Attempts to explain the observed liquid phase far-infrared intensities of benzene, hexafluorobenzene and 1,3,5-trifluorobenzene in terms of point quadrupole-induced dipole interactions result in failure to account for the extremely different absorption strengths. We consider the possible sources of (gross) error in this (simple) approach and conclude that the use of distributed charges to compute site-site interactions (including short ranged attractive (CT) forces) would be necessary in order to predict such spectra for non-polar molecules. The power of far-infrared absorption spectroscopy in studying short ranged "ordering" and dynamics in liquids is emphasised.

1. Introduction

It is now firmly established that the far-infrared (FIR) absorption spectra of non-polar molecules [1,2] arise from the transient dipole moments induced during molecular encounters. Furthermore, in large numbers of experimental, theoretical and computer simulation studies [1] the use of an idealised point quadrupolar-polarisability induction mechanism successfully accounts for the observed line-shape. At the same time, such studies also provide a deeper understanding of the collective dynamics (from 2, 3 and 4 body interactions) which give rise to spectra in this region. More recent computer (MD) simulations [3] have suggested that the use of a distributed quadrupole is needed to obtain satisfactory agreement between experiment and theory plus simulation. This situation arises from the fact that at liquid densities molecules sizes are comparable with average intermolecular distances leading to a breakdown of the point quadrupole/point polarisability approximation. Furthermore, molecular shapes will dictate that the charge distribution is anisotropic. The aim of this paper is to demonstrate experimental evidence to support the claim that distributed charge models are required for three non-polar molecules: benzene (A), 1,3,5-trifluorobenzene (B) and hexafluorobenzene (C). These three molecules have been selected for two main reasons.

Firstly, their quadrupole moments \( \Theta \) have been carefully measured by different groups and consistent "well-known" values are available [5,6]. The values quoted in table 1 have been obtained by the induced-birefringence technique either for the gas or in solution at infinite dilution. These \( \Theta \) values are therefore more closely related to the "true" monomolecular property than the corresponding ones obtained from far-infrared spectra of the neat liquids. The latter are merely effective values as they are also

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1. Buckingham [4] suggested that these liquids should be investigated by FIR spectroscopy as they might provide information of importance in relation to distributed interaction models.

2. We have used the definition of eq. (1) of ref. [6].
Table 1
Experimental and molecular properties of the three liquids studied

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>C₆H₆ (A)</th>
<th>C₆F₃H₃ (B)</th>
<th>C₆F₆ (C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>quadrupole moment Θ</td>
<td>10⁶⁰ C m²</td>
<td>-30</td>
<td>3.1</td>
<td>31.7</td>
<td>[5,6]</td>
</tr>
<tr>
<td>polarisability α</td>
<td>10⁶⁰ C m² V⁻¹</td>
<td>11.5</td>
<td>11.35</td>
<td>11.65</td>
<td>[7]</td>
</tr>
<tr>
<td>molar concentration</td>
<td>mol dm⁻³</td>
<td>11.22</td>
<td>9.67</td>
<td>8.67</td>
<td></td>
</tr>
<tr>
<td>density</td>
<td>g cm⁻³</td>
<td>0.8765</td>
<td>1.277</td>
<td>1.612</td>
<td></td>
</tr>
<tr>
<td>molecular weight</td>
<td>10⁻³ kg mol⁻¹</td>
<td>78</td>
<td>132</td>
<td>186</td>
<td></td>
</tr>
<tr>
<td>L₁, σ</td>
<td>Å</td>
<td>5.27</td>
<td>?</td>
<td>?</td>
<td>[8]</td>
</tr>
<tr>
<td>L₁, ε/k</td>
<td>K</td>
<td>440</td>
<td>?</td>
<td>?</td>
<td>[8]</td>
</tr>
<tr>
<td>hard sphere diameter (from density)</td>
<td>Å</td>
<td>5.366</td>
<td>5.64</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>moment of inertia I₄ = 1/4I₄</td>
<td>10⁶⁶ kg m²</td>
<td>14.75</td>
<td>47.5</td>
<td>82.1</td>
<td></td>
</tr>
<tr>
<td>nB</td>
<td>1.501</td>
<td>1.414</td>
<td>1.377</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1/n₀)[(n₀² + 2)/3]²</td>
<td>1.339</td>
<td>1.257</td>
<td>1.225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α²θp²</td>
<td>10¹⁵⁴ mol² dm⁻⁶</td>
<td>15.0</td>
<td>0.12</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>∫₀^(∞)α(ν) dν (obs)</td>
<td>cm⁻²</td>
<td>776</td>
<td>266</td>
<td>76</td>
<td>this work</td>
</tr>
<tr>
<td>∫₀^(∞)α(ν) dν (two body interaction)</td>
<td>cm⁻²</td>
<td>1367 b)</td>
<td>1.22 a)</td>
<td>38 a)</td>
<td>[9,10]</td>
</tr>
<tr>
<td>∫₀^(∞)β(ν) dν</td>
<td>cm⁻²</td>
<td>405 a)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Calculated values using eqs. (2) and (4) (two body interaction only) with a hard sphere interaction potential U(r₁₂) (eq. (5)).

b) Calculated values using eqs. (2) and (4) (two body interaction only) with a Lennard-Jones interaction potential U(r₁₂) (eq. (5)).

affected by multibody interactions among the molecules of interest. Secondly, as is readily seen from table 1 the QMs of C₆H₆ and C₆F₆ are nearly the same (but of opposite sign), whereas that of C₆F₃H₃ is at least one order of magnitude lower. This reflects a tendency of highly electronegative fluorine atoms to localize electron density on going from C₆H₆ to C₆F₆. For C₆F₃H₃ the net effect of the difference in electronegativities of F and H atoms is to produce an almost exactly spherical charge distribution [5]. As a consequence the integrated intensities of the far-infrared spectra of these molecules are expected to be very different and might be expected to provide a check on the effectiveness of quadrupole-induced interactions in this spectral region.

2. Theoretical background

The infrared power absorption coefficient measured in the far infrared is

\[ α(ω) = \left( \frac{n^2 + 2}{3} \right)^2 \frac{4π^2}{3hcV} \frac{ω}{n(ω)} \times [1 - \exp(-βhω)] I(ω) \],

(1)

where \( I(ω) \) is the absorption cross section [11] and \( n(ω) \) the refractive index (as a function of frequency) (the other quantities having their usual meanings). The \( \left( \frac{n^2 + 2}{3} \right)^2 \) represents an average Polo–Wilson [12] type internal field correction. In the classical approximation (i.e. using \( 1 - \exp(-βhω) \approx hω/kT \) for \( hω ≪ kT \)) one obtains from eq. (1):

\[ \int_{-∞}^{∞} α(ω) n(ω) dω = \left( \frac{n^2 + 2}{3} \right)^2 \frac{4π^2}{3kTeV} M_2, \]

(2)

where

\[ M_2 = \int_{-∞}^{∞} ω^2 I(ω) dω \]

(3)

is the measured second spectral moment of the absor-
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For non-polar liquids $M_2$ can be calculated [13,14] assuming that the molecules interact through a quadrupole-polarisability mechanism, i.e. using a multipole model potential of lowest order. Nevertheless, such calculations present a formidable task and simplifying assumptions are inevitably used. For example, the simplest expression is obtained if one considers only two body interactions [13] of linear or symmetric top molecules having a scalar (point) polarisability and assumes that translational and rotational motions are uncoupled. One then obtains [14]

$$M_2 = \alpha^2 \Theta^2 \rho^2 \left( \frac{72\pi kT}{T_\perp} J_8 + 336\pi \frac{kT}{m_{12}} J_{10} \right),$$

(4)

where $\alpha$ and $\Theta$ are respectively the point (scalar) polarisability and quadrupole moment and $\rho$ is the number density. $I_\perp$ is the moment of inertia about the main symmetry axis and $m_{12}$ is the reduced mass of the interacting part of particles 1 and 2. The $J_n$ factors are given [14] by

$$J_n = \int_0^\infty dr_{12} \exp \left(-\frac{U(r_{12})}{kT} r_{12}^{-1} \right),$$

(5)

for an isotropic interaction potential $U(r_{12})$.

If the second moments ($M_2$) of the three liquids are assumed to be similar to each other then, under identical experimental conditions, the integrated intensity should be

$$S = \int \alpha(\omega) n(\omega) d\omega \cdot \left( \frac{n^2+2}{3} \right)^2 \alpha^2 \Theta^2 \rho^2$$

(6)

(if $n(\omega)$ is constant, or assumed to be so, in the region of interest then is may be used as constant on rhs – see table 1). It is immediately apparent from the parameters given in table 1 that $S$ should be similar for $C_6H_6$ and $C_6F_6$ and approximately two orders of magnitude lower for $C_6F_3H_3$.

3. Experimental

FIR spectra of the three neat liquids (Aldrich Chemicals, hplc grade) were measured at room temperature in 3 mm polyethylene cells using Bruker 113 V and Nicolet 20F interferometers. Data were collected in the range 10–250 cm$^{-1}$ (Bruker) or 20–400 cm$^{-1}$ (Nicolet) at a resolution of 2 or 4 cm$^{-1}$. Both DTGS and liquid helium cooled bolometric detectors were used. Typical data collection times were 2–5 min (details of experimental conditions have been published elsewhere [15]).

4. Results and discussion

The FIR spectra of the three liquids are presented on the same scale in fig. 1. They were obtained under identical conditions and are directly comparable. It is immediately obvious (despite complications due to an intense (internal mode) band for $C_6F_6$ and $C_6F_3H_3$ and combination bands at 118 and 170 cm$^{-1}$ for $C_6H_6$ [16] that the order of experimental intensities is $S_A > S_B > S_C$. The $S$ values obtained by planimetry (after correction for the effects of internal mode absorption) are reported in table 1 (and for benzene are found to be in reasonably good agreement with previous data [9,10]). The most striking factor is that $S_B$ (for $C_6F_3H_3$) is of the same order of magnitude as that for the other molecules in direct contrast to what is expected on the basis of the simple theoretical arguments presented above.

Any (or all!) of several reasons may be involved in explaining these quite unexpected results. The most

![Fig. 1. Far infrared spectra (at room temperature) of benzene (---), 1,3,5-trifluorobenzene (● ● ●), hexafluorobenzene (---).](image-url)
obvious one is that one must not omit the second spectral moment in eq. (6). We have performed a calculation of $M_2$, as we reported previously [15] using either a Lennard-Jones or a hard sphere isotropic potential. As may be seen from table 1 the LJ potential does produce an intensity roughly in agreement with experiment for $C_6H_6$ and $C_6F_6$ (as might be expected for a potential of this type [8]) but completely fails to account for the $C_6F_3H_3$ result. Certainly, however, the $S_A \gg S_C$ result is predicted by such a calculation and it appears likely that the full expression should be used. One might, of course, expect that a more realistic theoretical treatment of the second spectral moment is required, arguing that three and four body contributions should be included [1,3,13]. However, this omission seems unlikely to explain our data. Indeed, it has been demonstrated on a number of occasions [1,13] that three body interactions are likely to decrease the overall intensity (more than the expected increase due to four body terms). Furthermore, the correct order of magnitude obtained for $C_6H_6$ and $C_6F_6$ using a LJ potential would seem to rule out this type of explanation.

The most likely explanation of these apparent anomalies in the far-infrared intensities is probably connected with differences in the details of the molecular "ordering" and short ranged dynamics of these molecules – to which the observed spectral density is known to be sensitive [13]. Using the measured quadrupole moments and known dimer geometries [17] in the gas phase, Vrbanich and Ritchie [5] predict that the 1,3,5-trifluorobenzene will have a plane-parallel arrangement in the (averaged) liquid phase "structure" a symmetrically staggered arrangement of the F atoms (fig. 2). This picture was, of course, based on considerations of stabilization of local C–F dipoles on one molecule with C–H and C–C bond polarisabilities on a neighbouring molecule. Such an arrangement would also lead to the possibility of electron donor–acceptor interaction between the electron "rich" F atoms on one molecule and electron "poor" H atoms on another (more realistically via orbital overlap between C–F and C–H groups on neighbouring molecules). Such short range potentials have already been invoked to explain the spectroscopic behaviour [18–20] of mixtures of benzene and hexafluorobenzene. Short range interactions (via orbital overlap), which are not possible for either of the $C_6H_6$ or $C_6F_6$ pure liquids, would certainly enhance the far-infrared spectral density of $C_6F_6H_3$ in the 40–120 cm$^{-1}$ region (as found, for example, for the pyridine–I$_2$ donor/acceptor complex [21,22]. It would help to explain the "unexpected" behaviour of the $C_6F_3H_3$ (molecule B) when only point quadrupoles are considered (eq. (2) and (4)). These interactions could not, however, explain the discrepancy between the data for $C_6H_6$ and $C_6F_6$ (i.e. $S_A \approx S_C$ – table 1, even though $\Theta_A \approx \Theta_C$). In this case it would appear necessary to take account of distributed charges in order to describe the short and medium ranged potentials and their anisotropy. Furthermore, it may be necessary to include the effects of orientational correlation [15] which may be important at short times, over the extremely short distances represented in our spectra. It may be thought that these effects contribute only to the far wing of the spectrum ($> 100$ cm$^{-1}$) but recent computer simulations [3] for liquid CO$_2$ suggest that no clear distinction (in frequency space) may be made between contributions from different sources (for example, from different multipole moments).

5. Conclusions

To summarise, it seems clear that the far-infrared absorption of liquid 1,3,5-trifluorobenzene may not be explained on the basis of a point quadrupole-induced dipole fluctuation. It is necessary to pay attention to the shortcomings of this model and to take account of the details of the electronic charge distribution (which lead in the first instance to a very low
quadrupole moment) and consider the possibility of donor–acceptor interactions caused highly differing electronic structures of C–H and C–F bonds. This work nicely illustrates how such short ranged potentials may be probed using far-infrared spectroscopy.

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References