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MOLECULAR DYNAMICS SIMULATION OF LIQUID CH_2Cl_2 WITH 3x3 AND 5x5 SITE-SITE INTERACTIONS

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ABSTRACT

A molecular dynamics simulation of liquid CH_2Cl_2 is compared with the far infra-red spectrum at the same state point (293K, 1 bar). Two representations of the force field are used, a 3x3 and 5x5 site-site interaction consisting of Lennard-Jones and charge terms. The far infra-red spectrum shows unambiguously that the 5x5 representation is more realistic in the sense that it reproduces the observed spectrum more closely.

INTRODUCTION

In this letter the results of a molecular dynamics simulation of liquid methylene chloride are compared with spectra in the range from zero to far infra-red (THz) frequences (ref. 1). We compare two different representations of the pairwise intermolecular force field in methylene chloride using the algorithms TRI2 (3x3 atom-atom potential with and without charges) and TETRA (5x5 atom-atom potential with and without charges). The zero-THz frequency power absorption data are simulated by Fourier transforming the orientational and rotational velocity auto- and cross-correlation functions from the molecular dynamics runs (ref. 2). The result is an unambiguous indication that the 5x5 force-field is the better of the two respresentations of CH_2Cl_2 pair interactions in the liquid.

Details of Algorithms

TRI2

This is based on a listing written initially (ref. 3) by Renaud and Singer which has been modified by Ferrario and Evans to include charge-charge interaction in the basic Lennard-Jones atom-atom potential. These are defined by $\sigma(Cl\text{-}Cl) = 3.35$ Å; $\varepsilon/k(Cl\text{-}Cl) = 173.5K$; $\sigma(CH_2\text{-}CH_2) = 3.96$Å; $\varepsilon/k(CH_2\text{-}CH_2) = 70.5K$ with cross-terms evaluated with the usual but empirical combining rules. Partial charges were used to reproduce a dipole moment (ref. 4) of 1.6D, i.e. the charge on the Cl unit is $-0.151|e|$ and that on the CH_2 unit is $+0.302|e|$. The complete pairwise potential has been tested out by McDonald using his own

algorithm at 287K (molar volume of V = 62.92 cm^3 $mole^{-1}$) and this provides us with a mean potential energy of -6.2 kcal $mole^{-1}$. This compares with measurements of -6.2 kcal $mole^{-1}$ to -6.3 kcal $mole^{-1}$. From this indication it seems that the 3x3 force-field is a good one but the far infra-red results reveal its limitations clearly.

After equilibration (which takes upwards of 30 ps with charges) the programme was run for 108 molecules with 0.005 ps time-steps over a total span of about 9 to 12 ps. The EMLG pilot-project state point of 293K, 1 bar (V = 64.0 cm^3/mole) was used. This enables preagreed comparison (refs. 4,5) with a range of experimental data measured at the same state point or points. A variety of auto-correlation functions have been computed using running-time averaging (ref. 6). Here we are interested mainly in a.c.f.'s of the dipole vector ($\underline{e}_A(t)$) and of its time derivative ($\dot{\underline{e}}_A(t)$). The latter a.c.f. gives us access to the far infra-red power absorption coefficient $\alpha(\omega)$ (in neper cm^{-1}) where ω is the angular frequency in radians s^{-1} (= $2\pi\bar{\nu}c$ where $\bar{\nu}$ is in cm^{-1}).

TETRA

This is an algorithm for pentatomic rigid molecules written originally by Singer and co-workers and modified by Ferrario. The Interactions are molecularly pairwise additive and made-up of 25 atom-atom Lennard-Jones components and 25 electrostatic terms between point charges fixed at the atomic sites of each molecule. A cut-off criterion is applied to the distance between the centres of mass of two interacting molecules in order to calculate the resultant force. Long-range corrections for this are evaluated in the usual way. The translational equation of motion (usually for 108 molecules) is integrated using the Verlet method. The rotational equations of motion are integrated using a fourth order predictor algorithm for the motion of the three unit vectors along the principal axes of the moment of inertia dyadic of the asymmetric top. We used 108 CH_2Cl_2 molecules inside a cubic box of length 22.56 Å, corresponding to a molar volume at 293K of 64.0 cm^3/mole. Periodic boundary conditions were used with a time step of $\Delta t = 5 \times 10^{-15}$ s as in TRI2. During the equilibration run (about 2500 or 3000 steps) linear and angular velocities are scaled to drive the system to a temperature of 293K. No scaling is used during the equilibrium run itself (up to 3600 time steps). Lennard-Jones parameters were taken from the literature (ref. 10) to check on whether these are in any sense "transferable" from one molecule and algorithm to another. This gives σ(H-H) = 2.75 Å; σ(Cl-Cl) = 3.35 Å; σ(C-C) = 3.20 Å; ε(Cl-Cl)/k = 175K; ε(H-H)/k = 13.4K; ε(C-C)/k = 511K; $\varepsilon(A-B)/k = \left(\frac{\varepsilon}{k}(A-A)\frac{\varepsilon}{k}(B-B)\right)^{\frac{1}{2}}$; $\sigma(A-B) = \frac{1}{2}(\sigma(A-A) + \sigma(B-B))$. Charges have been estimated using a simple m.o. calculation. These were adjusted to a dipole moment of 1.6D, as in TRI2. This gives $q_H = 0.098|e|$: $q_{Cl} = -0.109|e|$; $q_c = 0.022|e|$. After 2400 steps of equilibrating, the results were as follows (MRCC CDC 7600 computer, each time step taking about 1.5 s of CPU time).

Results from TETRA

Without Charges

T = temperature/K; P = pressure/bar; U = internal energy (kJ/mole); E_T = total energy (trans + rot) (kJ/mole); C_V = specific heat at constant vol. in J $mole^{-1}K^{-1}$. T = 292.7 K (< > denotes an average value calculated over the equilibrium span of 3600 time steps). This is 49.5% translational and 50.5% rotational.

$\langle T^2 \rangle^{\frac{1}{2}}$ = 9.2K. $\langle P \rangle$ = 382 bar; $\langle \Delta P^2 \rangle^{\frac{1}{2}}$ = 312 bar. $\langle U \rangle$ = -23.69 kJ $mole^{-1}$; $\langle E_T \rangle$ = -16.39 kJ $mole^{-1}$. $\langle \Delta E_T^2 \rangle^{\frac{1}{2}}$ = 0.21 kJ $mole^{-1}$. C_V = 37 J $mole^{-1}K^{-1}$ (cf 90 J $mole^{-1}K^{-1}$ experimentally (ref. 4)).

This is, of course, a fluctuation property ($\Delta U/\Delta T$) and ideally needs runs upwards of 20,000 steps for good statistics.

With Charges

$\langle T \rangle$ = 294.5K; $\langle T^2 \rangle^{\frac{1}{2}}$ = 11.0K (50.2% trans; 49.8% rot). $\langle P \rangle$ = 273 bar; $\langle \Delta P^2 \rangle^{\frac{1}{2}}$ = 300 bar. $\langle U \rangle$ = -25.46 kJ $mole^{-1}$ (-6.1 kcal $mole^{-1}$).

$\langle E_T \rangle$ = -18.11 kJ $mole^{-1}$; $\langle \Delta E_T^2 \rangle^{\frac{1}{2}}$ = 0.13 kJ $mole^{-1}$. C_v = 46 J $mole^{-1}K^{-1}$.

DISCUSSION

Without Charges

The far infra-red power absorption coefficient was evaluated from auto and multi-molecule correlation functions of $\dot{\underline{e}}_A(t)$ by numerical Fourier transformation of the curves of Fig. (1). As always in dynamics studies the band shape is the variable of prime interest but in order to obtain an idea of the intensity (in neper cm^{-1}) we used the Scaife/Fatuzzo-Mason relation (ref. 11) in the Fourier transform with the experimentally measured static permittivity $\varepsilon(o)$. Correlation functions such as $\langle \underline{e}_{Ai}(o) . \sum_{i \neq j} \underline{e}_{Aj}(t) \rangle$ were evaluated in a spherical sample tangential to the six faces of the cube of 108 molecules used. The far infra-red spectra are illustrated in Fig. (2) and despite the artifacts (introduced by the numerical f.t. routine having to cope with the slender but long negative tails of the $\dot{\underline{e}}_A(t)$ c.f.'s) the following points emerge clearly. Referring to the f.t.'s of the a.c.f. $\langle \dot{\underline{e}}_A(t) . \dot{\underline{e}}_A(o) \rangle$ the 5x5 result is considerably closer to the measured $\alpha(\omega)$ (from a variety of spectrometers and klystrons) than the 3x3. Here we are dealing, of course, with pure liquid CH_2Cl_2. Interestingly, however, the 5x5 simulation happens to match almost exactly the measured spectrum of 10% CH_2Cl_2 in carbon tetrachloride. In Fig. (2) we have scaled the data for bandshape comparison. The area beneath the orientational a.c.f. $\langle \underline{e}_A(t) . \underline{e}_A(o) \rangle$ is 1.2 ps, which is the same, fortuitously, as the dielectric relaxation time measured by Reid (ref. 9) for the 10% decalin solution of CH_2Cl_2, 1.2 $\pm$ 0.3 ps. This result probably signifies that the spectral details in solution are dominated by the auto c.f. of CH_2Cl_2 in the absence of electrodynamic interaction between CH_2Cl_2 molecules. We use

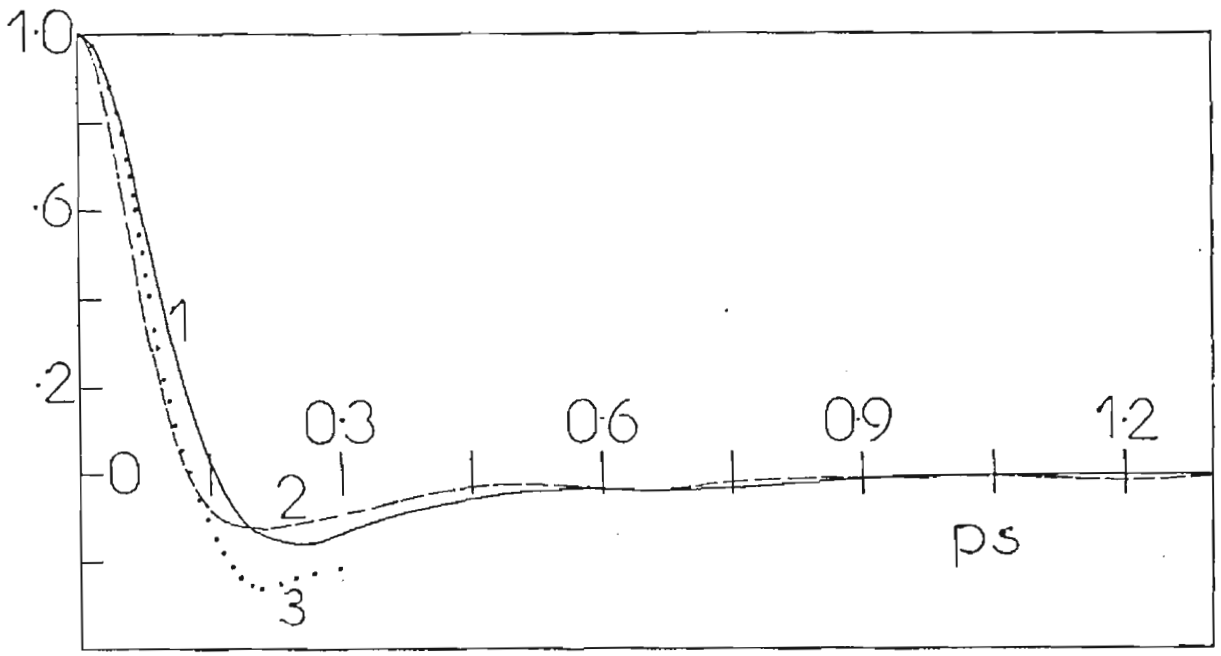

Fig. 1. Rotational velocity a.c.f.'s from (1) the 3x3 algorithm (no charges); (2) the 5x5 algorithm, (no charges). ● For comparison, a spectrum of a 10% dilute solution of CH_2Cl_2 in decalin directly Fourier transformed into the time domain.
Ordinate: C(t); Abscissa: time/ps.

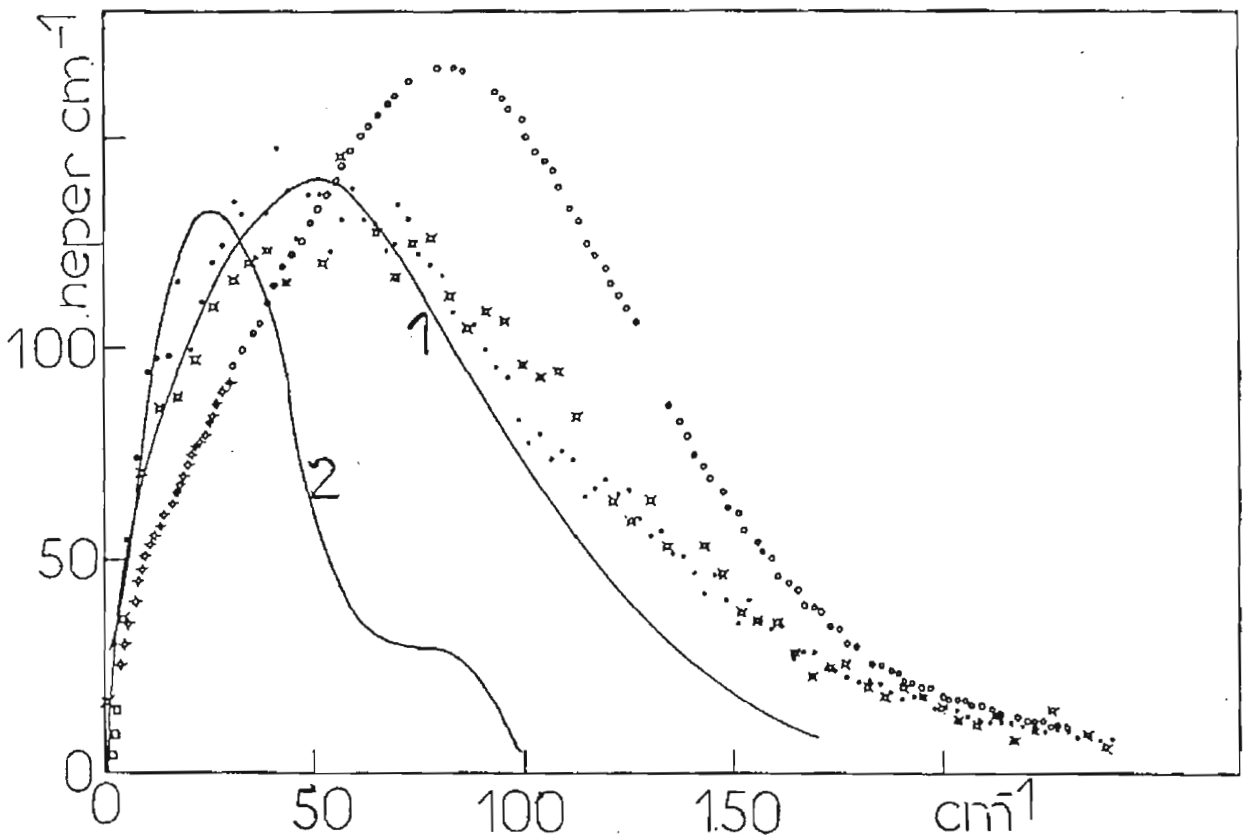

Fig. 2. Far infra-red spectra. □ , ⊹ and ⊙ Experimental (klystrons and interferometry). ● 5x5 simulation, no charges. ⊠ 5x5 simulation, with charges. ——(2) 3x3 simulation, no charges. ——(1) Spectrum of 10% CH_2Cl_2 in CCl_4 scaled up to match the intensity of ● .

(in this section) Lennard-Jones interactions only in the simulation. The 3x3 spectrum from $\langle \dot{\underline{e}}_A(t).\dot{\underline{e}}_A(o)\rangle$ is centred close to the gas-phase peak frequency of CH_2Cl_2 (about 25 cm^{-1}) and in this respect is unrealistic. The F.t.'s of the multi-molecule a.c.f. are not yet sufficiently high in quality for comment, and we are building up a 20,000 time step record to extract this spectrum accurately, and to study hydrodynamic long time tails.

With Charges

The effect of adding charges on the rotational velocity a.c.f. from TETRA is such as to shift the peak of the far infra-red power absorption coefficient by about 15% to higher frequency (65 cm^{-1} compared with 50 cm^{-1}). This is still 15 cm^{-1} below the observed peak at 80 cm^{-1} and the possible causes of this descrepancy are:

i) cross-correlations between dipole vectors on different molecules;

ii) shortcomings in the molecular dynamics simulation such as the empirical nature of the pair potential, and the assumption of pair-wise additivity.

It is clear that the far infra-red spectrum is a sensitive measure of the short time details of the simulation results, seemingly more so than the equilibrium thermodynamics results. Comparison in the latter area is made more difficult by the paucity of accurate experimental data. It will be interesting in future work to test the validity of the pairwise additive potential of this simulation by calculating from it the second dielectric virial coefficient B_ε. The latter is an extraordinarily sensitive measure of the pair potential and experimental measurements in this area are badly needed.

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