52$ cm^{-1}), whereas subtraction of the scaled pseudo-rotation band brings this value down to 1255 g ($\bar{v}_{max} = 39$ cm^{-1}). Torque estimates for pyrrolidine and methyl tetrahydrofuran are subject to the same uncertainties although the latter's value does again reflect the hindering effect of the CH$_3$ substituent.

SUMMARY OF RESULTS FOR THE CYCLIC MOLECULES

The molecules studied have been conveniently classified into five groups A-E and then into subgroups according to substituent. In the unsubstituted heterocyclic rings a general trend is seen as T_q increases with size and shape. The five-membered aromatics (table 1) have the smallest values (1500-2000 g). The six-membered aromatics and naphthalene derivatives are progressively hindered rotationally. For all these cyclic molecules the variation of group size or mass is still small compared with the mass of the ring; thus the halogenobenzenes all have T_q values around 3000 g. If such substituent comparisons are made for the smaller molecules much larger variations are expected. The majority of the above cyclic compounds have their dipole moments along the axes of smallest moment of inertia, or at least coplanar with the ring. In the smaller molecules, a change of substituent groups can greatly change the dipole direction relative to the axes of greatest and least inertia. This is reflected in greatly differing values of $I_r\bar{v}_{max}^2$ for molecules apparently similar in shape and size.

GROUP F. NON-CYCLIC (RIGID) MOLECULES

The results are summarised in table 2. We consider firstly the subset of molecules t-butyl chloride, 2-chloro-2-nitropropane and chloroform, where spectra are shown in fig. 4(a). The low value of $I_r\bar{v}_{max}^2$ for t-butyl chloride appears to indicate unhindered rotation due to a closely spherical shape without projections or indentations. Chloroform, however, is geometrically more planar than spherical, which results in a greater interaction with the medium. The bulky NO$_2$ group sets up a pronounced rotational hindrance, although only marginally larger than the CH$_3$ group and despite the fact that both t-butyl chloride and 2-chloro-2-nitropropane exhibit cubic rotator phases. Later in this paper a quantitative estimate of the volume displacement for rotation will be made within the context of Mori three-variable theory. In these molecules all three axial rotations contribute to dipole relaxation and it remains uncertain as to what effect the dipole direction has on the torque value. Finally for the nitro compound there is a possibility of rotation–vibration coupling simply because the rotation of the relatively heavy NO$_2$ group results in a variation of the principal inertial axes with time. It may be this high frequency jittering of the molecule which in this case increases the apparent torque exerted by the medium.

A second subset of non-cyclic molecules again chosen for descriptive convenience is made up of some of the smallest non-linear molecules dichloromethane, dibromomethane, sulphur dichloride and sulphur dioxide [fig. 4(b)]. The torque terms are very small, almost half the value found for $CHCl_3$ because the latter requires a larger volume to rotate. We can expect that intermediates such as CF_2Cl_2 will have intermediate values, or if the geometry is made more spherical even lower values of T_q are expected, such as appears to be the case for some mixed halogenated methanes
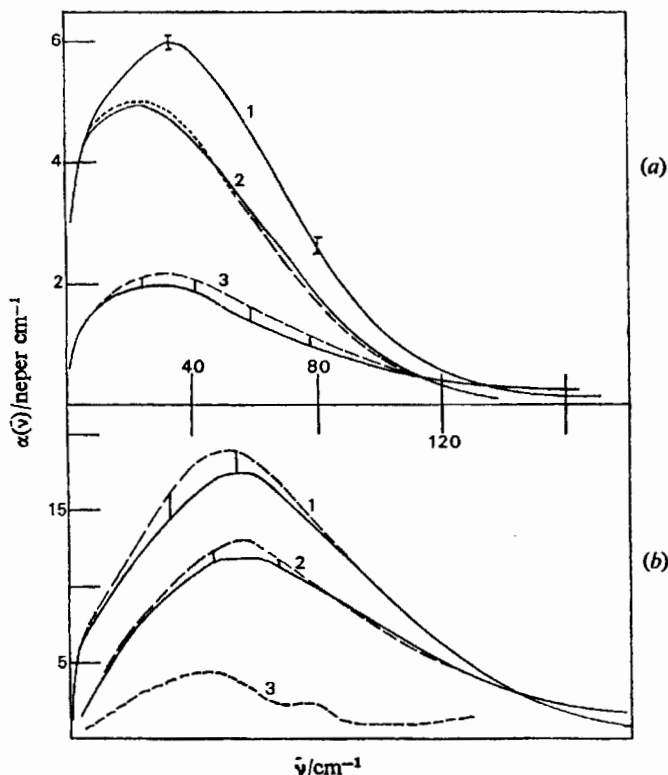

FIG. 4.—(a) (1) 2-chloro-2-nitropropane; (2) t-butyl chloride; (3) chloroform (10 % v/v in decalin). (b) (1) dichloromethane; (2) dibromomethane; (3) sulphur dichloride (10 % v/v in decalin).

such as $CClF_3$, CHF_3 and $CBrF_3$ and for methyl chloroform, studied in the pure liquid state under pressure [13] ($\bar{v}_{max} = 13, 26, 11$ and 22 cm^{-1}, respectively). Conversely, if two halogen atoms were removed to give a monohalogenomethane, the torque product might be expected to increase again as a linear geometry is approached (*i.e.*, the moment of inertia of the dipole axis tends to zero). For example, it is known [14] that the torque product for liquid propyne is 2540 g. This value can be directly compared [see fig. 5(a)] with the results of a study [15] of acetonitrile in CCl_4 ($I_r\bar{v}_{max}^2$) = 2281 g despite the large difference in dipole moment values ($\mu_{propyne} = 2.070$ D, $\mu_{acetonitrile} = 3.39$ D).

Solute molecules such as acetone and thionyl chloride [fig. 5(a)] are almost disc shaped, so that torque products higher than chloroform but lower than acetonitrile are expected and observed (table 2). A final subset of very small solute molecules such as HCl, H_2O, H_2S, NH_3 and HBr provide T_q values in the range below 300 g.

GROUP G. NON-RIGID MOLECULES

Molecules such as the halogenoalkanes with more than two CH_2 segments may possess a considerable degree of conformal variation dependent on structure and temperature. As a preliminary study, we present in fig. 5(b) spectral curves for 10 % solutions of 1-bromopentane and 1-bromo-3-methylbutane which both peak around 60 cm⁻¹. Some structural detail was observed for the latter which may be due to weak low frequency proper modes or otherwise a consequence of the existence
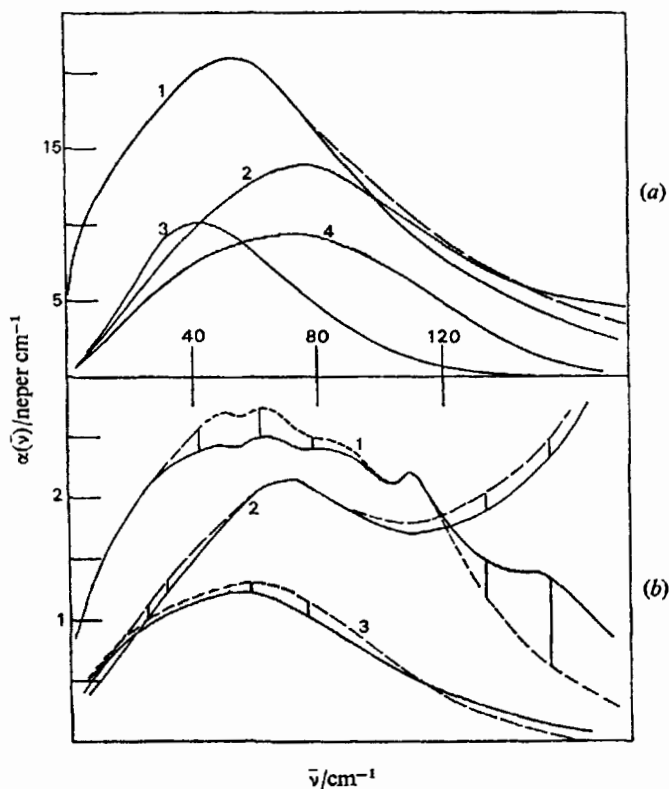

FIG. 5.—(a) (1) Acetone; (2) propyne;[14] (3) SCl_2; (4) acetonitrile.[15] (b) (1) 1-bromo-3-methyl-butane; (2) diphenylamine; (3) 1-bromopentane.

of conformal extremes. To determine I_r, the principal inertial axes were estimated for various low and high energy conformers. I_r for each case did not alter drastically between elongated and folded forms, so averaged T_q values were formed for each compound, both being ≈ 3500 g. Another type of non-rigid solute is the diphenyls of which only the amine has been found suitable for study (diphenyl ether and diphenyl ketone having intense overlapping proper modes). A value of I_r was obtained by averaging over all internal orientations of the phenyl groups which led to a very high value for T_q of 10 700 g, indicating a large degree of rotational hindrance to these " butterfly " molecules.

DISCUSSION

These results significantly increase the far infrared data available for liquid mixtures and are discussed in terms of the torque factor T_q. We demonstrate that $I_r \bar{\nu}_{max}^2$ is related to the mean squared torque acting on the dipolar solute molecule

and hence by a simple argument to the volume swept out on rotation of this molecule. The first relation above is " exact " to the same order of approximation used in the three parameter Mori formalism and providing that the underlying phenomenological description of this formalism, the so-called itinerant oscillator model, is a sufficiently valid description.[6] The further relation to volumes of rotation requires that a molecular surface can be defined in a manner appropriate to this dynamical problem.

The three variable Mori approximant to the orientational autocorrelation function $C_\mu(t) = \langle \mu(0)\cdot\mu(t)\rangle$ is well documented.[20] When this same approximant is applied to the angular velocity correlation function $C_\omega(t) = \langle \omega(0)\cdot\omega(t)\rangle$ for planar libration of the asymmetric top dipole and then model related [21] to C_μ, then one obtains for C_μ an expression formally identical with that obtained by Coffey et al.[22] for the planar itinerant librator.

Using the Mori expansion of the stochastic Liouville equation it may be shown [21] that one variable, $K_0(0)$, is the $t = 0$ value of the torque autocorrelation function, i.e., the mean squared torque $\langle \Gamma(0)^2\rangle$. We have:

$$K_0(0) = \langle \dot{\omega}(0)^2\rangle/\langle \omega(0)^2\rangle$$
$$= \langle \Gamma(0)^2\rangle/\langle \omega(0)^2\rangle I_r^2 \qquad (1)$$
$$= \langle \Gamma(0)^2\rangle/I_r kT.$$

By consideration of planar itinerant oscillation in terms of the stochastic equations of motion we have:

$$\omega_0^2 = K_0(0) = 4\pi^2 c^2 \bar{v}_{max}^2. \qquad (2)$$

The model imposes also the further conditions:

$$\frac{kT\tau_D}{I_1} > \beta_2, \qquad \beta_1 = \frac{kT}{I_1}\tau_D,$$

where τ_D is the Debye relaxation time, β_2 is the disc–cage friction coefficient and β_1 is the cage–environment friction coefficient. Therefore:

$$\langle \Gamma(0)^2\rangle = 2\omega_0^2 I_r kT$$

or

$$I_r \bar{v}_{max}^2 = \langle \Gamma(0)^2\rangle/(8\pi^2 c^2 kT). \qquad (3)$$

A factor of 2 has been included to allow for the fact that the itinerant librator is strictly valid only for two dimensional motion, whereas the Mori expression can and has been given spatial dimensionality by the use of I_r, as opposed to using any real molecular inertia. Numerical investigation [6] of the equivalence of the Mori and i.o, models, when both are applied to real three dimensional problems, tend to confirm both the use of I_r and the factor 2.

Eqn (3) may be useful as it stands, but more incisive use of it may be made[23] by factorising the $\langle \Gamma(0)^2\rangle$ term into a solute dependent part V^2, where V is the volume of rotation of the molecule, and a solute independent term (at least to a first approximation), $P(0)$. Consider an isolated sphere of radius r constrained to rotate with its centre of mass a distance R from a given axis. At an instant t there is a force (P') per unit normal area parallel to the instantaneous velocity v of the sphere. The torque experienced by a surface element of this sphere will be $\delta\Gamma = (\delta S \cdot P') \times d$, where δS is the normal projection of the surface elemental area and d its distance from the axis. As the spherical surface is closed ($\Sigma \delta S_i = 0$) then by defining P as the net force per unit normal area on δS and its antipode, we need only consider the front hemisphere ($\forall \delta S$ such that $\delta S \cdot V > 0$). The volume generated by complete

rotation of this hemisphere about the axis is $V_s = \sum_i 2\pi d_i \cdot \delta S_i$ while the torque acting at any instant is $\Gamma_s = \sum_i (\delta S_i \cdot P_i) \times d_i$. By replacing P_i by an averaged value over the hemisphere we have $\Gamma_s = (2\pi)^{-1} V_s P_{av}$. As both relations involve summation over elemental areas they also hold for any closed surface such as that of a molecule rotating about a given axis (i). For an ensemble of identical systems we may form the correlation function $\langle \Gamma_i(t_1)\Gamma_i(t_2) \rangle = (2\pi)^{-2} V_i^2 \langle P_{i_{av}}(t_1)P_{i_{av}}(t_2) \rangle$ where $P_{i_{av}}$ is now an average over the considered molecule rotating about axis (i). The system is also presumed stationary. In general a molecule rotates about three axes, so that torque correlations of the form $\langle \Gamma_a(0)\Gamma_a(t) \rangle$, $\langle \Gamma_b(0)\Gamma_b(t) \rangle$ and $\langle \Gamma_c(0)\Gamma_c(t) \rangle$ etc. can be formed. The exact relation between these terms and the three dimensional torque correlation $\langle \Gamma(0) \cdot \Gamma(t) \rangle$ is not known, through mathematical intractability within the underlying Mori formalism, but some progress may be made by computer simulations. For the present we simply wish to define an effective average volume of rotation V about the two or three axes which correspond to modes of dipolar relaxation such that we may write $\langle \Gamma(0) \cdot \Gamma(t) \rangle = (2\pi)^{-2} V^2 P(t)$, where $P(t)$ is the three dimensional equivalent of $\langle P_{i_{av}}(0)P_{i_{av}}(t) \rangle$. To define V we arbitrarily suppose that at short times (of the order of the libration periods), the f.i.r. spectrum is a superposition of one dimensional librations of amplitudes θ_i determined by $\theta_i^2 = E/k_i$ where E is the energy of this mode ($\frac{1}{2}kT$ on average) and k_i is the " force constant " of the libration. From the above form k_i is associated with the mean squared torque acting in the plane so $k_i^2 = \langle \Gamma(0)_i^2 \rangle \propto V_i^2$. We further presume that $\langle P_{i_{av}}(0)^2 \rangle$ is reasonably independent of the axis chosen. If the dipole lies along a principal axis (a) then as the absorption intensities of librations about the b and c axes may be presumed proportional to θ_b and θ_c, respectively, it follows that spectral addition requires that $V^{-1} = (V_b^{-1} + V_c^{-1})$, i.e., a reciprocal average of the two mutually perpendicular volumes of rotation. In the more general case (μ not parallel to any principal axis) the form :

$$V^{-1} = (\mu_b^2 - \mu_c^2)V_a^{-1} + (\mu_c^2 - \mu_a^2)V_b^{-1} + (\mu_a^2 - \mu_b^2)V_c^{-1}$$

is expected to be applicable. Our final predictive equation is therefore :

$$I_r \bar{v}_{max}^2 \equiv 10^{-38} T_q = V^2 P(0)/(32\pi^4 kTc^2)$$

where for dilute solutions $P(0)$ is presumed to be independent of the solute molecule and so a constant for a given solvent at a given temperature. To estimate values of V for some of the molecules considered we recall that for the sphere $V_s = \sum_i 2\pi d_i \cdot \delta S_i$. If d_i is large compared with r, the radius, then the hemispherical surface may be approximated by its circular cross-section centred at R from the axis (i). The volume of rotation of such a circle can easily be shown to equal $V_i = 2\pi^2 R r^2$. By assuming that the molecule considered has an inpenetrable surface defined by the covalent radii spheres of the constituent atoms, then a particularly simple measure of V_i can be made by summing the volumes of each (non-overlapping) sphere. To simply account for the effects of " shielding " of one part of a molecule by another, the overlapping volume is subtracted from V_i for each sphere in turn before summation. This allows reasonably small V values to be obtained for the more spherical molecules compared with molecules of similar volume but more asymmetric geometry. van der Waals surfaces were considered less appropriate than the covalent radii in this application. Details of this choice and also details as to how to treat such aggregates as methyl groups or benzene rings using covalent radii spheres are published elsewhere.[6] When V values are squared and plotted against the torque product values as observed here
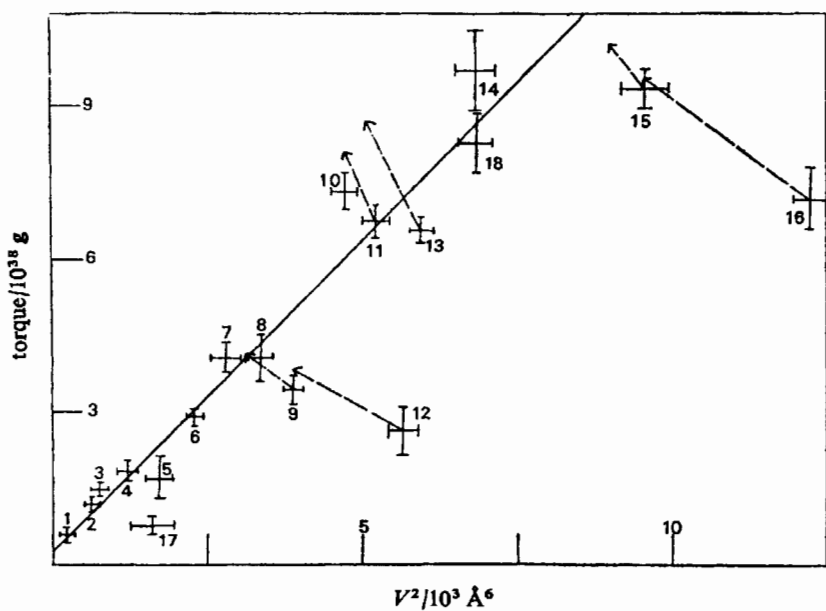
FIG. 6.—Plot of V^2 (10^3 Å^6) against torque ($\times 10^{38}$ g) for the following solutes in decalin (10 % v/v) at 293 K.   (1) CH_2Cl_2;   (2) chloroform;   (3) furan;   (4) pyridine;   (5) tetrahydrofuran;   (6) fluorobenzene;   (7) α-picoline;   (8) pentafluorobenzene;   (9) chlorobenzene;   (10) toluene;   (11) benzonitrile;   (12) bromobenzene;   (13) nitrobenzene;   (14) o-xylene;   (15) 1-chloronaphthalene;   (16) 1-bromonaphthalene;   (17) t-butyl chloride.
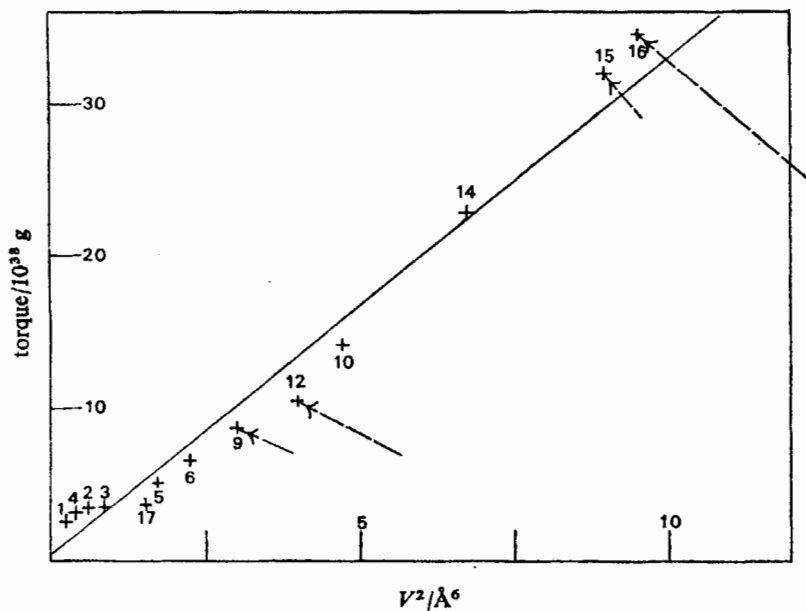

FIG. 7.—As for fig. 6, 10 % v/v in glassy decalin at 110 K.

for decalin solutions at 293 K a good correlation occurs as the above equation predicts (fig. 6). Despite the uncertainties inherent in the estimations of V^2 values we believe it is significant that molecules such as PhCl, PhBr, $PhNO_2$, $C_{10}H_7Cl$ and $C_{10}H_7Br$ give points that lie well below the drawn line that passes through the majority of remaining points. Our belief is that such molecules are examples where librational relaxation is strongly coupled to a translational mode in the following way. The moments of inertia and volumes of rotation have been calculated on the assumption that the principal axes are inertial and intersect at the centre of mass. Steele,[24] however, has remarked that in the condensed phase, the principal axes are torque determined and so are more likely to intersect at the centre of volume, a point rather indeterminate in nature. For most of the solutes on the graph, the centre of mass displacement from either the ring centre or central molecule [represented by $Z(A)$] is small. For the above five molecules and also for benzonitrile, these Z values are, however, higher. By choosing axes that intersect closer to the geometric centre, the V^2 value and hence the rotational hindrance can be reduced, although now the I_r value computed for such axes has increased. If, for example, V and I_r values are computed

TABLE 3.—T_q AND V^2 VALUES FOR INERTIAL AND RING CENTRE PRINCIPAL AXES

molecule	Z/Å	$I_r/10^{-38}$ g cm^2	V^2/Å^6	T_q/g	$I_r/10^{-38}$ g cm^2	V^2/Å^6	T_q/g	$\dfrac{\Delta T_q}{\Delta V^2}$
			(about centre of mass)			(about ring centre)		
bromobenzene	1.66	4.43	5700	2551	6.57	3840	3784	0.64
chlorobenzene	0.98	2.97	3958	3433	3.83	3117	4169	0.87
benzonitrile	0.85	3.07	5200	6781	3.7	4670	8173	2.60
nitrobenzene	1.22	3.9	5800	6555	5.18	5020	8711	2.76
1-bromonaphthalene	1.32	5.17	12 420	7077	7.06	9500	9665	0.89
1-chloronaphthalene	0.69	4.43	9510	9374	4.82	9000	10 200	1.68

for PhBr relative to axes about the ring centre, the corresponding point in fig. 6 falls much closer to the line. In the liquid state the actual centre of rotation–libration will be a compromise between those axes which minimise I_r and those that minimise V and dependent on the ratio of changes I_r/V^2. The extremes of these changes, i.e., the values of I_r and V for ring centre axes, are given in table 3 and correspond to the arrowhead coordinates in fig. 6. As benzonitrile has such a large ratio of changes compared with PhBr say, then rotation most likely occurs about the centre of mass rather than the ring centre and vice versa for PhBr. The arrows thus represent error bars with respect to the uncertainty of the principal axes.

The connection between this uncertainty and mode–mode coupling can now be seen more clearly. If a " libration " of PhBr is occurring about the ring centre (and in the ring plane for simplicity), then this motion may be decomposed into a libration of the dipole about the centre of mass and a translational oscillation of the centre of mass. Spectrally one may suppose that the libration will occur at some frequency closer to that predicted by the above rule (based on pure rotational motion), while the translation will give a weaker absorption band at a lower frequency. Our future work will be to incorporate the simple empirical correlations observed in this paper into a formal description of mode–mode coupling based on the itinerant librator model. At present we are continuing to assess the validity of the above equation for a greater variety of systems and over a range of temperature. Already data (fig. 7)

have been obtained for several molecules in decalin solvent at 110 K, well below the glass transition temperature. The indication is that not only does the rule $T_{\mathrm{q}} \propto V^2$ continue to be obeyed but that the value of $P(0)$ which is proportional to the gradient and the temperature is found to be identical with the value found for the liquid decalin systems, 1.38×10^{19} N^2 m^{-4}, the units indicating that $P(0)^{\frac{1}{2}}$ is the mean force per unit normal area of the molecule. If intermediate temperature studies show that $P(0)$ is independent of temperature then we have an important conclusion that the mean squared torque $P(0)V^2$ acting on a given molecule is also temperature independent, the f.i.r. peak frequency varying as $1/T$.

Comparison at constant temperature of the f.i.r. peaks of a given solute in different solvents indicates that P is solvent dependent, CCl$_4$ for example having a slightly higher value than that for decalin. However, for many solvents of interest, particularly liquid crystals where solute absorptions peak at higher frequencies than they do in decalin, it is uncertain whether P varies because of the change of solvent geometry or because of electrodynamic effects and this is a problem which needs further investigation.

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