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MOLECULAR DYNAMICS OF CH_2Cl_2: TEMPERATURE DEPENDENCES OF THE FAR INFRA-RED SPECTRUM.

PART 1: EXPERIMENTAL AND SIMULATION

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ABSTRACT

The temperature dependence of the rotational diffusion in liquid CH_2Cl_2 has been measured in the far infra-red from 10 to 220 cm^{-1} and 177K to 313K (f.p. to b.p. at 1bar). The results are interpreted at 177K and 293K with a molecular dynamics simulation using a 5 x 5 atom-atom potential with charge-charge electrodynamics. The simulation reproduces the basic features of the spectra but some experimental details of the dependency of $\tilde{\nu}_{max}$, the far infra-red peak frequency, on temperature is not followed by the simulation. The situation can be improved by accurately measuring the second dielectric virial coefficient B_ϵ of CH_2Cl_2 vapour in order to improve our knowledge of the intermolecular pair potential.

INTRODUCTION

In this paper we report the far infra-red spectra of liquid methylene chloride at 10K intervals from the freezing to the boiling point at 1bar. This forms part of the EMLG pilot project (refs.1-3) for CH_2Cl_2. The results are compared with a molecular dynamics simulation at state points 177K, 1bar and 293K, 1bar using a 5 x 5 atom-atom plus charge-charge potential described fully elsewhere (ref.11). The purpose of the paper is to investigate the extent to which the present molecular dynamics simulation (ref.4) is capable of following the more subtle details of the spectra which are known to reflect the short time details of molecular diffusion, details which are not always adequately described by phenomenological theories such as the classical ones of Langevin or Debye or the more recent ones of Gordon and Coffey and Calderwood.

A great advantage of molecular dynamics simulation is that it enables us to isolate various aspects of the dynamics and to investigate the consequence of

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neglecting, for example, cross correlations on the calculated spectrum. We have a control over the physics that, if used carefully, can provide us with information that is not accessible from current phenomenological theory or experimentation. Of course, the technique, particularly its application to those polyatomic molecular liquids, is still in its early infancy and we presently make assumptions that are obvious over-simplifications. We do, for example, neglect theoretically the role of polarisability (ref.5), so that collision induced absorption (ref.6) is not accounted for. The next stage of the evolution will indeed be to incorporate such effects. However, the present simulation does enable us to build up a cross-correlation function and thereby to test directly the macro-micro theorems (ref.7) of phenomenological theory. We will do this by comparison both with simulation and experiment. In this way we can investigate the basis of multibody dielectric theory, which is usually based on the consideration of spherical cavity regions of the dielectric under consideration (ref.8). The far infra-red spectrum is related only indirectly to dynamical auto-correlation functions, these being strict terms on outcome of fluctuations in the macroscopic polarisation. This makes the calculation of both the intensity cross-section and bandshape of a far infra-red spectrum very difficult and the simulation method at present is one of the most powerful and detailed techniques available, given some necessary checks on the form of the pair potential used. A particularly useful check is the measurement and calculation of second dielectric virial coefficient (ref.9) B_ϵ which we consider at the end of the paper.

EXPERIMENTAL

The spectra were obtained using Michelson interferometry (ref.10) with a variety of accessories designed to optimise the quality of the measured spectra. Temperature control is $\pm$ 2K, achieved with a cell specially designed for the purpose of optimising the accuracy of both $\bar{\nu}$, the wavenumber, and $\alpha(\bar{\nu})$, the power absorption coefficient.

RESULTS

The spectra at 10K intervals up to 298K from 178K are illustrated in comparison in Fig. 1. The absorptions near the freezing and melting points respectively are shown in Figs.2 and 3. The variation of peak position with temperature is sketched in Fig.4 and that of the peak absorption α_{max} in Fig.5. The latter apparently minimises at about 223K, indicating a complicated subsidiary mechanism of molecular interaction in the region approaching the freezing point.

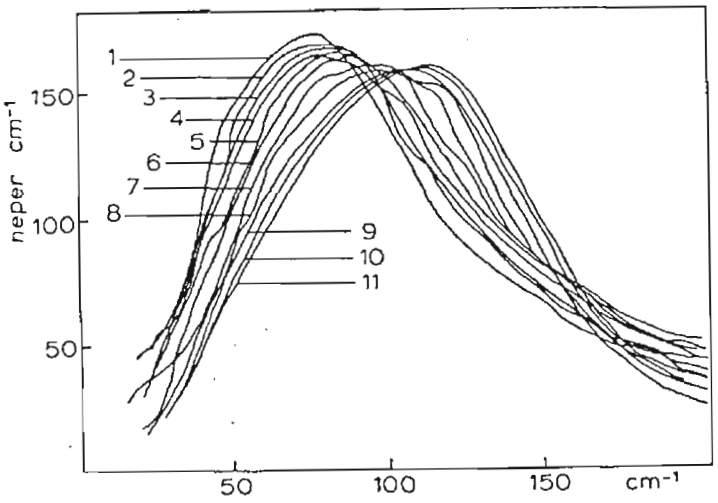

Fig.1. Power absorption coefficient $\alpha(\tilde{\nu})$ (neper cm^{-1}) vs. $\tilde{\nu}$ (cm^{-1}) for pure liquid dichloromethane. Curves as follows: I) 298K; II) 288K; III 278K; IV) 268K; V) 258K; VI) 248K; VII 238K; VIII 228K; IX) 218K; X) 208K; XI 198K. Note the intensity drop at 238K.
Ordinate: $\alpha(\tilde{\nu})$ (neper cm^{-1}); Abscissa: $\tilde{\nu}$/cm^{-1}.

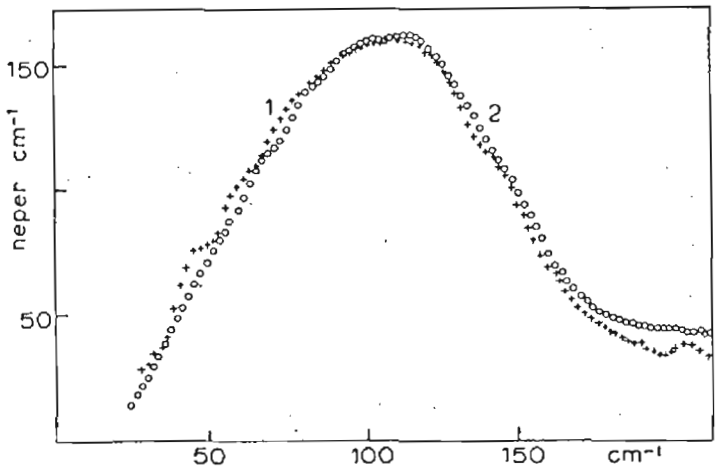

Fig.2. Absorption of liquid CH_2Cl_2 near the freezing point. I) 188K; II) 178K.
Ordinate: $\alpha(\tilde{\nu})$ (neper cm^{-1}): Abscissa: $\tilde{\nu}$ /cm^{-1}.

DISCUSSION

When dealing with spectra such as these which have their origin in the roto-translation of interacting molecules it is not strictly valid to interpret them in isolation of the increasingly wide range of data available from other spectral sources (refs. 1-3). In this particular case the dielectric measurements in the range up to 10 cm^{-1} (our low frequency limit) are needed, but are presently not available. It is anticipated that these gaps in the data will be rectified during the course of the EMLG project. Indeed, the whole intention of the project is to

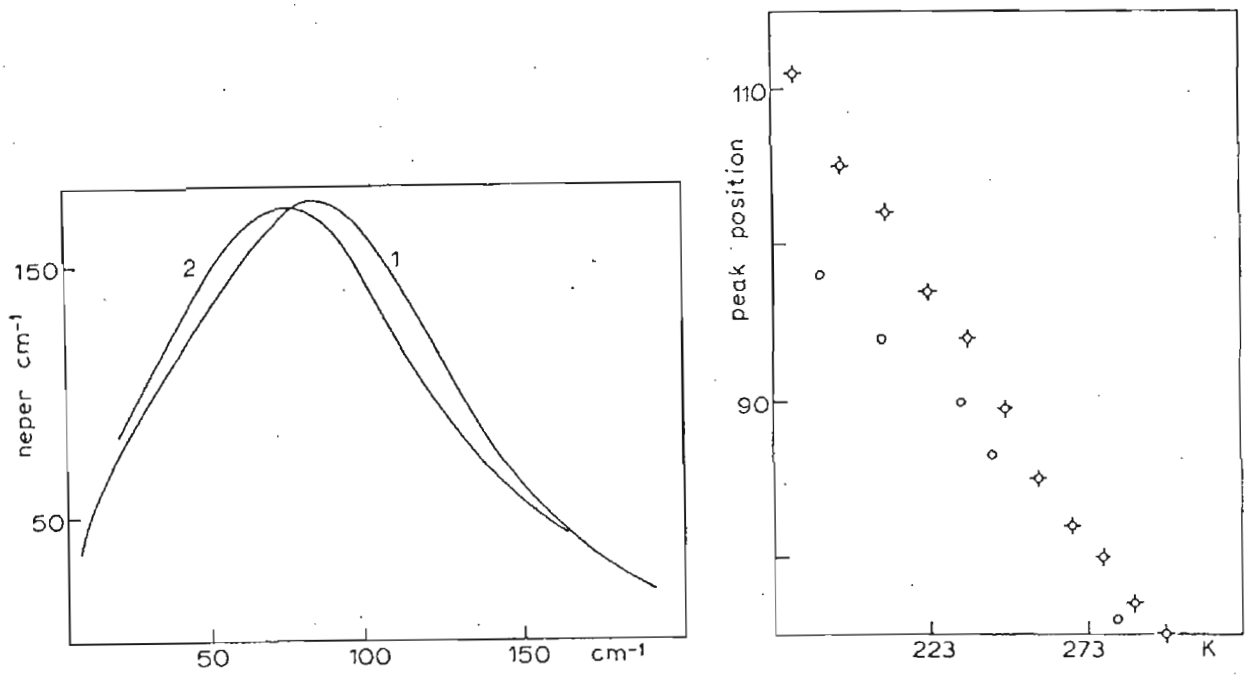

Fig.3. Absorption of liquid CH_2Cl_2 up to the boiling point. I) 308K; II) 312K.
Ordinate: $\alpha(\tilde{\nu})$ (neper cm^{-1}); Abscissa: $\tilde{\nu}$/cm^{-1}

Fig.4. Variation of peak position with temperature.
Ordinate: peak position, $\tilde{\nu}_{max}$; Abscissa: temp. (°K).

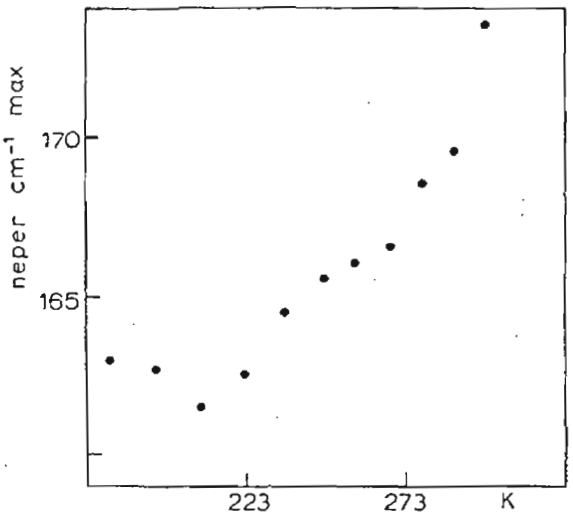

Fig.5. Variation of maximum absorption, α_{max} (neper cm^{-1}) with temperature. Note the minimum at about 220K.
Ordinate: max. abs., α_{max} (neper cm^{-1}); Abscissa: temp. (°C)

coordinate research so that full sets of experimental data using all of the current spectroscopies become available for the carefully selected liquids. The data are then to be compared with the simulation and theoretical techniques presently

available. In this present paper we make a first attempt to compare the results of experiment and simulation under the prescribed conditions of the proposed scheme of research. As more results become available our analysis will be extended to the other spectroscopies. We can use our molecular dynamics simulation of a given pair-potential to compute a wide variety of spectra and equilibrium thermodynamic averages. If it becomes possible to transfer the parameters in the pair potential from liquid to liquid then the basis of a predictive theory of the liquid state becomes available. The phenomenological theory is, by definition, purely descriptive. In contrast we have many independent checks on the form of the pair potential in a molecular dynamics simulation, among which may be listed the second dielectric virial, heat of sublimation, crystal structure, ab initio calculation and so on. If a certain pair potential is useful in the molecular crystal and (imperfect) gas then it may be used, via molecular dynamics simulation to produce theoretical liquid phase spectra, preferably a wide variety of spectra as measured by the different spectroscopies at the same state point.

Description of the pair potential. Using the m.d. algorithm TETRA, fully described elsewhere (ref.11), we aim to transform our pair-potential via the classical equations of motion for 108 interacting molecules, into far infra-red spectra. This is achieved by the construction of correlation functions and Fourier transformation, allowing for internal field effects with the Scaife/Fatuzzo/Mason equations (ref.12). These seem to have gained a measure of acceptance after some controversy. The pair potential is an atom-atom Lennard-Jones type (ref.5) with charges fixed at the atomic sites. The parameters are ϵ/k (C-C) = 51.0K; σ (C-C) = 3.2Å; ϵ/k (H-H) = 13.4K; σ (H-H) = 2.75Å; ϵ/k (Cl-Cl) = 175.0K; σ (Cl-Cl) = 3.35Å; with fractional charges of + 0.098e on H; -0.109e on Cl and + 0.022e on C. The former were chosen to optimise the thermodynamic conditions by slightly adjusting values already in the literature and the charges taken directly from a simple calculation by del Re (ref.13). This reproduces the gas phase dipole to within 0.1 D. A multipole expansion was not considered because of problems with convergence and complexity (the relatively low, C_{2v}, symmetry of CH_2Cl_2). Full details of the numerical method are published elsewhere (ref.11).

Auto and cross correlation function. The orientational dynamics of the CH_2Cl_2 molecules can be described (ref.11) in terms of three unit vectors $\underset{\sim}{e}_A$, $\underset{\sim}{e}_B$ and $\underset{\sim}{e}_C$ along the axes of the three principal moments of inertia. One of these axes coincides with the dipole axis, and consequently $\underset{\sim}{e}_A$ is the dipole unit vector. The available phenomenological theory (ref.3) usually produces $\langle \underset{\sim}{e}_A(t).\underset{\sim}{e}_A(o) \rangle$ and $\langle \dot{\underset{\sim}{e}}_A(t).\dot{\underset{\sim}{e}}_A(o) \rangle$, respectively the orientational and rotational velocity auto-

correlation functions of $\underset{\sim}{e}_A(t)$. The m.d. simulation produces these and also the $\underset{\sim}{e}_B(t)$ and $\underset{\sim}{e}_C(t)$ counterparts. These are illustrated at 293K and 177K (0.2° above the freezing point) in Fig.6. The simulated rotational diffusion is clearly anisotropic and this is an indication which should lead to further investigation with, for example, NMR relaxation and Rayleigh/Raman scattering of light[10].

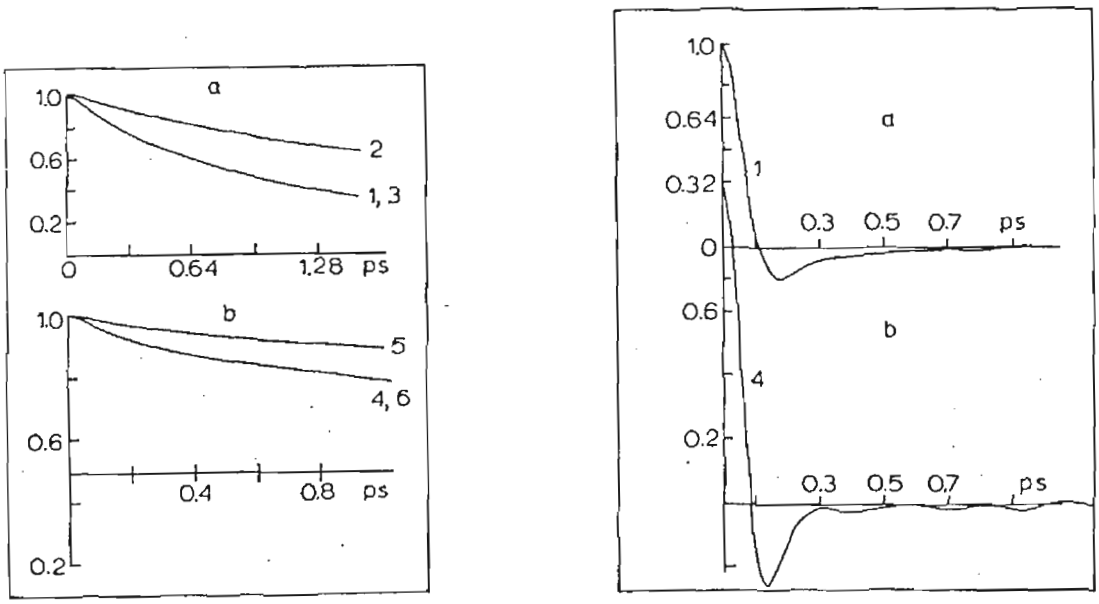

Fig.6. Rotational velocity and orientational a.c.f.'s for CH_2Cl_2, illustrating the anisotropy of rotational diffusion at 293K and 177K. M.d. simulation.
(a) (1) orientational a.c.f. of $\underset{\sim}{e}_A(t)$ at 293K; (2) of $\underset{\sim}{e}_B(t)$ at 293K; (3) of $\underset{\sim}{e}_C(t)$ at 293K; (4) of $\underset{\sim}{e}_A(t)$ at 177K; (5) of $\underset{\sim}{e}_B(t)$ at 177K; (6) of $\underset{\sim}{e}_C(t)$ at 177K.
b) (1) to (6). The same for rotational velocity.
Ordinates: Normalised a.c.f.'s; Abscissae: time/ps.

However, we somehow have to produce theoretically the time-dependent macroscopic polarization (ref.12) in order to describe both far infra-red and low frequency dielectric spectral data. This obviously requires more than 108 molecules, but it is nevertheless possible to obtain an indication of this quantity by simulating the so-called microscopic (cross) correlation functions:

$$C_1(t) = \left\langle \underset{\sim}{e}_{Ai}(o) . \sum_j \underset{\sim}{e}_{Aj}(t) \right\rangle ;$$

$$\text{and } C_2(t) = \left\langle \dot{\underset{\sim}{e}}_{Ai}(o) . \sum_j \dot{\underset{\sim}{e}}_{Aj}(t) \right\rangle .$$

In order to do this we have taken spherical samples inside our cube of 108 molecules and calculated $C_1(t)$ and $C_2(t)$ for different radii of these spheres up to 80 or

90% of L/2 where L is a side of the cube. The results for radii A_1 and A_2 are illustrated in Fig.7. These functions are broadly similar to their respective auto-correlation functions and are therefore describable fairly satisfactorily by known (analytical) methods of macro-micro cirrelation (ref.7). By Fourier transforming $C_2(t)$, taking care to involve an internal field correction, we arrive finally at the results of Fig.8. It is clear that the measured spectra peak at a higher frequency at each temperature than the simulated spectra. There are

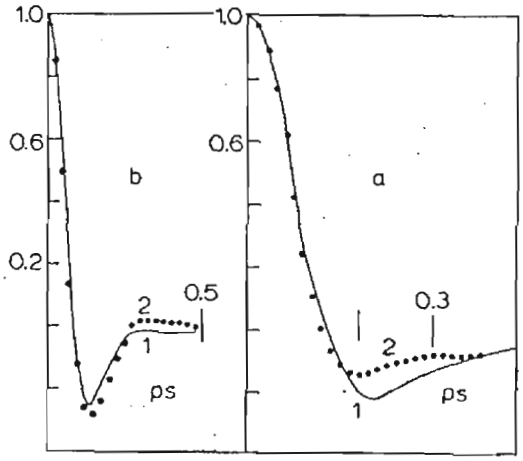

Fig.7. Comparison of auto and microscopic rotational velocity correlation functions at a) 293K; b) 177K.
a) 1) a.c.f., 2) microscopic c.f. for a sphere or radius R = Å; 3) R = Å.
b) Correspondingly at 177K.

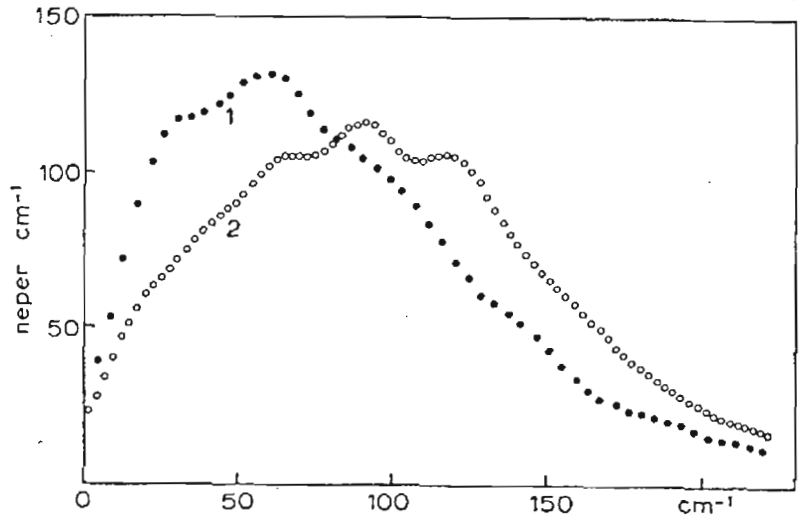

Fig.8. Fourier transforms of the microscopic correlation functions from the molecular dynamics simulation.
1) At 293K; 2) at 177K.
Ordinate: $\alpha(\tilde{\nu})$/neper cm^{-1}; Abscissa: $\tilde{\nu}$ /cm^{-1}.

several possible reasons for this, and one or two suggestions for further work are listed below.

i) An extrapolation method could be developed analytically which relates the macroscopic polarization to the microscopic correlation function, following the recent suggestion of Brot and co-workers (ref. 12).

ii) A scheme of refinement of the pair potential could be undertaken involving the accurate measurement of B_ϵ, the second dielectric virial coefficient, for CH_2Cl_2 over a range of temperature wide enough to be useful. This is work in progress using $1:10^9$ accuracy for the gaseous dielectric permittivity ϵ and $\pm$ 0.01° accuracy in temperature. The quantity B_ϵ is extremely sensitive to model pair potentials.

iii) The simulation technique could be improved by taking into account polarizabilit effects, intra-molecular vibration and by using more molecules (ref. 14).

iv) A course of measurement in dilution could be undertaken for CH_2Cl_2 in CCl_4 at different temperatures. This would provide insight to electrodynamics (ref.7) vis à vis kinematics (ref.15).

v) Finally these results should always be considered in the light of the many other a.c.f.'s which have recently been simulated for CH_2Cl_2 with this and other potentials. These should, according to the scientific method, stimulate renewed experimental investigation.

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