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CROSS CORRELATION BETWEEN ROTATION AND TRANSLATION IN LIQUID MENTHOL

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ABSTRACT

The theory of rotating frame cross-correlation between molecular centre of mass linear velocity and molecular angular velocity recently reported [4,5] for the three-dimensional diffusion of the asymmetric top predicts that correlation between molecular rotation and translation is responsible for the difference in dynamical behaviour between enantiomers and their racemic mixture. In this paper experimental evidence is reported for liquid, supercooled, and rotator phase menthol of statistical correlation of this type being responsible for distinct features in the far-infra-red power absorption. These can be used, under carefully controlled conditions, to measure the strength of the correlation.

INTRODUCTION

Recent advances in computer simulation [1-5] have shown that there is a well defined difference between the dynamical properties of a left handed and right handed molecule, i.e. enantiomers. The way in which the rotation of a right handed molecule depends on its own centre of mass translation is different from the equivalent in the left hand, mirror image, molecule. It is known now that there are many ways in which this statistical cross correlation can occur, but every one of these so far identified [4,5] is the same for either enantiomer; except one. The dynamical difference between the R and S enantiomer resides exclusively in one off-diagonal element of the cross-correlation function:

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$$C_{tr} = \langle \underset{\sim}{v}(t)\underset{\sim}{\omega}^T(o)\rangle$$

and in that element alone.

Conversely, it follows that spectral, and in general physical, differences between the lab. frame properties of either enantiomer and their equivalents in the racemic mixture must provide information on the switching function described above. One of the easiest ways to see this is that were the properties of each enantiomer identical in all respects then there would be no difference in the properties of the racemic mixture of any kind, one would simply be making up a 50/50 solution of identical components. It is well known however, that the enantiomer and its racemic mixture are physically different, [6,7] but the explanation for this is almost never given in terms of the theory of diffusion. In other words it has been impossible to pinpoint analytically the reason for modifications in molecular dynamical behaviour due to chiral symmetry. In this respect the failure of the great theoretical advances made early in this century by Einstein, Debye, Langevin and many others has been complete. As far as we know, the theory of diffusion [8,9] still cannot account for our computer simulation results in this context, first published some years ago. [1,2] It is anticipated that the new rotating frame theory of three dimensional, asymmetric top diffusion will be able to provide the first analytical results in due course through the intermediary of analogue circuit simulation.

In this paper we present results for the far infra-red power absorption coefficient of liquid, supercooled liquid and rotator phase menthol which show conclusively that spectral features in this frequency region can vary greatly in amplitude and position, respectively the power absorption coefficient in neper cm^{-1}; and the wavenumber, $\bar{\nu}$, in cm^{-1}, between enantiomer and mixture. These differences have been isolated experimentally by careful choice of conditions, and it is reasonable to assume on the grounds of the evidence from computer simulation, that they are embodied exclusively in the switching function defined already. By taking the Fourier transform of these differences, a rotational velocity correlation function is obtained which is an indirect, but experimental, measure of the strength of rotation to translation cross correlation in menthol.

It is anticipated that computers will become rapidly more powerful and speedy, so that there is nothing to stop the technique of molecular dynamics computer simulation from being used to build up far infra-red spectra directly in future work.

EXPERIMENTAL

The power absorption coefficients were obtained as a function of frequency [8,9] using a Grubb-Parsons/N.P.L. "Cube" Mark III interferometer interfaced with a Research Machines 380Z microprocessor linked to a Honeywell 6080 mainframe at Aberystwyth. The interferograms were Fourier transformed using an alogirthm developed and adapted especially for this system. Aliasing effects were eliminated with filters and the system evacuated to eliminate background features due to water vapour and atmospheric material.

The optical configuration was identical for sample and background interferograms, the only difference being path length of absorber in the sample cells, situated outside the plano-convex lens of the Michelson interferometer. When comparing the power absorption of enantiomers and racemic mixture great care was taken in maintaining all conditions in the laboratory constant, so that a direct and accurate comparison of the respective far infra-red power absorption could be made. In this respect the temperature was controlled to within $\pm 1^{\circ}C$, all mirrors carefully dried, and silica gel used to remove spurious liquid water or water vapour.

The frequency dependence of the power absorption coefficient in the L enantiomer of menthol (IR,2S,5R) and of that in the racemic mixture was determined at 320 ± 1K; 311 ± 1K; 296 ± 1K; and at 293 ± 1 K. At these temperatures the two liquids (i.e. enantiomer and mixture) are in the following conditions.

i) At 320K both the L enantiomer and the mixture are ordinary liquids.

ii) At 311K the L enantiomer is a supercooled liquid, 7K below the normal melting point of 318K. The racemic mixture is still a regular liquid 10K above its normal melting point of 301K. Therefore the rotational and translational kinetic energy of both enantiomer and mixture is the same, but the intermolecular and configurational (potential) energy is clearly not the same. The total hamiltonian is therefore different and therefore the ensemble molecular dynamics as well.

iii) Further cooling to 296K causes a phase transition in the L enantiomer into what is probably a rotator phase, although no experimental evidence for this supposition seems to be available. On the other hand the racemic mixture can be supercooled to 296K, which is only about 5K below the normal melting point of the mixture. In contrast we are now about 22K below the normal melting point of the enantiomer, and it seems that the molecular ensemble can no longer at this temperature, support super-cooling. The kinetic energies (i.e. the temperature) are again the same, but the phase change means that the inter-molecular energies and forces are now quite different. Facts like these cannot be explained with the standard theoretical approach to molecular diffusion. [8,9] Our computer work [1-5] has shown that the phase change is caused by the different correlations in enantiomer and racemic mixture between a molecule's centre of mass translation and its own rotation. At 296K therefore we are in the ideal position to observe the spectral consequencies of this cross-correlation. If the L enantiomer is really in a rotator phase, then it is relatively free to rotate but translation of the molecular centre of mass becomes much less free than in the liquid. In the mixture in contrast, both rotation and translation are relatively easier, and it follows that the statistical cross-correlation between molecular rotation and molecular translation will be affected greatly by the phase change.

RESULTS AND DISCUSSION

Figure 1 shows that at 320 ± 1K the power absorption differences between

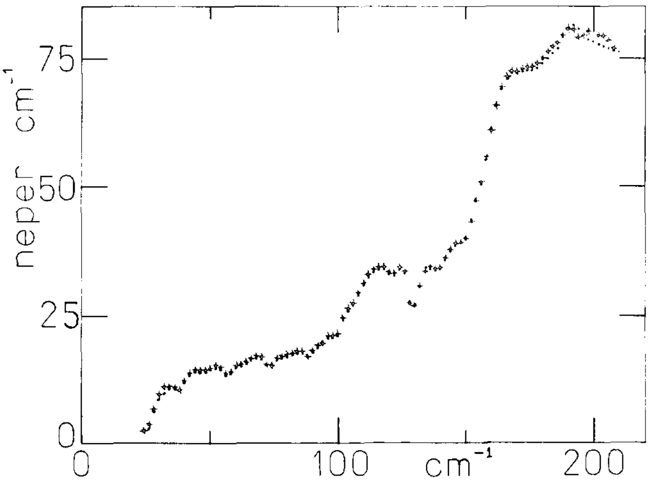

Fig. 1. Far infra-red power absorption of the L enantiomer (●) and racemic mixture (✧) of liquid menthol at 320 ± 1 K.

enantiomer and mixture are small, so that the effect of the switching off-diagonal element in C_{tr} does not work through into the laboratory frame in a clearly observable way. This is well known, insofar that it is well known [6,7,10] that the differences in physical properties, such as refractive index, between an enantiomer and its racemic mixture can be very small. We can take advantage of the result in Fig. 1 to demonstrate the accuracy of our observations both on the ordinate and abscissa, and also to demonstrate the chemical purity of the samples of menthol used in this work. In other words the differences in power absorption between the L enantiomer and mixture that begin to become observable in Fig. 2 are unlikely to be due to experimental uncertainty or impurity. The power absorptions in this work have been defined very accurately on the ordinate by the use of quartz windows and carefully defined sample path lengths.

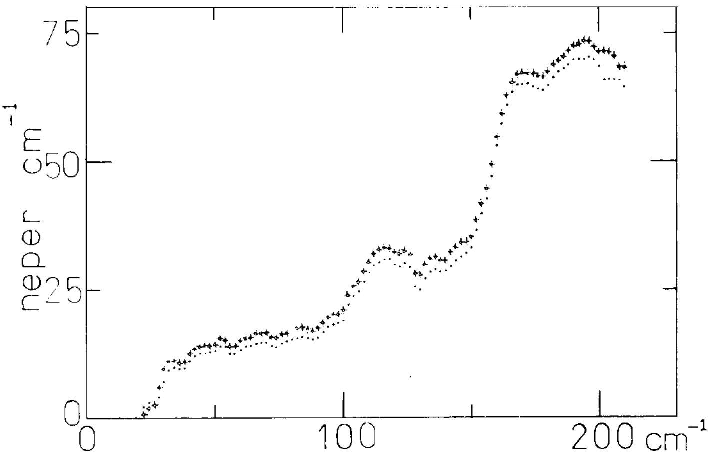

Fig. 2 As for Fig. 1, ✛ liquid racemic mixture at 311 ± 1 K;
● the L enantiomer in the supercooled liquid state at the same temperature.

In Fig. 2 the power absorption of the supercooled enantiomer begins to separate from that of the liquid mixture, but again the difference in frequency dependence of the power absorption is slight. If the two spectra were to be superimposed they would be indistinguishable within the experimental uncertainty.

However, in Fig. 3, at 296 K, the spectra of enantiomer and mixture are easily distinguishable. In these differences reside the information we seek concerning the off-diagonal switching elements of C_{tr} the cross-correlation function between rotation and translation. It is clear from the phonon mode at 75 cm^{-1} in the assumed rotator phase L enantiomer at 296 K that the molecular dynamics have become cooperative. In contrast the phonon mode is missing from the spectrum of the supercooled racemic mixture in this figure, which cannot therefore propagate sound in the same way. If these spectral differences are accepted as being due to the cross correlation in

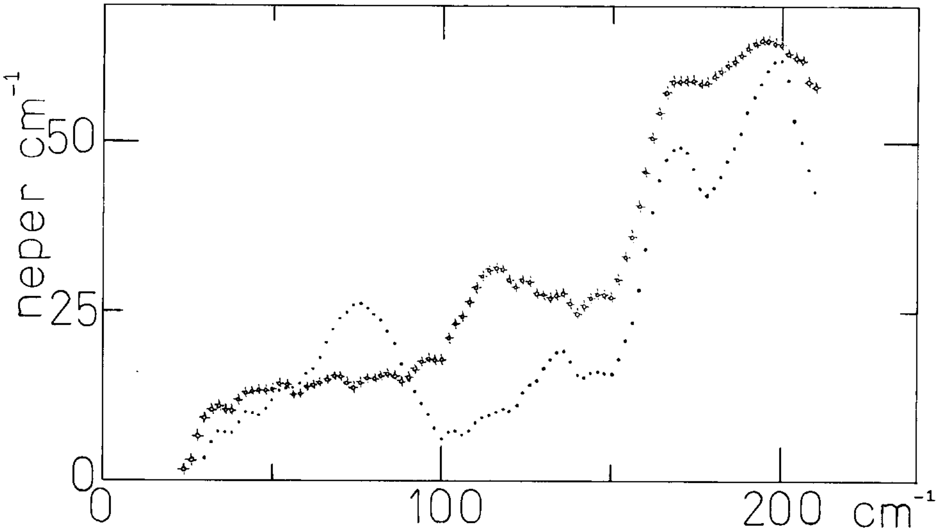

Fig. 3.

-✧- Racemic mixture in the supercooled liquid at 296 ± 1 K

● L enantiomer in the rotator phase at the same temperature.

which we are interested it follows that sound propagation itself is also a phenomenon that could be used to investigate rotation/translation coupling. There are various well known [11,12] spectral methods of doing this such as the study of the dispersion of hyper-sound or by taking advantage of the various light scattering techniques now available.

DATA ANALYSIS

By scaling and taking the difference between the power absorptions in the L enantiomer and the racemic mixture in Fig. 3 it is possible to derive by Fourier transformation a rotational velocity correlation function [8,9] which is illustrated in Fig. 4. This measures indirectly the role of translation/rotation cross correlation in the laboratory frame of reference. A much more detailed analysis will be possible with computer simulation, and by reference to the literature, [1-5] it can be shown that the off diagonal cross correlation function identified in this paper as the switching function will be measurable through a positive or negative time dependence in the L enantiomer, and that in the racemic mixture it will vanish. The technique of computer simulation is able, furthermore, to make the necessary transformation [1-5] to the principal molecular moment

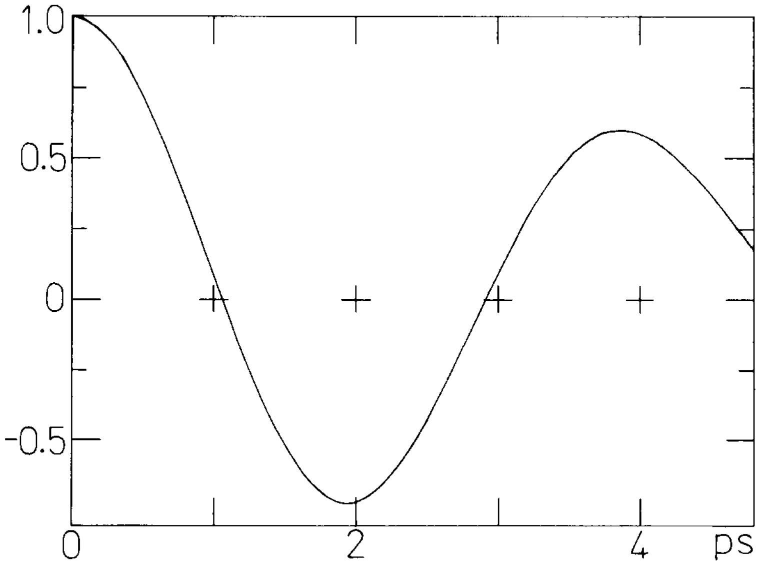

Fig. 4. Direct normalised Fourier transform of the phonon mode of the L enantiomer in the rotator phase at 296 K corrected for the equivalent absorption, shown in Fig. 3 of the racemic mixture at the same temperature.

of inertia frame in order to measure this time quantitatively. The trajectories generated during the simulation could also be used in principle to build the far infra-red spectrum. The only factor prohibiting this at present is lack of computer power.

CONCLUSIONS

The L enantiomer of menthol supports a phonon mode in the rotator phase which is absent in the supercooled racemic mixture at the same temperature. On the basis of previous results from computer simulation, this is taken to mean that the correlation between rotation and translation is primarily responsible for the significant spectral differences identified in this paper.

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REFERENCES

1 M.W. Evans, Phys. Rev. Lett., 50 (1983) 371

2 M.W. Evans, J. Chem. Soc., Chem. Comm., (3), (1983) 139

3 M.W. Evans, Phys. Rev., A, 30A, 2062 (1984) in press (1986)

4 M.W. Evans and G.J. Evans, Phys. Rev. Lett., 55 (1985) 818

5 M.W. Evans, Phys. Rev. Lett., 55 (1985) 1551; Phys. Rev. A, Rapid Comm., in press.

6 S.F. Mason, "Molecular Optical Activity and the Chiral Discrimination", (Cambridge Univ. Press, 1982).

7 J. Jacques, A. Collet and S.H. Willen, "Enantiomers, Racemates and Resolutions", (Wiley/Interscience, New York, 1981).

8 M.W. Evans, G.J. Evans, W.T. Coffey and P. Grigolini, "Molecular Dynamics and Theory of Broad Band Spectroscopy", (Wiley/Interscience, New York, 1982).

9 W.T. Coffey, M.W. Evans and P. Grigolini, "Molecular Diffusion", (Wiley/Interscience, New York, 1984).

10 "Handbook of Chemistry and Physics" (Chemical Rubber Co., Minneapolis, yearly).

11 G.J. Evans and M.W. Evans in vol 63 of "Advances in Chemical Physics", ed E.W. Evans, series ed I. Prigogine and S.A. Rice (Wiley/Interscience, New York, 1985).

12 E. Dickinson, Chem. Socl. Rev., 14 (1985) 421.