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COMPUTER SIMULATION OF FAR INFRA-RED PEAKS IN LIQUID AND GLASSY CH_2Cl_2

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ABSTRACT

The observation of spectral structure in the far infra-red power absorption coefficient of molecular liquids is supported in CH_2Cl_2 by a molecular dynamics computer simulation.

INTRODUCTION

This brief communication reports the first computer simulation of far infrared liquid peaks (in supercooled and superheated CH_2Cl_2), and lends qualitative support both for their recent spectral observation by G J Evans [1], using Michelson interferometry, and for an analytical explanation, using the theory of molecular diffusion in the low friction limit. [2,5]

The appearance of these peaks is important for our basic understanding of the molecular dynamics and interactions in the liquid state, and therefore for reaction rates and other dependent phenomena in physical and physical organic chemistry. They were first reported [6] in the nematogen n heptyl n'cyano biphenyl (7CB) aligned with an electric field, and have recently been confirmed as a feature of far infrared absorption in both dipolar and non-dipolar liquids at field-off equilibrium.

They occur in the vicinity of the well-known far infrared lattice modes in the equivalent molecular crystals, but appear to be more numerous in the liquid [1]. This can be understood with the theory of molecular diffusion and chemical reactions in cosine potential wells [7], or more generally, wells with arbitrary periodic symmetry built up with a Fourier summation [8]. Conversely, therefore, the far infrared liquid peaks provide us with detailed information on the intermolecular potential in the molecular

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liquid state.

It is shown in this note that a careful computer simulation of liquid dichloromethane over a wide range of thermodynamic conditions (pressure and temperature) produces a number of sharp far infrared peaks (by careful numerical Fourier transformation of the appropriate rotational velocity autocorrelation function) provided this is computed out to long enough times from the origin t=0.

Algorithm and Numerical Methods

The available knowledge of the intermolecular potential of CH_2Cl_2 is sparse [9], and open to improvement. The representation used for this work aims to show that an acceptable (contemporary) CH_2Cl_2 pair potential provides qualitative evidence for far infrared liquid state peaks. This is a 3 x 3 site-site potential. Each site-site term is comprised of Lennard-Jones and charge-charge components, defined by:

$\sigma(Cl\text{-}Cl) = 3.35$ Å; $\varepsilon/k(Cl\text{-}Cl) = 173.5$ K;

$\sigma(CH_2\text{-}CH_2) = 3.96$ Å; $\varepsilon/k(CH_2\text{-}CH_2) = 70.5$ K;

$q_{Cl} = -0151|e|$ and $q_{CH_2} = +0.302|e|$

This model provides a mean potential energy of -6.2 kcal $mole^{-1}$ at 287 K (molar volume = 62.92 $cm^3 mole^{-1}$). This compares [10] with experimental measurements of -6.2 kcal $mole^{-1}$ to -6.3 kcal $mole^{-1}$.

The rotational velocity autocorrelation functions [9] (r.v.c.f.'s) $\langle \dot{\underset{\sim}{e}}_i(t) . \dot{\underset{\sim}{e}}_i(0) \rangle / \langle \dot{e}^2_i \rangle$ were then evaluated at equilibrium in the supercooled condition, at room temperature, and in the superheated condition under kbars of hydrostatic pressure. An innovation of this work is to take samples of about 900 records (2700 time steps of 5×10^{-15} secs each), and to use these data to compute the r.v.c.f.'s right out from the origin (t=0) to 6.0 ps (400 records). This means that the resolution of the Fourier transformation (the far infrared power absorption) is increased and so also are the chances of seeing fine structure in this spectrum - the far infrared peaks.

Fourier Transform Method

Great care is necessary [11,12] to avoid introducing spurious numerical features into the far infrared spectrum equivalent to the r.v.c.f., and therefore the techniques of double-side Fourier transformation were used [11], as in commercial interferometric spectrometers such as the Grubb-Parsons/NPL "Cube". Spurious oscillations in the spectrum due to finite integration interval were removed with a window function, a standard procedure in Fourier transform spectroscopy. [11,12]

RESULTS AND DISCUSSION

The results are typified (fig. 1) by a rotational velocity a.c.f.

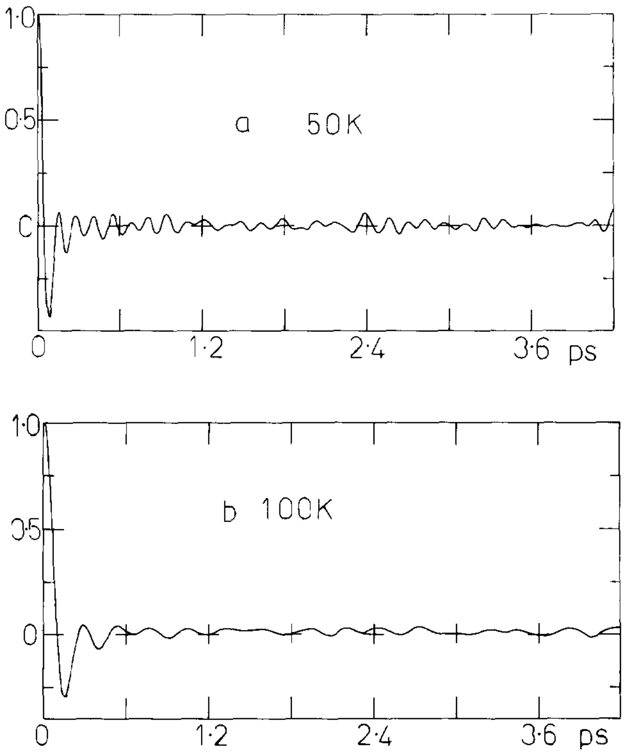

Fig. 1. Rotational velocity a.c.f. $\langle \dot{\underset{\sim}{e}}_1(t) . \dot{\underset{\sim}{e}}_1(o) \rangle / \langle \dot{e}_1^{\,2}(o) \rangle$ at a) 100 K; b) 50 K. $\underset{\sim}{e}_1$ is a unit vector in the principal moment of inertia frame of the CH_2Cl_2 molecule.

$\langle \underset{\sim}{\dot{e}}_1(t).\underset{\sim}{\dot{e}}_1(o)\rangle/\langle \dot{e}_1^{\,2}\rangle$ in supercooled or glassy CH_2Cl_2 at 50 K, molar volume = 3.9×10^{-5} m^3/mole; and at 100 K, molar volume = 5.0×10^{-5} m^3/mole. It can be seen that these are oscillatory in the long time tail, out to the 6.0 ps limit. These long-tail oscillations [9,13] are qualitatively similar to the experimentally derived r.v.c.f.'s from peaked spectra in the far infrared, and reported elsewhere. [14,15] The Fourier transforms of these two r.v.c.f.'s are shown in fig. (2) - the far infrared power absorption spectra. The spectra are clearly full of detail, which can be traced at both temperatures, and is not, therefore, arbitrarily distributed on the frequency scale, i.e. is a real spectral outcome of the CH_2Cl_2 molecular dynamics computer simulation.

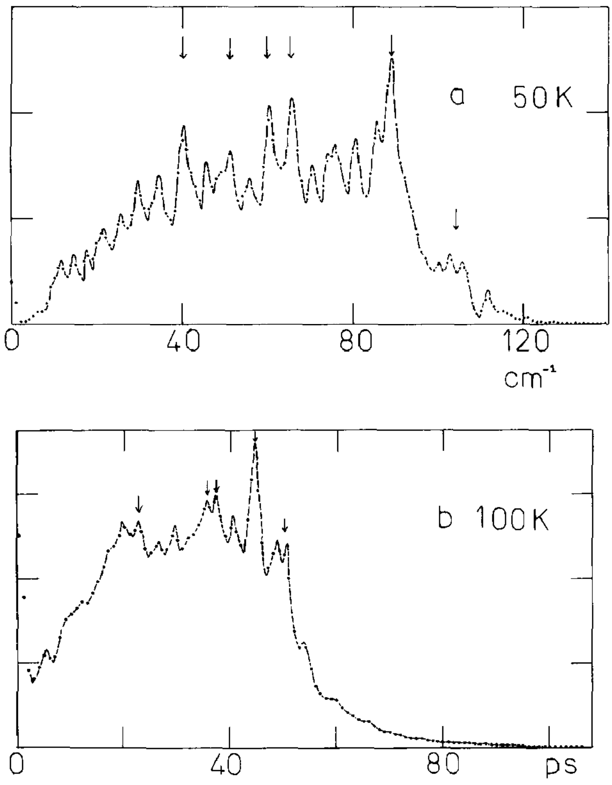

Fig. 2. 800 point double sided Fourier transforms of the r.v.c.f.'s in figs 2(a) and 2(b). The arrows mark groups of peaks that appear at both temperatures at the same frequencies relative to each other.

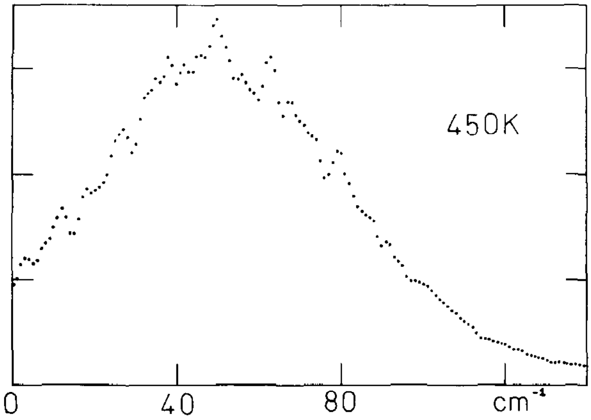

Fig. 3. Far infrared power absorption of superheated CH_2Cl_2 at 450 K under kbar of external pressure.

At the opposite end of the scale in thermodynamic terms, fig. (3) shows that small tail oscillations and far infrared structural detail exist in the "superheated" CH_2Cl_2 liquid at 450 K; molar volume = 4.15×10^{-5} m^3/mole: equivalent to kbar of external hydrostatic pressure. We have checked that this is also the case at room temperature and density.

Therefore, this provides qualitative numerical evidence for the existence of far infrared structure for the 3 site model used for the CH_2Cl_2 intermolecular potential. This supports the recent observations [1] of such structure in a number of dipolar and non-dipolar molecular liquids, and the previous report [6,9] of numerous far infrared peaks in nematic 7CB aligned with electric fields.

The importance of this work is that the so-called "broad band Poley" absorption of liquids in the far infrared can now be resolved, for the first time, into its individual components, providing unique insight into the intermolecular pair potential and the nature of the liquid state in general. [16,17] This is of obvious importance also for our understanding of chemical reaction rates in solution.

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