The analysis of molecular dynamics with a range of microwave/far infrared spectra

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A Mori approximation for zero-THz absorption of dipole solutes in tested thoroughly with several examples. A number of points emerge from the data correlation.

1) It is advantageous to analyse the complicated theoretical expressions before attempting a best fit analysis. Curve matching should be performed in both time and frequency domains.

2) The theory is sufficiently at short and long times but the evolution at intermediate times is not followed satisfactorily. This shows up clearly in the 10-50 cm⁻¹ region of the far infrared.

3) The far infrared peak frequency is not related straightforwardly to the theoretical mean square torque, but via parameters grouped about 2.6 for the two halogen- or as systems studied.

4) The measured Debye relaxation times (this work) are reproduced theoretically from the far infrared to within about 30 per cent of their values for most solutes, but progressively poorer results are obtained as the molecular size increases, and as the molecules become more anisotropic.

5) It is essential to consider the effects of collision-induced absorption and other mechanisms of permanent dipole enhancement. The failure of the Gordon sum rule cannot be attributed solely to this cause and intermolecular interaction probably plays a significant role.

1. INTRODUCTION

In previous publications [1-3] we have used a three variable Mori continued fraction approach for the orientational autocorrelation function, to describe the spectral features of dipolar liquids and liquid mixtures over the zero to the THz frequency range and hence emphasize the causal link between classical dielectric and far infrared (F.I.R.) behaviour. This approach, referred to as method (i), is a development of a method first used by Nee and Zwanzig [4], and includes memory and inertial effects which are needed to reproduce even the most basic features of absorption spectra in the F.I.R.—the Poly absorption.

In the short-time domain [2, 3], the formalism has clear advantages over earlier models which correspond to lower order approximants in the Mori formalism.

More recently we have been developing an analytical model [6-9] whereby this formalism is applied to the angular velocity autocorrelation function of a dipole vector which is then constrained to move in a plane (in order to calculate
2. THEORETICAL

The Mori-O model, so called to emphasize the dual interpretation that this model affords and also to distinguish this three-variable formalism from a generalized version of the I.O. model [7] which we have studied in connection with viscoelastic and glassy media [14], has been discussed in the literature from several theoretical points of view [6-12]. To aid in our discussion, the main features of this theory together with the relations required for the present application are grouped in an appendix. Of primary importance is equation (A.11) for the rotational velocity autocorrelation function $C_{ij}(t)$ which is to be

$$C_{ij}(t) = \frac{N_{ij}}{N_{ij}} \frac{\langle m_i m_j \rangle}{m_i m_j} \sum_{\alpha, \beta} \cos(\omega \alpha t)$$

where $\omega$ is the inverse pre-exponential factor and $\alpha$ is the I.R. refractive index.

Several basic points need to be considered in such a comparison. Firstly the analytic equation (A.11) derived for planar reorientation of a dipole in a disc in inertis $I$ is assumed (to be) valid for real systems when the reduced inertis $I_i$ is used as the appropriate measure of inertia. Secondly the proportionality factor in (1) may not be entirely adequate in view of the uncertainty of internal field effects so that we prefer to match the theoretical and experimental time curves only in profile. As regards the actual fitting procedure, the time unit is chosen to be $(\epsilon/(\Delta T))^2$. This removes the factor $\Delta T$ from (A.7) and (hence $A_1$) and also factors of $10^9$ from the coefficients. Iteration is best performed on the initially guessed values of $\alpha_0$, $\beta_0$, and $\beta$ rather than on $\nu_{01}$, $p$, and $\beta$ (the bars denoting normalized units) as it is easier to determine the latter from the former using relations (A.6) than it is to do the reverse using Cardon's formula [6]. The particular influence on the iteration procedure, of $\nu_{01}$, $\alpha_0$, and $\beta_0$ can also be more easily assessed. Thus, appearing in the dominant (off) term, determines the position of the minimum of $C_{ij}(t)$ while $\nu_{01}$, the damping factor $\exp(-\nu_{01}t)$ determines the depth of the minimum. The parameter $\nu_0$ is found only to significantly affect the slope of $C_{ij}(t)$ if its value is comparable with or smaller than the $\nu_{01}$ of $\beta$, otherwise it becomes redundant. This makes it necessary to consider both time and frequency domain data in the determination of optimal values for $\nu_{01}$, $\nu_0$, and $\beta$ although as will be shown later, the interplay spectral peaks generated by the Mori-O model complicates this procedure. For the present it is convenient (and suitably accurate) to summarize our attempts at spectral curve matching by stating that the value of $\nu_{01}$ should be chosen to equal the best fit value of $C_{ij}(t)$. Using this empirical result as an assumption valid for all the systems studied here, best-fit values of $\nu_{01}$, $\nu_0$, and $\beta$ can now be obtained from the single operation of curve matching in the short-time domain. These results are summarized in table 1 and the adequacy of the fit shown in figure 1. The systems studied were chosen for the accuracy for which the experimental $C_{ij}(t)$ curves may be extrapolated, those to 20 cm$^{-1}$ region and so only extrinsic dielectric behavior. Such predictions are confirmed by spectro measurements performed in the 4 to 70 GHz region and further indicate the basic validity of the Mori-O approach.
Table 1. Best-fit data for solution experiments at 20 K.

<table>
<thead>
<tr>
<th>Species</th>
<th>$K_C$ (per cent)</th>
<th>$K_C$ (mole fraction)</th>
<th>$γ$</th>
<th>$β$ (induced time units)</th>
<th>$K_T$</th>
</tr>
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<tr>
<td>O</td>
<td>0.65</td>
<td>0.81</td>
<td>1.31</td>
<td>0.24</td>
<td>0.45</td>
</tr>
<tr>
<td>(C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ClO₃⁻</td>
<td>0.67</td>
<td>0.81</td>
<td>1.31</td>
<td>0.24</td>
<td>0.44</td>
</tr>
<tr>
<td>(C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃OH</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(C)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CH₃OH₂</td>
<td></td>
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<tr>
<td>(C)</td>
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<tr>
<td>CH₃OH₃</td>
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<tr>
<td>(C)</td>
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<td>CH₃OH₄</td>
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<td></td>
</tr>
<tr>
<td>(C)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Figure 1. Time curve matching on data for selected solvents in deuterium solution (20 K). Illuminating on a range of interpretation. (a) Preeilided-dashed; (b) experimental data; (c) over frequent amendment factor. 0.5; 0.6; 0.7; 0.8; 0.9; 1.0; 1.1; 1.2; 1.3; 1.4; 1.5; 1.6; 1.7; 1.8; 1.9; 2.0. As for figure 2 (a) with the experimental curve obtained from: (1) the spectral mean of seven experiments; (2) an intermediate; (3) CH₃OH₄-diluted. As for figure 2 (a).

We emphasize that the form of $C(f_{20})$ is adequately determined from the data over the 35-200 cm⁻¹ range by the pol if infrared and microwave experiments. For the numerical transformation the bandwidth is extrapolated (within consideration of microwave data) down to zero frequency, reasonable extreme of extrapolation giving negligible error. The best fit parameters so obtained may be used to generate the forms of other correlation functions including that of $\phi$-electron (equation A7) which underlies the microwave behaviour below about 30 cm⁻¹. This allows a prediction of deuterium behaviour described primarily by the microscopic relaxation time $\tau_{\phi}(1/\omega_0)$, $\tau_{\phi}$ being given specifically (as less $\gamma C/(\omega_0)$) by (A 11).

The trends in parameters $\gamma$, $\phi$, and $K_1$ are analysed here in terms of statistical concepts (the mean square torque and the causal linking of losses and absorption $\gamma_{abs}$) and through the concept of orientational oscillation.
3. Experimental

Spectra were taken with a phase modulated Grubb-Parsons N.P.L. interferometer using standard techniques of Fourier transform spectroscopy [16] and some have been presented before [9]. The data acquisition was spread over a period of twelve months in order to minimise instrumental uncertainty. Microwave ammonia measurements employed standard wideband for 35 and 70 GHz points and the sweep frequency method of Price [17] for the range from 4 to 18 GHz. The numerical transformations were performed using a Simpson's rule algorithm.

4. Results and Discussion

The best fit results are summarised in table 1 and provide adequate descriptions of the experimental rotational velocity correlation functions exemplified in figure 1. Have the experimental curves (full lines) decay initially as cosines and are followed by the Mori-T.O. fits until they deviate beyond the first half period of the oscillation. These further points on the curve matching analysis are exemplified in the figure and will be considered in turn.

We have already pointed out [8, 9] that the principal axes of rotation in the condensed phase may not correspond to the principal inertia axes through the centre of mass but rather axes about the centre of volume swept out by the rotating molecule. This involves a coupling of rotation and translation and the value for \( I_z \) becomes larger. For the monosubstituted phenyl group, the centre of volume is essentially close to the ring centre and is the centre of mass so that computing \( I_z \) for axes about the former origin gives an upper bound for \( I_z \). Both values of \( I_z \) have been used in fitting the data for the chloride, bromide and nitrobenzene solutes and the alternative fits for chlorobenzene are illustrated in figure 1(c).

In figure 1(b) two sets of data [12] for CH₂Cl₂ have been transformed and fitted to indicate the extent of instrumental uncertainty on the derived parameter values. Here curve 1 is the transform of a spectrum averaged over different runs, curve 2 is the extremum of this set, caused by a known optical misalignment. Such machine errors inherent in the Michelson instrument are not obvious from the spectra and are only now beginning to be tackled systematically. The \((K_n, K_m, \gamma)\) set for curve 2 vary by up to 22% per cent of the mean values and this taken as the maximum possible uncertainty for the results of table 1. Finally we note that for some systems the experimental correlation function is broadened and cannot be simulated very well by (A 11). This is due to the chlorobenzene (figure 1(d)) where induced absorption in liquid paraflin contributes and our simulated curve is consequently chosen to match the region of the minimum rather than the initial conical decay.

4.1. The best-fit parameters of table 1

The position of the minimum in the rotational velocity autocorrelation function (and therefore \( \beta \)) depends essentially on the spectral band center position while the depth of the minimum (and \( \alpha \)) depends on the spectral band width. The latter quantity can be confirmed from table 1 by taking the ratio \( \alpha/\beta_{\max} \) (with \( \beta \) in unnormalized units) which is then found to be almost constant. This property provides a consistency check for the computed \( \beta \).

The most important parameter from a statistical point of view is the mean square torque \((\langle T \rangle)^2\) which can in principle be determined from a priori calculation or by computer simulations. This is obtained from (A 5) as

\[
\langle T \rangle^2 = kT/2(\gamma_0)^2 \alpha
\]

and, at constant \( P \), is therefore proportional to \( \alpha \). From table 1 we see that this parameter increases in value with the size of the solute, so supporting our previous rationalization developed [8, 9] between \((\langle T \rangle)^2\) and the solute volume of rotation. Actual values of torque are evaluated conveniently as the root mean square torque per mole.

Next we consider to what extent the statistical parameters of table 1 promote the concept of planar itinerant oscillation as outlined in the Appendix. If \( \eta \) is taken to be larger than \( 2 \pi \), and if \( \beta \) and \( \alpha \) are given from the observed Debye and librational peak positions, then, as illustrated in figure 3 (a) for the pyridine-decalin system (curve 3), the resulting far infrared peak is too

![Figure 2. Absorption spectra for solvents in decalin (253 K) on normalized scales: (1) aniline (5.5 ps); (2) CH₂Br₂ (5.4 ps); (3) chlorobenzene (5.4 ps); (4) CH₂Cl₂ (6.4 ps); (5) furan (6.3 ps); (6) pyridine (6.9 ps); (7) chlorobenzene (5.5 ps); values in parentheses are \( \alpha \) and reflect spectral width.](https://example.com/figure2.png)

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\]

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Figure 3. Analytical formula illustrating for two systems of widening differing relaxation times. (a) Absorption for pyridine-decalin (w=11 ps); (b) theoretical; (c) experimen-tal; (d) analytical fitting; (e) fit using parameters of table 1 (optimal fit at a short time); (f) fit using parameters based on internal connotations model (a=1.5); (g) fit using parameters based on internal connotations model (a=1.5); (h) intermediate fit (K_a=90, K_b=250, g=12). (1), (2), and (3) are for curves (1) and (2) in figure 3 (ac); (1) and (2) are for curves (1) and (2) in figure 3 (ac); (3) and (4) are for curves (1) and (2) in figure 3 (ac). Improve immediately the root mean square frequency of vibration in the molecular ensemble. An explanation involves the transverse and long-time behavior of the theoretical absorption spectra as illustrated in figure 3 (a) for pyridine-decalin. From this example, which is typical, we note that the

Inertia I_1 must be smaller than that of the uncaged dipole, I_2, and so on average contains less than one solvent molecule. This density of the cage points to the following interpretation. The second-order dipole in the occasional pairing or clustering of solute with solvent molecules interdispersed with periods of greater rotational freedom. Evidently, we do not have cooperative translation of several molecules fixed in a planar orbit around the solute.

Our next consideration arises from the result that K_{12}^{(3)}(t) = (2v_{12}^{(3)}t)^{1/2} for optimal fitting. This indicates that the absorption maxima cannot be ascribed immediately to the root mean square frequency of vibration in the molecular ensemble. An explanation reveals itself through the features of the optimum theoretical absorption spectra as illustrated in figure 3 (a) for pyridine-decalin. From this example, which is typical, we note that the

Figure 4. Variation of mean square torque to peak ratio (K_a^{2}v_{12}^{(3)}t)^{1/2} with peak frequency (v_{12}^{(3)}t) for decalin solutions at 298 K. (Numbered as in table 1.)

Table 2. The effect of K_2 on spectral fitting, by reference to FNOx-decalin data, figure 3 (a).

<table>
<thead>
<tr>
<th>Curve</th>
<th>w</th>
<th>v</th>
<th>( (K_{a}^{2}v_{12}^{(3)}t)^{1/2} ) ps</th>
<th>( K_{a} ) ps</th>
<th>( K_{b} ) ps</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>40</td>
<td>17</td>
<td>56</td>
<td>252</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>15</td>
<td>18</td>
<td>31.5</td>
<td>251</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>11</td>
<td>18</td>
<td>20.6</td>
<td>185</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>19</td>
<td>22.4</td>
<td>68</td>
<td>189</td>
</tr>
</tbody>
</table>

Table 1. The parameters for the parameters in table 2 are given in table 2. A more satisfactory, though not perfect, spectral simulation is obtained from the use, in (A 15), of the parameters given in table 1, and is by virtue of the parameters being fully equivalent to the Mie theory (16).

From the table it is apparent that to reproduce the breadth of the Peley absorption we have to use \( K_{a} = K_{b} \) for all the systems. The equivalence of the parameters (A 12) then forces us to the conclusion that the cage moment of
curve is twin peaked and underestimates the intensity in the 10-50 cm⁻¹ region. Reasons for this failure are given later, but for the present we may interpret the analytical curve [(4)] as a blend of librational absorption centred at \( K_\text{lib} \) [8],\(^8\) (about 70 cm⁻¹), superimposed on the invariants corrected Debye plateaus absorptions which give the lower frequency peak. Clearly these two peaks merge completely in practice giving an observed 2\( v_{\text{lib}} \) from less than \( K_\text{lib} \) [8] so that the ratio \( K_\text{lib} / 2v_{\text{lib}} \) of table 1 are greater than unity because of the proximity of the Debye process. The ratio for the present systems are grouped around a value of 2.3 and in fact there is a degree of correlation of their \( v_{\text{lib}} \) with \( \tau_\text{lib} \) (but not with \( \tau_\text{lib} \)) figure 4. This is not expected from the modelling and is in variance with our relation [8, 9] derived between the peak positions and the solute volumes of rotation, which depends on \( K_\text{lib} / 2v_{\text{lib}} \) being constant. Deviations from this law are therefore useful pointers to the following:

(a) the invariance of the Mori/I.O. model, especially when attempts are made to describe zero-T THz spectra consisting of widely separated Debye and Folev peak frequencies. In this case \( K_\text{lib} / 2v_{\text{lib}} \) has to be large, forcing on unnatural narrowness on the theoretical F.I.R. curve. In the extreme of solid-phase librations the Mori/I.O. model cannot be made to produce a broad far infrared curve whilst accounting for the known loss features of the THz region;

(b) the presence of association, typified by hydrogen-bonding, e.g. aniline and acetone solutions in figure (4);

(c) the presence of induced absorption [18] in the far infrared.

As the bands of most non-polar systems are centred at comparatively high frequency [2], deca tion for example at 70 cm⁻¹ and benzene at 80 cm⁻¹, it is expected that similar contributions are present in the dipolar bandshape. If the spectrum of 10 per cent bromobenzene in deca tion is corrected by subtraction of a fraction (less than 10 per cent) of the pure benzene spectrum then the

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Figure 5. Ammoniation/frequency spectra for selected deca tion solutions at 293 K. (1) Bromobenzene; (2) chlormon; (3) chloroform; (4) formic.

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Figure 6. Microwave and far infrared for CH₃CCl₂-deca tion: Fossan-Rickwood curve and analytic fit. (a) \( \sigma / f^2 \) spectra (approximating dielectric loss) • • • • • • • experi mental points. (b) Fossan-Rickwood curve through all data. (c) Debye curve through low frequency data. (d) Mori/I.O. analytic best fit (parameters as in table 1). (e) Fossan-Rickwood plot of curves (3) and (2) above. (1) Plot for chlorobenzene-deca tion for comparison.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \text{V} )</th>
<th>( \text{E} )</th>
<th>( \text{E}_{\text{a}} )</th>
<th>( \text{V} \text{K} )</th>
<th>( \text{E}_{\text{a}} )</th>
<th>( \text{E}_{\text{a}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CHCl₃</td>
<td>2.29</td>
<td>1.2</td>
<td>0.6</td>
<td>0.1</td>
<td>0.9</td>
<td>0.95</td>
</tr>
<tr>
<td>(2) Chloroform</td>
<td>2.56</td>
<td>4.9</td>
<td>0.8</td>
<td>0.3</td>
<td>0.4</td>
<td>94.6</td>
</tr>
<tr>
<td>(5) Fluorine</td>
<td>2.82</td>
<td>3.0</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>94.6</td>
</tr>
<tr>
<td>(9) Benzene</td>
<td>2.56</td>
<td>9.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.4</td>
<td>94.6</td>
</tr>
</tbody>
</table>

(7) Fluorine | 2.7 | 4.9 | 1.0 | 0.9 | 0.9 | 94.6 | 2724 |

(10) Chlorobenzene | 2.46 | 10.1 | 1.0 | 0.9 | 0.9 | 94.6 | 2724 |

(11) (20 per cent) THF | 2.5 | 9.0 | 2.5 | 1.0 | 0.9 | 94.6 | 2724 |

(12) (20 per cent) pyridine | 2.57 | 10.1 | 1.0 | 0.9 | 0.9 | 94.6 | 2724 |

(13) Naphthalene | 4.18 | 2.6 | 1.0 | 0.9 | 0.9 | 94.6 | 578 |

(14) (5 per cent) tetrachloroethylene | 3.0 | 10.1 | 1.0 | 0.9 | 0.9 | 94.6 | 1203 |

(17) 1-Chlorohexadecane | 3.0 | 10.1 | 1.0 | 0.9 | 0.9 | 94.6 | 1203 |

(16) 1-Hexadecanol | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(17) 1-Butanol | 2.82 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(20) 1-Octanol | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(25) 1-Octene | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(18) 1-Decene | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(19) 1-Dodecene | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(21) 1-Tetradecene | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(22) 1-Hexadecene | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(23) 1-Octadecene | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(24) 1-Hexadecyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(25) 1-Octadecyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(26) 1-Hexyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(27) 1-Octyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(28) 1-Dodecyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(29) 1-Tetradecyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(30) 1-Hexadecyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

(31) 1-Octadecyne | 2.72 | 3.0 | 0.3 | 0.4 | 0.9 | 94.6 | 1203 |

To obtain accurate values of \( \varepsilon_{\text{a}} \), a modified Fussxi-Kirkwood equation [7] is used

\[
\varepsilon_{\text{a}} = \frac{1}{1 + \frac{\varepsilon_{\text{a}}}{\varepsilon_{\text{a}}}}
\]

For systems with short relaxation times, the Debye process overlaps with the far infrared absorption and can no longer be found with a Fussxi-Kirkwood plot (figure 6). (The distinction between far infrared and microwave is of course arbitrary.) In this case only the low frequency points can be used to determine \( \varepsilon_{\text{a}} \). The integrations of these points from the frequency axis (at \( \varepsilon_{\text{a}} \)) experimental relaxation times have been calculated and are shown in table 3, together with \( \varepsilon_{\text{a}} \) parameters and \( \varepsilon_{\text{a}} \). Some literature solution values [20] are given for comparison in column four but except for 1-chlorohexadecane [21] and chloroform [22] none of the solvents has previously been studied in

decanol and no data were found for 1-octene, CHCl₃, tetrahydrofurane or \( \text{C}_6\text{H}_5\text{F} \).

These values are compared with the Mochi/Io model predictions from the far infrared as follows. A field correction was made using the Cole factor [23] (not the Debye-Lorentz field factor) to obtain the molecular \( r_{\text{a}} \) times:

\[
r_{\text{a}} = \frac{r_{a,0} + \Delta r_{a,0}}{r_{a,0}}
\]

The values of the experimental \( r_{\text{a}} \) are bracketed in the table and are only significantly smaller for the more polar solvents. The theoretical \( r_{\text{a}} \) values are nearly all within 30 per cent of the observed values except for fluorobenzene-decalin and \( \text{C}_6\text{H}_5\text{F} \)-decalin, which are within 30 per cent, and for solutions of benzoic acid and 1-chlorohexadecane whose long relaxation times are reproduced theoretically to within a factor of two only. For chloro-, bromo- and nitrobenzene solutions the parameters obtained by choosing the larger reduced inertia appropriate to torque-determined axes, give significantly larger and more realistic values of \( r_{\text{a}} \). This further evidence for the ability of zero-field spectroscopy to investigate into-translational couplings in detail.

In conclusion, the Mochi/Io model can be used to simulate both the long and short time details of a large number of solutes in deca1in at 293 K and is an improvement over the Wylie version [24] of ionomer oscillation or the Bran-Larkin model [25], both of which give an unrealistic fast decay (non-covalent) for \( \varepsilon_{\text{a}} \) at short time. The theoretical spectra, however, do not behave satisfactorily in that they are generally too-pre-aid and do not merge completely to give the observed single absorption band (figure 4). The region of breakdown of the Mochi/Io theory can therefore be identified as the intermediate frequency region, 10-80 cm⁻¹. This may be rationalized as follows:

(i) The earliest approximations used in the model probably does not allow sufficient consideration of the transition from the deterministic (short-time) to stochastic (long-time) regimes.

(ii) There is an unresolved question of the importance of rotation/translation coupling, especially regarding the cooperative nature (cou-wheeling) of large angled motions.

(iii) The onset of dispersive internal-field elements below the 10 cm⁻¹ region does not allow us to exceed the validity of our autocorrelation function modelling without considering eventually the problem of cross-correlations (e.g. using the theorem of Maddin and Kivelson [26]).

Figure 7. Graph of mean squares: \( \varepsilon_{\text{a}} \) (benzene); \( \varepsilon_{\text{a}} \) (chlorobenzene); \( \varepsilon_{\text{a}} \) (pyridine); \( \varepsilon_{\text{a}} \) (hexyl chloride); \( \varepsilon_{\text{a}} \) (CHCl₃).
4.2. Spectral analysis and the problem of collision induced absorption

We have already briefly considered, in figure 3 (a), two spectral simulations of the pyridine-decyl system, both described by (A 13) but with parameter sets derived from opposing points of view. Curve 1 is based on the parameters given in table 1, and is consequently well representative of the short-time details of the motion (figure 1 (a)). This is reflected in figure 3 (a) as a correct simulation of the width of the librational profile and its high frequency fall off. The adequacy of the analytic extrapolation to low frequency, already inferred from table 3 where $v_0$ and $v_{max}$ can be seen graphically in figure 3 (b) where curve 1 of figure 3 (a) is compared with microwave data in the loss representation. Curve 2 of figure 3 (a) in contrast illustrates the typical spectral form generated when the parameters are determined from knowledge of the experimental $v_0$ and $v_{max}$ and with the supposition $I_0=I_{max}$. This curve can then reproduce the two essential features of the spectrum, the Debeye and Polanyi peaks, in position but not in profile. Clearly neither curve is completely satisfactory in the far infrared and if spectral fitting were divorced from temporal considerations a curve such as 3 in figure 3 (a) closely matching the observed peak in position and intensity might be more appropriate. All these curves give identical profiles in the loss representation (figure 3 (c)) below about 5 cm$^{-1}$ (150 GHz) which are narrower than those observed. Conversely, as already discussed, the redundancy of $v_0$ in the temporal curve matching exercises of table 1 makes it necessary to consider a set of curves such as curves 1 to 3 in figure 3 (c) in connection with data for nitrobenzene-decyl. Of these three curves, all identical at high frequency or short time, curve 2 is considered to be optimal in this representation and coincidently also in the loss. The two systems pyridine and nitrobenzene in decyl are extreme in having very different relaxation times of 3.3 ps and 20 ps respectively. Comparison of the fits for each system thus indicates how the I.O. model can reasonably fit the overall spectra (in profile or not intensity) even when the Debeye and Polanyi peaks are well separated in frequency (figure 8). An opposite extreme occurs for dichloro- methane in decyl solution where now the loss peaks well above 100 GHz, figure 6 (a). An extrapolation, made by fitting both the microwave and far infrared data points on a Fenns-Kirkwood plot (curve 1 of figure 6 (b)) indicates a maximum intensity of greater than $\epsilon_{\text{max}}=2.6(\epsilon_{\text{max}}=2.5)$ in this case. This was observed for three other systems (chloroform, tetrahydrofuran and furan) whose loss peak in this region and occurs despite the fact that $\beta_{\text{rep}}<1$, indicating a broadening of the experimental loss curve. Qualitatively, this is due to a large overlap between the Debeye peak and the Polanyi absorption of the far infrared, and for CH$_2$Cl$_2$ the low frequency data drawn in figure 7 on a Debeye curve as seen by curves 2 in figures 6 (a) and (b). The Fenns-Kirkwood plot for the chloroform-decyl system is also shown for comparison (with its $\epsilon_{\text{max}}^\text{obs}$ scaled down) and is typical of data for systems whose loss peaks at lower frequency ($\beta_{\text{rep}}>0.7$ to 0.9).

The failure of the Mor(I) model to account adequately for the far infrared inorganic relates to a similar failure of the Gordon sum rule [27]. It is assumed usually that the additional absorption is due to induced contributions. In table 4 we list the sum rule predictions, $\mathcal{A}_0$ (corrected by a Pekeris-Wilson factor for the internal field) against the measured integrated absorptions ($\mathcal{A}_{obs}$) for some of our solutions. The aromatic ring compounds have smaller ratios $\mathcal{A}_{obs}/\mathcal{A}_0$ below 65 per cent compared with those for the saturated molecules and aldehydes. This is notable in the light of the large induced absorption of benzene itself. Tetrahydrofuran is an exception, with an observed absorption over three times that predicted by Gordon, indicating another underlying absorption mechanism (pseudostationary). These ratios for 10 per cent $\nu/v$

<table>
<thead>
<tr>
<th>Solution</th>
<th>$\mathcal{A}_0$/cm$^{-1}$</th>
<th>$\mathcal{A}_{obs}$/cm$^{-1}$</th>
<th>$\mathcal{A}_{obs}/\mathcal{A}_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PrF$^3$</td>
<td>214</td>
<td>100</td>
<td>0.47</td>
</tr>
<tr>
<td>PrCl$^3$</td>
<td>125</td>
<td>76</td>
<td>0.61</td>
</tr>
<tr>
<td>PhNO$^2$</td>
<td>82</td>
<td>47</td>
<td>0.57</td>
</tr>
<tr>
<td>PhNO$_2$</td>
<td>600</td>
<td>356</td>
<td>0.59</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>210</td>
<td>95</td>
<td>0.45</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>748</td>
<td>316</td>
<td>0.41</td>
</tr>
<tr>
<td>CH$_3$COCH$_2$</td>
<td>1300</td>
<td>408</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 8. Predicted and observed Debeye times and their correlation with $\beta_0$ ($\nu$=volumetric number). Number as in table 3. X-Mon predictions from far infrared data. Observed microrelaxation times.
solutions in desalts are very similar to those obtained for the pure liquids by Hindle et al. [25] (detailed in table 4). The apparent constancy of the ratio of the hexamethylene, despite their different absorption intensities suggests that the induced components in these systems is not simply the same cross-section absorption as for pure benzene. Rather, we assume that it is a true dipole due to induced dipoles whose instantaneous dipole magnitude is with respect to the present molecular axes but that there is an additional enhancement of the permanent dipole. In other words the instantaneous value of the molecular dipole moment which is responsible for far infrared absorption is larger than the dipole moment observed instantaneously (with an Orme [29] or Guggenheim [30] equation for example). This could be due to a variety of mechanisms, the following being typical:

(i) According to Dreyfus [31], the solution static permeability is due to a field orientation of dipoles in uncharacterized with thermal rotational diffusion. Each diffusing molecule will appear to contain a dipole of moment \( \mu \), but on a shorter time scale the molecules are "dipolar", the actual dipole at each instant being a random function of \( \mu \). The relaxation time of this dipole moment will be determined by the distribution of orientations \( \mu \) and the mean square value of the mean angle of orientation. A calculation shows that the dipole orientations are to be "free radius" the effective moment observed over times larger than the relaxation time may be 4 times smaller than the instantaneous moment.

(ii) The effect of collisions on the dipole may cause its values to fluctuate. Again at longer times a mean value is effective but in the far infrared the absorption intensity depends on the instantaneous moment. As Grant's work shows \( \mu \) and the random fluctuation of \( \mu \) is due to the mean value will give a mean square value larger than the square of the mean. If a dipole of unit mean value is equally likely to take values of 0.1 D and 1.5 D, i.e. 10 per cent fluctuation, then the mean square dipole is 1.9 D. In addition the effects of dipole-dipole interaction is known to reduce the Orme determined dipole moment in solvents such as nitrobenzene or hexamethylene. Assuming that this occurs in many liquid systems (inferred from computed solution gas dipole moment moments) then again we must consider a static (Orme) dipole moment in the electric field range 0-10 cm\(^{-1}\), and an effective dipole moment, i.e. essentially free of dipole-dipole effects, giving enhanced absorption, in the far infrared.

5. RELATING THE POLING AND DESALTS ABSORPTION PEAK

In this section we obtain a simple empirical relation linking these two frequencies. This is useful because these separation of the frequency scale is a direct measure of the mean square torques. It is convenient to normalize the frequency with the square root of the reduced inertia. Figure 2 shows the peak separation as a function of molecular geometry. A similar trend is observed with increasing temperature for a given solvent.

The model predictions of \( \tau_0 \) used earlier may be developed to account for the peak separations in a simple empirical way. Comparing the correlation functions \( C(\tau) \) it becomes clear that the position of the minimum is generally determined from the spectral peak position, while its depth depends on spectral width. Therefore the unrealized value of the parameter \( \beta \) is approximately proportional to \( \tau_{\text{rms}} \), for the majority of systems. Further the unrealized value of \( \tau_0 \) is approximately constant, about 6 \pm 6 \text{ ps}^{-1}, which is an indication of the similarity in bandshape for most of the solute/desalts systems we have studied. Using the approximation \( \tau_0 \approx \tau_{\text{rms}} \) (here we are indicating normalization) then \( T \approx (\tau_0 - \tau_{\text{rms}})^{-1} \approx \tau_{\text{rms}}^{-1} \). Because \( \beta \) is proportional to \( \tau_{\text{rms}} \), therefore \( \tau_0 \) is constant with \( \tau_{\text{rms}}^{1/2} \), and consequently the relaxation time is proportional to the square of the solute volume of rotation. These relations assert that the master far infrared bandshape (cf. figure 3) does not vary appreciably from solvent to solvent.

A similar result may be derived from the Langevin equation for rotational motion. For brownian motion in the absence of a field

\[ \tau_0 \approx (\tau_{\text{rms}})^{-1} \]

where \( \zeta \) is the friction coefficient. The mean square displacement (\( \langle D^2 \rangle \) is related to \( \tau_0 \) by \( \langle D^2 \rangle = 2AD^2 \tau_0 \) and Einstein's relation for the diffusion coefficient follows, i.e., \( D = kT/\langle \tau \rangle \).

The relaxation time \( \tau_0 \) is approximately that for the molecule to have rotated, on average, through an angle of 1 rad from its t=0 position, and is proportional to \( D^{-1} \). For planar motion \( \tau_0 \) is related to the auto-correlation function of the random torque acting on the molecule.

\[ \langle D^2 \rangle = 2(kT) \cdot \tau_0 \cdot \langle \tau \rangle \]

The basis of the present three variable theory is a generalized Langevin equation where \( \langle \tau \rangle \) is not independent of previous values of \( \tau \) and is replaced by

\[ \langle \tau \rangle = \langle \tau \rangle \cdot \langle \tau \rangle \]

The random torque correlation function may be decomposed into a solute dependent term \( \tau_{\text{rms}} \) and a fast approximation \( \langle \tau \rangle \) which is the linear function of \( \tau \).

For long time intervals where the rapid fluctuation (free) of \( \tau \) is not considered the generalized form reduces to that involving the single friction constant \( \zeta \). The random torque correlation function may be decomposed into a solute dependent term \( \tau_{\text{rms}} \) and a fast approximation \( \langle \tau \rangle \) such that we have

\[ \tau_0 \approx \tau_{\text{rms}}^{-1/2} \cdot \langle \tau \rangle \]

or for a set of solvents in a common solvent at a given T, \( \tau_0 \approx \tau_{\text{rms}}^{-1/2} \cdot \langle \tau \rangle \).
that in figure 8 to predict the relative values of \( r_{2} \), from a simple consideration of solute geometry and to a better accuracy than that predicted by Stokes' law:

\[ r_{2} = 4 \pi \eta \frac{B_{2}}{M^{2}} \]

where \( \eta \) is the solvent viscosity.

The Science Research Council is thanked for an equipment grant and a studentship to C.J.R.

Appendix

The Mori representation of the Langevin equation describing the evolution of a random variable \( \dot{S}(t) \) has the form [18, 2]

\[ \mathbf{A}(t) - \mathbf{B}(t) = \left[ K_{d}(t) - \mathbf{B}(t) \right] dt + \mathbf{D}(t), \]  

where \( \mathbf{A}(t) \) is the stress tensor which is null for simple molecular motion, \( K_{d}(t) \) is the memory function of \( \mathbf{A}(t) \) and \( \mathbf{B}(t) \) is the random component of \( \mathbf{A}(t) \). On multiplying by \( \mathbf{A}(t) \) and averaging, equation (A.1) is transformed into

\[ \frac{d\mathbf{C}^{(p)}(t)}{dt} = \mathbf{C}^{(p)}(t) \mathbf{K}_{d}(t) \mathbf{B}(t) \]  

where \( \mathbf{C}^{(p)}(t) = \mathbf{A}^{(p)}(t) / \mathbf{A}(t) \) (A.3) and has a solution in Laplace space:

\[ C^{(p)}(s) = \frac{1}{\mathbf{p} + \mathbf{K}_{d}(s)}. \]  

The memory function is shown in Mori's work [18] to be itself a correlation function (of the variable \( \mathbf{R}(t) \)) and may also be described by an equation similar to (A.2) with a second memory function \( \mathbf{K}_{m}(t) \). Sequential use of this logic generates a continued fraction expression for \( C^{(p)}(s) \) which truncates at first order by assuming that \( K_{d}(t) \approx K_{m}(t) \exp(-s t) \). With angular velocity \( \Omega \) as the variable, the correlation function expression in Laplace space is now

\[ C^{(p)}(s) = \frac{K_{0}^{(p)}}{s + K_{0}^{(p)}} \]  

\[ = \frac{1}{s^{2} + \omega_{0}^{2}} \]  

As chemically, the correlation functions are time-even their Taylor expansions at short times are of the form

\[ C^{(p)}(t) = \omega_{0}^{2} \frac{\omega_{1}^{2}}{6} \frac{\omega_{2}^{2}}{4} \cdots \]  

and likewise for \( K_{d}(t) \) and \( K_{m}(t) \). Substitution into equation (A.2) and comparing terms gives

\[ K_{0}^{(p)} = -\omega_{0}^{2} \frac{\omega_{1}^{2}}{2!} \frac{\omega_{2}^{2}}{4!} \cdots \]  

Transformation of (A.4) generates the angular velocity correlation function in terms of the roots, \( -\omega_{0}, \pm \omega_{1}, -\omega_{2}, \cdots \) of the cubic denominator rather than in terms of \( K_{d}, K_{m} \) and \( \gamma \) directly. The two sets of parameters are interrelated by [12]:

\[ \gamma = 2 \Omega_{0} \omega_{0}^{2} \quad K_{d} = K_{m} = \omega_{0}^{2} + B_{2} \omega_{1} \gamma \quad (A.5) \]

The orientational correlation function \( \langle \phi(0) \phi(t) \rangle \), where \( \omega \) is the unit dipole vector, must now be derived from the form for \( \langle \phi(0) \phi(t) \rangle \), and can only be obtained in closed form for the case of planar orientation [10]. We have in this case:

\[ \langle \phi(0) \phi(t) \rangle = \exp \left( -B_{1} t \right) \left( \exp \left( -B_{2} t \right) - 1 \right), \]  

\[ \langle \phi(0) \phi(t) \rangle = \exp \left( -B_{1} t \right) \left( \exp \left( -B_{2} t \right) - 1 \right), \]  

\[ \gamma = 2 \Omega_{0} \omega_{0}^{2} \frac{\omega_{1}^{2}}{6} \frac{\omega_{2}^{2}}{4!} \cdots \]  

The most square angular velocity, \( \langle \phi(0) \phi(t) \rangle \), is for this case. For a spherical top having the same moment of inertia \( I \) as in the case, the form for \( \langle \phi(0) \phi(t) \rangle \) [30] is essentially identical to equation (A.7) but with \( \langle \phi(0) \phi(t) \rangle = 2 B_{2} t^{2} I \). It would then appear that equation (A.7) could be generalized to apply to spatial rotation of asymmetric tops by using the result \( \langle \phi(0) \phi(t) \rangle = 2 B_{2} t^{2} I \), where \( I \) is the reduced inertia:

\[ I = \omega_{0}^{2} \frac{\omega_{1}^{2}}{6} \frac{\omega_{2}^{2}}{4!} \cdots \]  

A similar argument may be applied to \( \langle \phi(0) \phi(t) \rangle \) in [4] to reveal the mean square torque \( \langle T(0) T(t) \rangle = 4 B_{2} t^{2} I \langle \phi(0) \phi(t) \rangle \) and hence the useful result:

\[ \langle T(0) T(t) \rangle = 4 B_{2} t^{2} I \langle \phi(0) \phi(t) \rangle \]  

At long times, (A.7) becomes purely empirical with a relaxation time the inverse of \( B_{2} / I \). Algebraic manipulation shows that \( C_{1} \) can be simplified to \( \kappa_{1} / \kappa_{0} \), which is the zeroth power term in (A.4). We thus have an important result:

\[ \nu_{12} = \nu_{1} \kappa_{1} I, \quad \kappa_{1} / \kappa_{0} \]  

More relevant to far infra-red behaviour is the ramanian velocity correlation function [12] which is the direct Fourier transform of the absorption spectrum, and is given analytically as (minus) the second derivative of (A.7). To simplify this function it is useful to work in reduced units of \( (K_{d} / I)^{1/3} \). Denoting reduced time by \( \tau \) we have [12]:

\[ \langle \phi(0) \phi(t) \rangle = \left[ \langle \phi(0) \phi(t) \rangle \right] \left[ \cos \beta \Omega_{0} (1 + K_{d} / I)^{1/3} \sin \beta t \exp \left( -\gamma \Omega_{0} (1 + I) \right) \right], \]  

\[ \langle \phi(0) \phi(t) \rangle = \left[ \langle \phi(0) \phi(t) \rangle \right] \left[ \cos \beta \Omega_{0} (1 + K_{d} / I)^{1/3} \sin \beta t \exp \left( -\gamma \Omega_{0} (1 + I) \right) \right], \]  

\[ \langle \phi(0) \phi(t) \rangle = \left[ \langle \phi(0) \phi(t) \rangle \right] \left[ \cos \beta \Omega_{0} (1 + K_{d} / I)^{1/3} \sin \beta t \exp \left( -\gamma \Omega_{0} (1 + I) \right) \right], \]  

\[ \langle \phi(0) \phi(t) \rangle = \left[ \langle \phi(0) \phi(t) \rangle \right] \left[ \cos \beta \Omega_{0} (1 + K_{d} / I)^{1/3} \sin \beta t \exp \left( -\gamma \Omega_{0} (1 + I) \right) \right], \]
where now all coefficients are reduced (but not barred for clarity). The parameters $K_0$, $K_1$, and $\gamma$ derive from the coefficients, in (A 6) are denoted by $K_0$, $K_1$, and $\gamma$.

The phenomenological model of isotropic oscillation described and analyzed by Calderwood and Coffey [11] consists of a central disc of moment of inertia $J_0$ harmonically bound to an annulus of inertia $J_1$ the latter undergoing brownian rotation through the influence of the surroundings. The characteristic fre-

quency of the disc librating within the annulus is $\omega_{\text{ann}}$ the motion giving rise to resonant absorption in the far infrared. The brownian rotation gives rise to relaxational behaviour with a characteristic time $\gamma$ determined by the friction coefficient $\nu = (K_0/\gamma)$. In applying this model to liquid systems $K_0$ is identified (in this case) with the solvent reduced-inertias. On intutive grounds $K_1$ is identified with $2\nu \varepsilon_{\text{int}}$, the far infrared peak position, $I_1$ is adjustable but larger than $I_0$ and $\gamma$ is determined from the observed Debye time. Solution of the equations of motion for this system lead [21, 6] to equations identical in form to (A 4), (A 7) and (A 11), with the substitutions:

$$K_1 \rightarrow K_1' \quad J_1 \rightarrow J_1' \quad \omega_{\text{ann}} \rightarrow \gamma \rightarrow \nu.$$  \hspace{1cm} (A 12)

The equations evolved from the Mori approximant or the isotropic oscillator theories are thus equivalent although the two approaches are distinct but complementary.

The form for the analytic spectrum may be derived in the manner of Calderwood and Coffey [11] via the complex polarizability:

$$\alpha(s) = \frac{K_0}{i \omega - s + i \nu} = \frac{K_0}{i \omega - s + \nu \varepsilon_{\text{int}}} (\varepsilon(s + i \nu)).$$

We have, in this work, derived the expression for the absorption spectrum to obtain [12] (in terms of the Mori parameters):

$$n(\omega) = \omega (K_0 + K_1 + K_2 + \gamma K_1 K_2)$$

$$= \omega \varepsilon_{\text{int}} (K_0 + K_1 + K_2) + \gamma K_1 K_2$$

$$\rightarrow \frac{K_0}{i \omega - s + \nu \varepsilon_{\text{int}}} (\varepsilon(s + i \nu))\left(\omega - B(s + i \nu)\right),$$

where $\varepsilon_{\text{int}}$, the refractive index is almost constant in the far infrared region for the diben solutions studied.

References