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CORRELATION TIMES FOR LIQUID CH_2Cl_2

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ABSTRACT

The overall consistency of experimentally available correlation times for liquid CH_2Cl_2 is tested with the aid of a new computer simulation at 293K, 1bar, using a 5×5 Lennard-Jones atom-atom potential with charges situated at the atomic sites. The various N.M.R. correlation times and the dielectric relaxation time are satisfactorily in line with the computer simulation. The infra-red correlation time reported by van Konynenberg and Steele is consistent with the simulation, but those reported by Rothschild are over 100 too short. The correlation time from depolarised Rayleigh scattering is over 3 times longer than the simulation result, and the neutron-scattering correlation time of Brier and Perry is about 100. shorter. The computer simulation reproduces the far infra-red spectrum of liquid CH_2Cl_2 fairly well and is therefore considered to be reliable.

A coordinated project, such as the EMLG Delta Project is needed to improve the overall consistency of these basic features of liquid phase molecular dynamics, exemplified by liquid CH_2Cl_2 .

INTRODUCTION

In this short note we report and compare correlation times for liquid dichloromethane at room temperature with computer simulated correlation times from the algorithm [1] TETRAH. The results show quite clearly that the literature results for some techniques are more seriously inconsistent than from others. A coordinated project such as the EMLG Delta Project [2,3] on CH_2Cl_2 , CH_3F and CH_3I is therefore needed to improve the consistency of the basic features currently available.

SIMULATION METHOD

This is based [4-7] on a 5×5 atom-atom + charges representation of the pair potential in CH_2Cl_2 with the parameters taken directly from those already in the literature. It is necessary to model the intermolecular potential energy

surface of two CH_2Cl_2 molecules because there has been no attempt (prior to Delta) at measuring sensitive coefficients such as the dielectric second virial (B_ϵ) which may be used to parameterise the pair potential experimentally. (For CH_3F the situation is much better, due to the careful measurements of Cole and coworkers on a range of virial coefficients and transport properties of CH_3F gas.)

The full details of TETRAH and spectral results available from it so far have been reported elsewhere [4-7]. Spectra such as the power absorption coefficient in the far infra-red [9] are reproduced satisfactorily, and this seems to indicate that Lennard-Jones parameters for atom-atom interaction are to an extent transferable between molecules. A parallel simulation of liquid CHCl_3 , using the same atom-atom Lennard-Jones parameters, has confirmed this indication. This seems to be encouraging for atom-atom + charges models of intermolecular potential, but second dielectric virial coefficients, when available will provide a further, very severe, test because it is known [10] that some model potentials give the wrong sign for B_ϵ .

Whatever the form of the pair potential used in the molecular simulation the range of spectral results will be self-consistent for that potential. Therefore the simulation in turn provides us with a measure of the overall consistency of the available experimental data. In this paper we aim to test the consistency of the experimentally available spectral correlation times for CH_2Cl_2 using the simulated correlation times of the first (P_1) and second (P_2) Legendre orientational autocorrelation functions for three unit vectors of CH_2Cl_2 . These are the dipole unit vector, \underline{e}_A , and the two perpendicular unit vectors in the principal moment of inertia frame, denoted by \underline{e}_B and \underline{e}_C .

The three principal moments of inertia of CH_2Cl_2 are then defined such that $I_A \doteq I_C \doteq 10I_B$, i.e. CH_2Cl_2 is, fortuitously, nearly an inertial symmetric top.

RESULTS AND DISCUSSION

There are correlation times available in the literature from infra-red [11] and RAMAN spectroscopy; Rayleigh scattering [12]; inelastic and incoherent neutron scattering [13]; various forms of N.M.R. relaxation [14-18]; and from dielectric/far infra-red spectroscopy [19-21]. The most detailed study has been carried through by N.M.R. spectroscopy, and these results have been analysed by Brier and Perry [13]. The diffusion of CH_2Cl_2 is anisotropic, as may be discerned by ^1H (proton) N.M.R. relaxation, ^2D nuclear quadrupole relaxation; and ^{35}Cl nuclear quadrupole relaxation. These techniques provide information on the motion of different axes, and this is summarised in table 1.

There are some fairly consistent features of this table. For example the ^1H (intramolecular) correlation time of 0.53 ± 0.06 ps agrees with the computer simulation result for motion about the \underline{e}_C vector of 0.51 ps. The latter has been calculated as the time taken for the $P_2(\underline{e}_C)$ correlation function to fall to $1/e$ of

its initial ($t = 0$) value, when this is normalised to unity. The ^{35}Cl (quadrupole relaxation, magnetic resonance) correlation time is a measure of the motion about the C - Cl axis, roughly parallel to the \underline{e}_B vector in the computer simulation. The two time correlation times are, respectively, 1.20 ± 0.10 ps and 0.90 ps. The NMR times refer, theoretically speaking [2], to strictly single particle auto-correlation functions, as do the computer simulations.

The inverse of the dielectric loss peak frequency (τ_D) is, on the other hand, a multi-molecular correlation time [22], often confused with the Debye relaxation time. For pure liquid CH_2Cl_2 at 293K, 1bar τ_D is 1.45 ps. The single particle correlation time of the a.c.f. $\langle \underline{e}_A(t) \cdot \underline{e}_A(0) \rangle$ of the computer simulation is 1.2 ps. We have attempted to calculate a multi-particle correlation time in the computer simulation using 4 small sub-spheres, and this turns out to be about 1.3 ps. Even this is not directly comparable with τ_D for a variety of well-known reasons [2], among which is the necessity for correcting the experimental τ_D for the internal field. An excellent account of the relationship between the dielectric relaxation time and single particle correlation time (of $\langle \underline{e}_A(t) \cdot \underline{e}_A(0) \rangle$ is given by E. Kluck [23]. Bearing these factors in mind we record without further comment that the experimental τ_D is 1.45 ps and the simulated correlation time is 1.2ps. It may not be irrelevant to record that the inverse of the dielectric loss peak frequency in a 10% CH_2Cl_2 solution [2,21] in CCl_4 is 1.2 ± 0.3 ps. In the latter, cross-correlations between CH_2Cl_2 molecules are probably much smaller than in pure CH_2Cl_2 .

van Konynenberg and Steele [12] have extracted a P_2 correlation time for the \underline{e}_B vector from Rayleigh scattering to 100 cm^{-1} shift from the exciting line. This type of spectrum is also multimolecular in origin and is probably more significantly affected by collision-induced effects than the far infra-red spectrum because it deals more directly in the molecular polarisability. van Konynenberg and Steele attempted, in an early paper, to correct for collision-induced effects and indicated a $P_2(\underline{e}_A)$ correlation time of ~ 1.85 ps. This compares with a single particle N.M.R. time of only 0.5 ps and a $P_2(\underline{e}_A)$ (single particle) from our computer simulation also of 0.5 ps.

The most inconsistent features of table 1 are those involved with infra-red bandshapes. The experimentally derived correlation times $P_1(\underline{e}_A)$ are different. Rothschild [11] lists $P_2(\underline{e}_A)$, $P_2(\underline{e}_B)$ and $P_2(\underline{e}_C)$, and in comparison with the computer simulation results, these are over 100% too short. This emphasises that neutron scattering data cannot be analysed without a sufficient theoretical back-up, and computer simulation seems to provide this for any future work in this field.

TABLE 1

^{13}C .N.M.R. etc. and Computer Simulation P_1 and P_2 .
Correlation Times for liquid CH_2Cl_2 (293, 1bar).

Technique	Vector	Correlation Time/ps	
^1H (intra)	H - H (ll to \underline{e}_C)	0.53 ± 0.06	
^2D (quadrupole)	C - D	0.80 ± 0.10	
^{13}C -H (dipolar)	C - H	0.70 ± 0.07	P_2
^{35}Cl (quadrupole relaxation)	C - Cl (approx. ll \underline{e}_B)	1.20 ± 0.10	
Computer simulation [4-7]	\underline{e}_A	0.50	
" "	\underline{e}_B	0.9	
" "	\underline{e}_C	0.51	
Neutron Scattering [13]	centre of mass to H	0.56	
Dielectric [19-21] Relaxation	\underline{e}_A	1.45	
Infra-red (Rothschild) [11]	\underline{e}_A	0.5	
	\underline{e}_B	1.1	P_1
Infra-red (van Konynenberg and [12] Steele)	\underline{e}_A	1.1	
Computer Simulation 19-21	\underline{e}_A	1.2	
" "	\underline{e}_B	3.8	
" "	\underline{e}_C	1.21	
Rayleigh Scattering (van Konynenberg and Steele) [12]	\underline{e}_A	≈ 1.85	P_2

FUTURE WORK

The confused and incoherent state of the literature results typified by liquid CH_2Cl_2 may be clarified only by computer simulation, together with further, coordinated, experimental investigation and theoretical analysis. This is what the EMLG Delta project proposes to attempt.

The computer simulation method rests on an adequate knowledge of the pair-potential which will be forthcoming only when accurate B_e and C_p (third pressure virial) coefficients become available. The TETRAH results reported here are in line with some of the data, and are reasonably close to the sensitive far infra-red results [2] on liquid CH_2Cl_2 .

The whole of the comparison exercise reported here needs to be repeated at different (pilot project) state points. Full details are available in the

literature or from the EMLG Secretary, Dr. Jack Yarwood, Chemistry Department, University of Durham, DH1 3LE, U.K.

REFERENCES

1. K. Singer, D. Fincham, D. Heyes, W. Smith and S. Thompson, SERC CCP5 Group. The ALGORITHM TETRAH is available from the CCP5 Group, R. Holloway College.
2. M.W. Evans, G.J. Evans, P. Grigolini and W.T. Coffey, "Molecular Dynamics", Wiley/Interscience, New York, 1982.
3. J. Yarwood and M. W. Evans, *Ad.Mol.Rel.Int.Proc.*, 21 (1981) 1 - 87.
4. M.W. Evans and M. Ferrario, *Adv.Mol.Rel. Int.Proc.*, in press.
5. M. Ferrario and M.W. Evans, *Chem.Phys.*, in press, 1982.
6. *Ibid.*, submitted, 1982.
7. M.W. Evans, M. Ferrario and P. Grigolini, *Physica A*, submitted 1982.
8. T.G. Copeland and R.H. Cole, *J.Chem.Phys.*, 64, (1978) 1741, 1747 (and references therein)
9. J.K. Vij, C.J. Reid, M. Ferrario, G.J. Evans and M.W. Evans, *Adv.Mol.Rel. Int.Proc.*, in press, 1982.
10. H. Sutter, "Dielectric and Related Molecular Processes", Vol. 1, (1972), The Chem. Soc., London.
11. W.G. Rothschild, *J.Chem.Phys.*, 53(3), (1970) 990.
12. P. van Konynenburg and W.A. Steele, *J.Chem.Phys.*, 56 (1972) 4775.
13. P.N. Brier and A. Perry, *Adv.Mol.Rel.Inter.Proc.*, 13 (1978) 1 - 46.
14. F. Heatley, *J.Chem.Soc., Faraday Trans. II*, 69 (1973) 831.
15. H.S. Sandhu, *J. Magn.Res.*, 29 (1978) 563.
16. W.G. Rothschild, *J.Chem.Phys.*, 53 (1970) 3265.
17. D.E. O'Reilly, E.M. Peterson and E.L. Yasaitis, *J.Chem.Phys.*, 57 (1972) 890.
18. J.R. Lyerla, D.M. Grant and R.D. Bertrand, *J.Phys.Chem.*, 75 (1971) 3967.
19. G.J. Evans, C.J. Reid and M.W. Evans, *J.Chem.Soc. Faraday Trans.II*, 74 (1978) 343.
20. W.T. Coffey, G.J. Evans, M.W. Evans, and G.H. Wegdam, *ibid.*, 74 (1978) 310.
21. C.J. Reid, Ph.D. Thesis, Univ. of Wales, (1979).
22. Ref. (2), Chapter (1).
23. E. Kluk, *Acta Physica Polonica*, 58A (1980) 51.
24. P.C.M. van Woerkom, J. de Bleyser, M. de Zwart, and J.C. Leyter, *Chem.Phys.*, 4(2) (1974) 236.