*Journal of Molecular Liquids*, 30 (1985) 157–163
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

# ROTATIONAL VELOCITY CORRELATION FUNCTIONS FROM THE PSEUDO-LATTICE FAR INFRA-RED PROFILES OF MOLECULAR LIQUIDS

M. W. EVANS

U.C.N.W., Bangor, Gwynedd, Gt. Britain

(Received 31 October 1984)

## ABSTRACT

The observation of absorption peaks in the far infra-red power absorption profiles of molecular liquids is analysed with the rotational velocity correlation function. These are oscillatory and much longer lived than their equivalents from "conventional" broad band data for molecular liquids in the far infra red.

## INTRODUCTION

The far infra red absorption [1] of dipolar and non-dipolar molecules in the liquid and condensed states of matter provides the most important evidence to date of collective, lattice like motion in the otherwise mobile liquid state or melt. This has been emphasised by the recent report of peaks in the far infra red power absorption profile of dipolar and non-dipolar molecular liquids using improved methods of interferometry [2,3]. In a series of theoretical papers the origin of these peaks has been explained using the reduced model theory (R.M.T.) of Grigolini [4]. The R.M.T. provides, essentially speaking, a rigorous framework for applying the fundamental equations of motion to molecular motion in the liquid state and a variety of other important rate processes. An example of the R.M.T. at work is the rigorous derivation of the well known and much used [1] itinerant oscillator model from the Liouville equation for the probability density function.

If these peaks, observed by G.J. Evans, are all real, they provide [5,6] one of the biggest challenges to the computer simulation method since the instigation of this technique by Rahman twenty years ago. This paper attempts to pave the way for the computer simulation of far infra-red peaks by taking some of the new data for chlorobenzene, acetone, chloroform and deuterated chloroform as a basis for Fourier transformation into the time domain to

0167-7322/85/$03.30

extract the rotational velocity correlation function. This function can also be built up by computer simulation given a big enough sample of molecules, enough time steps, and a fine enough time step interval.

## NUMERICAL METHOD

Some peaked spectral data were digitised every one wavenumber over the complete frequency range from zero to the upper limit of the absorption profile, inclusive of all peaks. The power absorption coefficient was extrapolated to zero on the high frequency side. The profile was then Fourier transformed [1] for the rotational velocity correlation function, normalised to unity at the time origin. This correlation function is essentially that of the total dipole moment $\underset{\sim}{\mathbf{m}}$, i.e.

$$\langle \dot{\underset{\sim}{\mathbf{m}}}(t) \cdot \dot{\underset{\sim}{\mathbf{m}}}(o) \rangle$$

In the first approximation this could be calculated as the equivalent auto-correlation function (A.C.F.)

$$\langle \dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o) \rangle$$

where $\underset{\sim}{\mu}$ is the dipole moment of one molecule of the complete assembly. The analytical work (using R.M.T.) [7] has shown that far infra-red power absorption profiles from the analytically calculated A.C.F. $\langle \dot{\underset{\sim}{\mu}}(t) \cdot \dot{\underset{\sim}{\mu}}(o) \rangle$ also shows peaks [8]. Therefore there is a sound basis for them in the equations of motion [4,9] and they ought to be observable, under the right conditions, with computer simulation.

The cosine Fourier transform was evaluated with a very simple Simpson's rule algorithm written by the author. It has been checked carefully that this algorithm produces the same results as the Cooley-Tukey fast Fourier transform algorithm when evaluating time-correlation functions from far infra-red frequency domain data [10]. (The reverse procedure - that of Fourier transforming correlation functions for far infra-red spectra - is considerably more troublesome due to the oscillatory nature of the C.F. This is true even with the most sophisticated F.T. software and therefore this point should be remembered when using computer simulation to look for far infra red peaks above the "traditional" or "classical" broad band [1].)

The spectral data were digitised (sampled) at an unusually closely spaced wavenumber interval of 1 $cm^{-1}$. This puts an upper bound of 8.4 ps on the validity of the computed Fourier transform, the experimental rotational velocity correlation function. The importance of this point lies in the fact that the effect of peak structure in the frequency domain data on the correlation function is to introduce long lived oscillations into the correlation function, and therefore to increase the lifetime of dynamic correlation dramatically in comparison with broad band data of the "conventional" type [1]. (The clearly defined positions of these peaks on the frequency scale also means that it becomes possible to resolve modes of motion in the liquid state akin to the lattice-mode analysis of far infra-red collective modes in the crystalline solid. The far infra-red therefore gives us a new insight into the liquid and molten states of matter).

## RESULTS AND DISCUSSION

The results are illustrated by means of figures showing the data observed by G. J. Evans and the computed rotational velocity correlation functions. For liquid chlorobenzene (Fig. 1), two Fourier transforms have been made, one of the complete profile, and one of the individual peaks at 38 $cm^{-1}$. In both cases the R.V.C.F. is long lived in comparison with those from 'conventional' broad band data, illustrated, for example, in ref [1] , Chapter 1.

Both correlation functions are oscillatory in nature, reflecting the fact that the correlation persists over a far longer period of time than hitherto suspected from broad band data alone. If the peaks reported by G. J. Evans are all real, molecular dynamics in the liquid state can be modelled closely on the lattice modes observable in the molecular crystalline state in the far infra-red, with the important difference that there are more peaks in the liquid than in the crystalline solid. This can be explained by R.M.T. as described elsewhere [7]. The highly oscillatory nature of the correlation function from the 38 $cm^{-1}$ peak is reminiscent of crystal like structure. In the ideal lattice mode, such behaviour would persist indefinitely, and the correlation function would be a perfect cosine.

Therefore in order to simulate peaks by computer in the far infra-red power absorption of molecular liquids, it is necessary to go out to 8.0 ps, at least, in the simulation, using a minimum of about 15,000 time steps. It would also be necessary to take a sample of molecules large enough to account accurately for the presence of lattice modes, without introducing artificial effects due to periodic boundary conditions. It would probably be best to start with water, where there are several Evans peaks in the region up to about 300 $cm^{-1}$. The time step itself should be kept to a minimum, because this is the sampling interval of the Fourier transform into the peaked frequency domain.

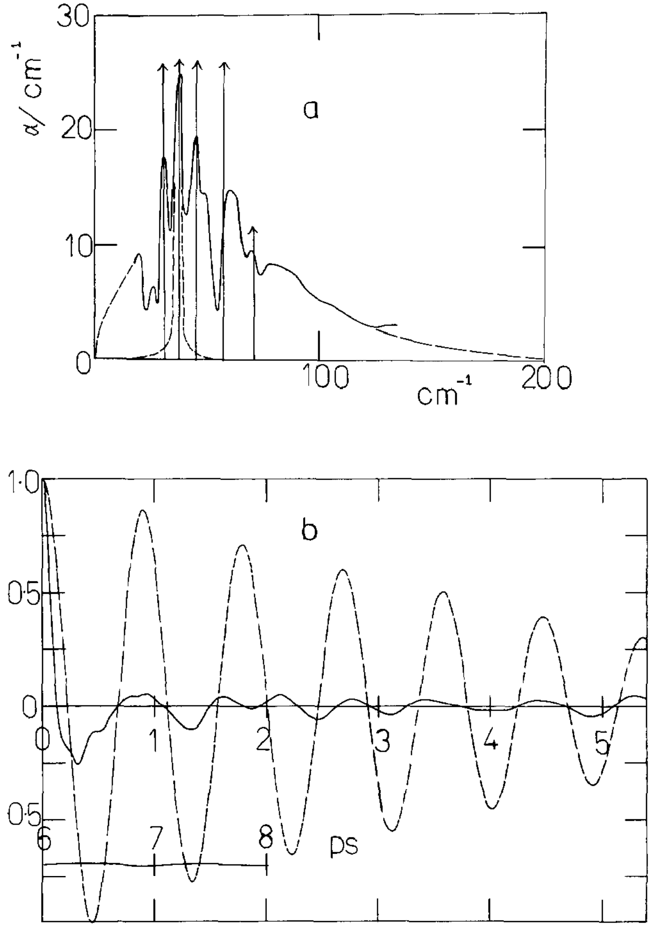

Fig. 1 a) Peaked far infra-red spectrum of liquid chloroform, due to G.J.Evans. Known lattice modes in the molecular crystalline state of chlorobenzene. These match five of the liquid peaks. b) Cosine Fourier transform of the complete far infra-red band, including all the peaks visible in Fig. 1a and using the extrapolations illustrated in that figure with dashed lines.

- - - - cosine Fourier transform of the 38 $cm^{-1}$ peak, extrapolated in Fig.1a.

The exercise is repeated in Fig. 2 for acetone, where, according to G. J. Evans, peaks are observable as shown in Fig. 2a. The rotational velocity correlation function is oscillatory about the time axis, but less so than for chlorobenzene. It will be necessary therefore to discriminate carefully in the computer simulation between R.V.C.F.'s that produce broad bands when Fourier transformed and those that produce peaks, and to carry out the transform itself with great care to prevent spurious peaks appearing in the spectrum.

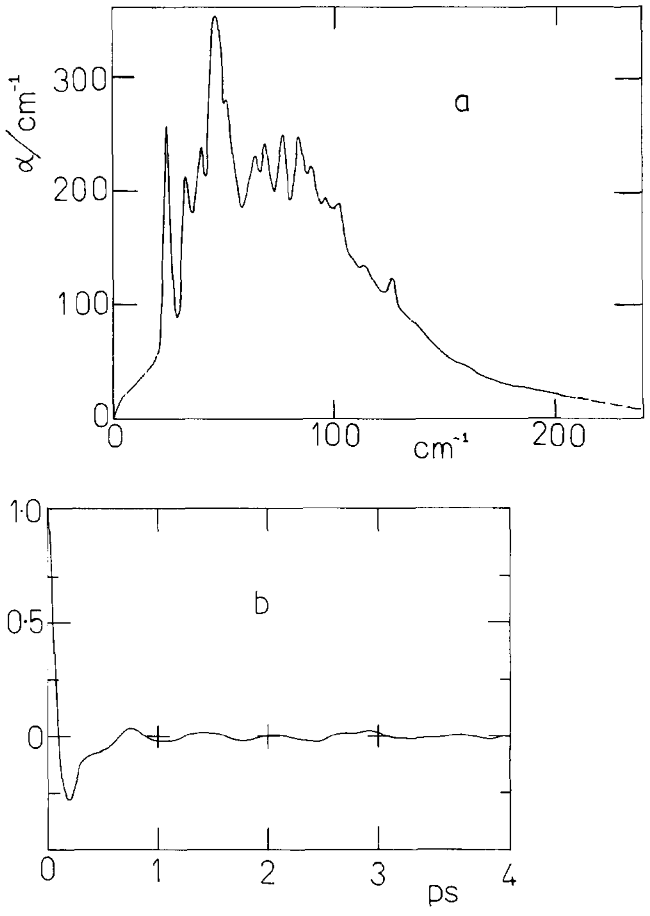

Fig. 2 a) peaked far infra-red spectrum of liquid acetone, due to G.J. Evans. b) cosine Fourier transform of the complete profile of Fig. 2a. The oscillations persist to about 4.0 ps, but are not much more pronounced than those typical of a broad band [1]. Therefore careful computer simulation work would be needed to see the far infra-red peaks properly.

In Fig 3. the peaks reported by G. J. Evans in liquid chloroform and deuterated chloroform at room T and P have been Fourier transformed to provide the oscillatory correlation functions shown in Fig. 3b. The correlation function for protonated chloroform is slightly the less oscillatory because the peaks in the power absorption are more evenly distributed. Again the rotational velocity correlation functions exist out to at least 6.0 ps or more, i.e. are much longer lived than those from conventional broad bands. There is a single lattice mode observable [11] in molecular crystalline protonated chloroform at 53 $cm^{-1}$ the liquid data by G. J. Evans shows that this single

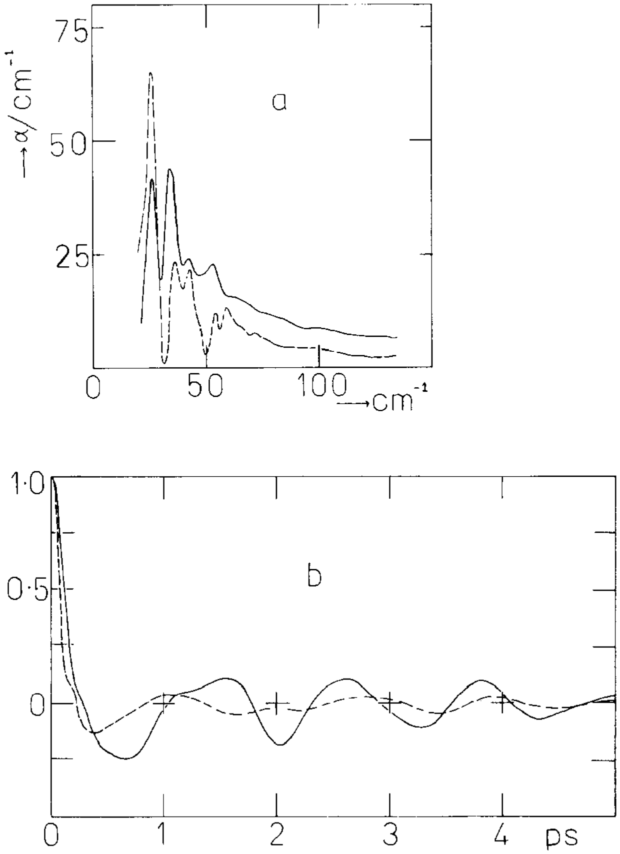

Fig. 3. a) Far infra-red spectrum of liquid chloroform of deuterated chloroform. These spectra are due to G.J. Evans, using the author's spectrometer on loan to Aberystwyth Chemistry Department.
b) The equivalent cosine Fourier transforms, (—— deuterated,
- - - - undeuterated).

lattice mode is supplemented in the molecular liquid by several satellite peaks at lower frequencies (Fig. 3a). It is significant that the relative intensities of these peaks change upon deuteriation, but their positions do not. This argues for their existence, and against the possibility that they could be artifacts of the observational method.

Finally we mention that the existence of satellite peaks in the molecular liquid can be explained [7] on the basis of R.M.T., using, for example the important itinerant oscillator which can be derived rigorously from the Liouville equation [1,4,9]. The number and relative intensity of far infra-red satellite peaks depend on the type of effective intermolecular potential used in the itinerant oscillator or other R.M.T. - allowed equations of motion.

## ACKNOWLEDGEMENTS

The University of Wales is acknowledged for a temporary Fellowship. Dr. G. J. Evans is thanked for copies of some of his new spectra, some of which are illustrated in this paper. These spectra were obtained on the author's N.P.L./Grubb-Parsons cube interferometer on loan to U.C.W., Aberystwyth, Chemistry Department.

## REFERENCES

1 M.W. Evans, G.J. Evans, W.T. Coffey and P. Grigolini, Molecular Dynamics, Wiley/Interscience, New York, (1982), Chapter 4.

2 G.J. Evans, J. Mol. Liq. In press.

3 G.J. Evans, J. Chem. Soc., Faraday Trans. 2, submitted, 79 (1983) 547.

4 P. Grigolini, in 'Memory Function Approach To Stochastic Problems In Condensed Matter', A Special Issue of 'Advances In Chemical Physics'. Ed. M.W. Evans, P. Grigolini, and G. Pastori-Parravicini, In press. Gen. Ed. Prigogine and Rice, Wiley/Interscience, New York, (1985).

5 G.J. Evans, A Review in Ref (4), Vol 2, Ed. M.W. Evans, In Press, (1985).

6 G.J. Evans and M.W. Evans, J. Chem. Soc., Chem. Commun., p. 267 (1978). In this paper many far infra-red resonance peaks were observed in a newmatic liquid crystal aligned with an electric field.

7 M.W. Evans, P. Grigolini, M. Leoncini and B. Zambon, Four papers in J. Mol. Liquids, Submitted for publication.

8 M.W. Evans, Phys. Scripta, 30 (1984) 222.

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

10 M.W. Evans, J. Chem. Soc., Faraday Trans 2, 71 (1975) 843.

11 G.W. Chantry, 'Submillimetre spectroscopy', Academic, (1971).