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SUBMILLIMETRE WAVES AND MOLECULAR MOTION IN FLUIDS AND SOLIDS

M. W. EVANS and G. J. EVANS
Edward Davies Chemical Laboratories, University College of Wales,
Aberystwyth SY23 1NE, U.K.

Abstract—The submillimetre spectrum gives direct evidence about the rotational and collisional motion of molecules in the gaseous state. It is natural therefore to use this spectral region to monitor the progressive inhibition of free rotation as the gas is compressed into the liquid and then the solid state. Examples which are discussed include compressed dipolar gases, quantised rotation in liquids, dilute solutions of water in organic solvents, disordered phases of solids, and induced absorption in compressed non-polar gases.

INTRODUCTION

The submillimetre region is rich in information about the rotational motions of molecules in the gaseous, liquid and plastic crystalline phases, and it is natural therefore to use the wavelengths to monitor the progressive inhibition of free rotation as the gas is compressed into the liquid. Although the total rotational absorption cross-section per molecule (A/N) should remain constant through various changes of phase it is affected by the internal field, short and long range dynamic correlations between molecules, and induced absorption.(2)

Therefore, to obtain information on the motion of the molecule's permanent dipole μ unhindered by electrodynamic factors, it is necessary to use in dilute solution a very strongly dipolar species of molecule. The effect of molecular dynamic cross-correlations can be exemplified for CH_2Cl_2,(1) where the maximum absorption frequency $\bar{\nu}_{max}$ is seen to shift to lower frequencies with CCl_4 dilution.(3) A/N remains constant on dilution so that induced absorption is negligible.

With these constraints the types of information available from broad-band submillimetre spectroscopy of the fluid and plastic crystalline phases is summarized in Table 1.

It is emphasized strongly that the far-infrared absorption is the high frequency part of the total zero–THz absorption expressed in terms of $\alpha(\omega)$, the power absorption coefficient and known as the Poley absorption for dipolar molecules. In this region the classical Debye equations produce a plateau absorption and are unusable.(9) It is needless to emphasize, therefore, that experimental data taken over the whole zero–THz range provide a difficult test for popular stochastic theories of the condensed planes of matter. For example, in the extreme of charge carrier hopping in semiconductors, or chalcogenide glasses,(10) the low frequency loss peak is virtually at zero frequency, but by general statistical considerations the Poley type absorption will remain as a secondary peak at submillimetre frequencies. In what follows we give a brief theoretical appraisal of the various types of absorption.

COMPRESSED DIPOLAR GASES

In the compressed, highly dipolar gases studied by Gerschel,(11) for example, the above point is illustrated by the fact that even though the loss and dispersion data are reproduced by an apparently semicircular Cole–Cole plot, the extrapolation to far-infrared frequencies shows up clearly the limits of an extended diffusion model such as *J*-diffusion,(12) which is barely capable of producing an $\alpha(\bar{\nu})$ in excess of the Debye plateau because the return to spectral transparency at high frequencies is theoretically much too slow. Thus, even at gas-like densities, this type of binary collision approxima-

Table 1. Information available from far-infrared broad bands of rotational and intermolecular significance in fluids and plastic crystals

Measurement		Model independent physical significance
A/N	(i)	Indicates presence of induced absorption[4]
	(ii)	Constancy with dilution indicates absence of short and long range dynamic correlations
	(iii)	Measure of molecular multipole moments in all phases
$\bar{\nu}_{max}$	(i)	Measurement of mean square torque[5]
	(ii)	Displacement from $J \rightarrow J+1$ (max), characteristic and useful feature of far-infrared studies of energy wells of libration[6]
	(iii)	Intercomparison of liquid and plastic crystalline phases especially useful in this context
$\alpha(\bar{\nu})$ (power absorption coefficient	(i)	Fourier transform related to $C_2(t) = \langle \dot{u}_i(0) \cdot \sum_{i \neq j} \dot{u}_j(t) \rangle$
	(ii)	In its ability to yield this information directly, accurately and in detail[7] the submillimetre region is an uniquely incisive probe into the molecular dynamics
	(iii)	$\alpha(\bar{\nu})$ very sensitive to short time details compared with the dielectric loss $\epsilon''(\omega)$, or the Rayleigh wing,[8] $\epsilon''(\omega)/\omega$

tion is not capable of reproducing loss and $\alpha(\bar{\nu})$ data *used in unison*. The advantage of submillimetre measurements is that they produce accurate data in the region corresponding to the far wings of bands observed, for example, with dipolarised Rayleigh scattering,[8] where the signal intensity is low and the data noisy, and, as with $\epsilon''(\omega)$ measurements in isolation of $\alpha(\omega)$, fitted easily with *very different* models of molecular motion.

QUANTISED ROTATION IN LIQUIDS HBr/SF$_6$

It is clear from the attempts to fit the broadened $J \rightarrow J+1$ loss observable[13] in *liquids* of this type in the far-infrared that the Poley absorption cannot be reproduced unless it is assured[12] that successive collisions are correlated (i.e. a dynamic memory is carried forward from one encounter to the next and beyond). In fact, the most conspicuous feature of the far-infrared, its shifted $\bar{\nu}_{max}$, demands this, otherwise the model absorption maximum remains static at the gas phase ($J \rightarrow J+1$) maximum. Thus the submillimetre is a *direct* way of evaluating stochastic molecular dynamical models.

DILUTE SOLUTIONS OF WATER IN ORGANIC SOLVENTS

Submillimetre data obtained by Pardoe and Gebbie[14] for very dilute solutions of water in organic solvents when analysed by a suitable approximation[15] of the Liouville equation of motion reveal that rotational diffusion is far from an adequate description of the water molecules reorienting *free from hydrogen bonding*. Using $\alpha(\omega)$ data, the estimated loss curves peak at *ca.* 200 cm^{-1} in stark contrast to the MHz frequency maximum of pure liquid water.[16] This is an illustration of the usefulness of submillimetre data in combination with theoretical ideas on liquid state dynamics used in a practical semi-empirical fashion. This methodology has been extended to liquids such as the monohalogenobenzenes, or tert butyl chloride, where the Poley absorption is more typical of the fluid state. For further details we refer to the original paper.[17] We emphasize here that A/N is usually in excess of the theoretical sum rule value(18) due to temporary, induced dipoles, internal field corrections, and electrodynamic and kinematic cross-correlations.

THE DISORDERED SOLID PHASE OF DIPOLAR HEXASUBSTITUTED BENZENES

Here the two features in the continuous zero–THz loss or absorption profile are separated by many decades of frequency. A model of planar itinerant torsional oscillation is suitable in this case since the molecules rotate about their hexad axes. The loss and $\alpha(\bar{\nu})$ curves may then be calculated as a continuous profile. In practice a distribution of librational frequencies exists, a consequence of the small but definitive differences between the depths of accessible potential energy wells. A broadening (as observed in the THz remnant of the Poley absorption), may be simulated by considering damping and collisional torques on a given molecule and its nearest neighbour cage, whose motion is considered theoretically as the libration of a rigid annulus.

The dielectric behaviour of disordered (amorphous) solids in general has been reviewed by Lewis,[10] where it was shown that the factor $\sigma(\omega) = \omega\epsilon''(\omega)$, the a.c. conductivity, varies according to an *apparently* simple law below *ca.* 10^{10} Hz. In dielectric terms the response in these solids is coming from the high side of a loss peak inaccessibly low in frequency. Theoretically, its description demands the unification of the concepts of charge carrier hopping and rigid dipole reorientation. Such models must also be realistic in the submillimetre region, where the Poley remnant still remains as it must on fundamental statistical grounds, and on grounds of actual observations made by Pardoe and Fleming in inorganic glasses. Much theoretical work remains to be done here.

INDUCED ABSORPTIONS IN THE SUBMILLIMETRE REGION

These are due in some measure, and are measurements of, the intermolecular potential energy.[4] Given a form for this they are alternatively useful for the estimation of the electrodynamic field in terms of multipole moments. For example, the broad, far-infrared collision induced spectrum of oxygen gas may be reproduced[20] using the idea of quadrupole ($J \rightarrow J+2$) and hexadecapolar ($J \rightarrow J+4$) induced dipole absorptions in bimolecular collisions of Lennard–Jones potentials. Alternatively, a $J \rightarrow J+2$ contour for compressed cyanogen[21] misfits the observed induced broad band due to the use of an oversimplified intermolecular potential. The Lennard–Jones function needs to be supplemented by a quadrupole–quadrupole term.

The compressed gas-to-liquid transition is accompanied by a decrease in the induced A/N. This reflects the change from two-body to multibody interactions in the fluid, which means that a molecule is surrounded more symmetrically by fields with a tendency to cancel each other's dipole inducing effect. Carrying the argument and observation into the plastic crystalline phase (e.g. of CBr$_4$) has the consequence[22] that the interaction-induced band is less intense than in the liquid, and that the rotation is apparently freer in the *solid*. Given a great deal of simulation by computer and theoretical development, this is a field which may be used fruitfully to elucidate the details of multi-body condensed-phase interactions.

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