100

Advances in Molecular Relaxation and Interaction Processes, 20 (1981) 47—62
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

INTERMOLECULAR PAIR AND TRIMER POTENTIALS FOR METHYL FLUORIDE

AHMED A. HASANEIN*, MAURO FERRARIO and MYRON EVANS

Chemical Department, University College of Eales, Aberystwyth, SY23 1NE
(Gt. Britain)

(Received 22 August 1980)

ABSTRACT

Ab initio calculations of the pair and trimer interaction energy of methyl fluoride are reported in various approach configurations. These are based on the 6 - 31G and 4 - 31G basis sets of the Gaussian 76 program of Pople and co-workers. The potential energy surface of pair interaction is compared with that of Copeland and Cole, based on gas viscosity, second pressure virial and second dielectric virial data, and with an unoptimised 5 x 5 atom-atom potential. The ''experimental'' Copeland/Cole potential and the ab initio calculations are more often in better agreement for different dimer configurations than with the atom-atom potential. Non-pair-additivity energy in the minimised cyclic trimer of CH_3F is of the order of 10% of the total trimer interaction energy and is expected to become more important in bigger (multimer) clusters.

The results indicate that a parameterisation of the ab initio results or alternatively a straightforward use of the Copeland/Cole form is more likely to be realistic in a molecular dynamics simulation of CH_3F when using the assumption of pair interaction. However it is best to avoid this assumption in the manner of Finney et al.

INTRODUCTION

The purpose of this paper is to report briefly a comparison of pair interaction potential forms for use in molecular dynamics simulations. We deal specifically with methyl fluoride, but the method is general in applicability. The difficulties associated with extending the Lennard-Jones representation to anisotropic molecules have been tackled in different ways. For example, electrodynamic (or, more accurate-

---

[*] Permanent address: Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

ly, electrostatic) terms have been added to account for interaction between ''net charges''. Kihara et al [1] and Buckingham et al [2] have introduced shape factors for the anisotropy of repulsive parts of the potential. The problem for m.d. simulation is of course that the extra terms contribute more in the condensed phase than in the dilute gas. Probably the most comprehensive pair potential for methyl fluoride is that derived by Copeland and Cole [3] by fitting data simultaneously from three sources: the pressure and dielectric second virial coefficients and gas viscosity, via the theory of Monchik and Mason [4]. The Copeland/Cole potential involves six parameters, adjusted so that the measured data are all reproduced to within approximately ±5% limits. However the validity of the pair-interaction method for liquid CH_3F is in doubt, as evidenced by the recent work of Finney et al [5] and of Singh and Singh [6]. The latter have used third pressure virial coefficients to take into account three body effects.

With the easily accessible molecular orbital algorithms now available such as Gaussian 76 and ''atmol'' it is possible to make detailed calculations of the potential energy surfaces of dimers and trimers made up from methyl fluoride monomer segments. In this article we report briefly on our work on CH_3F dimers using different split valence basis sets such as 4 - 31G and 6 - 31G, to build up potential energy surfaces. Provided that the basis sets can be tested extensively against experimental data (and this is the case [7 - 12] for CH_3F)an analytical representation of the $(CH_3F)_2$ pair interaction can be extracted for direct use in molecular dynamics algorithms. Our molecular orbital calculations are compared with model pair potentials such as the 5 x 5 atom-atom and the Copeland/Cole [13] representation. Lastly ab initio calculations are reported on a cyclic trimer of CH_3F. This shows, albeit in one particular configuration only, that ''non-pair-additivity'' is important. We discuss ways in which a ''multimer potential representation'' for CH_3F can be built up from molecular orbital theory.

Method of Calculation

The ab initio calculations were carried out using the Gaussian 76 program of Pople and co-workers [14]. We used the well characterised split valence basis set N-31 G (N = 4 to 6) [15-17]. The monomer geometry is kept at its experimental value [18]. The calculations were carried out on the Honeywell 6080/CDC system of Aberystwyth/UMRCC, using the dimer geometries detailed in table 1. In the trimer calculations, reported below, advantage was taken of such a technique when dealing with the cyclic configuration used to estimate the effect of non-pair-additivity in intermolecular potential energy differences.

TABLE 1

Coordinates of Atoms in Dimer Approaches / Å

APPROACH (1)	F	3.5	0.0	0.0
	C	4.1926	1.1996	0.0
	H	5.2784	0.9892	0.0
	H	3.9202	1.7734	-0.9055
	H	3.9202	1.7734	0.9055
	F	1.75	-3.0311	0.0
	C	1.0574	-4.2307	0.0
	H	1.7825	-5.0658	0.0
	H	0.4243	-4.2817	-0.9055
	H	0.4243	-4.2817	0.9055
APPROACH (2)		1.0	0.	0.0
		1.5530	0.9578	0.0
		0.6448	2.0038	0.0
		2.1914	1.0236	-0.9007
		2.1914	1.0236	0.9007
		2.9669	-2.2653	0.0
		3.9928	-1.8522	0.0
		4.9010	-2.8981	0.0
		4.1475	-1.2293	-0.9007
		4.1475	-1.2293	0.9007
APPROACH (3)		1.0	0.0	0.0
		1.6926	1.1996	0.0
		2.7784	0.9892	0.0
		1.4202	1.7734	-0.9055
		1.4202	1.7734	0.9055
		1.0	0.0	-4.5
		1.6926	1.1996	-4.5
		0.9675	2.0347	-4.5
		2.3257	1.2506	-3.5945
		2.3257	1.2506	-5.4055

APPROACH 4	1.0	0.0	0.0
	1.6926	1.1996	0.0
	2.7784	0.9892	0.0
	1.4202	1.7734	-0.9055
	1.4202	1.7734	0.9055
	-1.3385	2.9496	0.0
	-2.0311	1.75	0.0
	-1.3060	0.9149	0.0
	-2.6642	1.6990	0.9055
	-2.6642	1.6990	-0.9055
APPROACH 5	1.0	0.0	0.0
	1.6926	1.1996	0.0
	2.7784	0.9892	0.0
	1.4202	1.7734	-0.9055
	1.4202	1.7734	0.9055
	-0.9055	2.6996	0.0
	-1.5981	1.5	0.0
	-2.6839	1.7104	0.0
	-1.3257	0.9263	-0.9055
	-1.3257	0.9263	0.9055
APPROACH 6	1.0	0.0	0.0
	1.6926	1.1996	0.0
	2.7784	0.9892	0.0
	1.4202	1.7734	-0.9055
	1.4202	1.7734	0.9055
	4.7237	-0.5504	0.0
	4.0311	-1.75	0.0
	2.9453	-1.5396	0.0
	4.3035	-2.3237	-0.9055
	4.3035	-2.3237	0.9055

APPROACH 7	F	1.0	0.	0.0
	C	1.6926	1.1996	0.0
	H	2.7784	0.9892	0.0
	H	1.4202	1.7734	-0.9055
	H	1.4202	1.7734	0.9055
	F	0.1555	-3.5539	0.0
	C	-1.0442	-2.8613	0.0
	H	-0.8338	-1.7755	0.0
	H	-1.6179	-3.1337	-0.9055
	H	-1.6179	-3.1337	0.9055
APPROACH 8		1.0	0.	0.0
		1.6926	1.1996	0.0
		2.7784	0.9892	0.0
		1.4202	1.7734	-0.9055
		1.4202	1.7734	0.9055
		4.7784	4.4533	0.0
		3.5788	5.1459	0.0
		2.7437	4.4208	0.0
		3.5278	5.7790	0.95
		3.5278	5.7790	-0.9055
APPROACH 9		1.0	0.0	0.0
		1.6926	1.1996	0.0
		2.7784	0.9892	0.0
		1.4202	1.7734	-0.9055
		1.4202	1.7734	0.9055
		5.1567	-0.8004	0.0
		5.1567	-0.8004	1.3852
		4.6339	-1.7058	1.7459
		6.2022	-0.8004	1.7459
		4.6339	0.1051	1.7459

APPROACH 10	1.0	0.	0.
	1.6926	1.1996	0.
	2.7784	0.9892	0.
	1.4202	1.7734	-0.9055
	1.4202	1.7734	0.9055
	4.7237	-0.5504	0.0
	4.7237	-0.5504	1.3852
	3.8182	-0.0276	1.7459
	4.7237	0.4952	1.7459
	3.8182	-1.0731	1.7459
APPROACH 11	1.0	0.0	0.0
	1.6926	1.1996	0.0
	2.7784	0.9892	0.0
	1.4202	1.7734	-0.9055
	1.4202	1.7734	0.9055
	5.5897	-1.0504	0.0
	6.2823	0.1492	0.0
	5.5572	0.9844	0.0
	6.9154	0.2002	0.9055
	6.9154	0.2002	-0.9055
APPROACH 12	1.0	0.0	0.0
	1.6926	1.1996	0.0
	2.7784	0.9892	0.0
	1.4202	1.7734	-0.9055
	1.4202	1.7734	0.9055
	-2.2045	3.4496	0.
	-1.5119	4.6492	0.0
	-0.4261	4.4388	0.0
	-1.7843	5.2230	-0.9055
	-1.7843	5.2230	0.9055

APPROACH 13	F	1.0	0.0	0.0
	C	1.6926	1.1996	0.0
	H	2.7784	0.9892	0.0
	H	1.4202	1.7734	-0.9055
	H	1.4202	1.7734	0.9055
	F	3.5981	-1.5	0.0
	C	2.9055	-2.6996	0.0
	H	1.8197	-2.4892	0.0
	H	3.1779	-3.2734	-0.9055
	H	3.1779	-3.2734	0.9055
APPROACH 14		1.0	0.0	0.0
		1.6926	1.1996	0.0
		2.7784	0.9892	0.0
		1.4202	1.7734	-0.9055
		1.4202	1.7734	0.9055
		3.5981	-1.5	0.0
		2.9055	-2.6996	0.0
		3.6306	-3.5347	0.0
		2.2724	-2.7506	0.9055
		2.2724	-2.7506	-0.9055

For attractive curves: at the minimum.

For repulsive curves: R(centre to centre) ≈ 4.829Å.

Details of the Dimer Calculation

The following basis sets were used to check for self-consistency.

In fig. (1) we compare the m.o. potential energy curves with the following representations:

(i) 5 x 5 Lennard-Jones atom-atom (no electrodynamics):

(ii) the Copeland/Cole potential for CH_3F.

Nine configurations are shown out of those considered. The atom coordinates defining the monomers relative to each other are listed in table (1).

The atom-atom potential is used with the following unoptimised parameters:

Atom Interaction	σ(Å)	ϵ/k(K)
H .... H	2.8	15
C C	2.8	50
F .... F	2.8	60
H .... F	2.8	30
H C	2.8	27
C .... F	2.8	55

In fig.1(a) we consider the minimum energy configuration of the dimer of CH_3F as calculated by ab initio. The potential well depth is considerably deeper than that of either the other two, although the Copeland/Cole representation is the closer to the ab initio results. The deep m.o. well may be the result of the fact that the ab initio method overestimates the monomer dipole moment on both basis sets, giving 2.5D compared with the gas phase value [19] of 1.85D. The long and intermediate range dipole-dipole interaction may then be over-represented in the ab initio calculation. The position of the minimum is well grouped around 3Å for each potential.

In fig. 1(b) the highest energy dimer configuration brings out the fact that the atom-atom potential contains a negative portion which is not the case in the other two, which agree very closely, but probably fortuitously. The important point here is that the consideration of polarisability by Copeland and Cole (via multipole-multipole interactions) seems to be important in accurately representing dimer interaction in CH_3F, and even more so in consequence when considering multimer clusters and non-pair-additivity (vide-infra).

In fig. 1(c) the parallel ''fish bone'' approach brings out the greatest discrepancy in the three potential representations. The atom-atom representation is over sensitive to the position of the hydrogen atoms, while in this case the Copeland/Cole potential is too attractive in comparison with the ab initio representation. In view of the similarity illustrated in fig.1(b) it seems that either the ab initio calculation is in turn over-sensitive to what we may term multipole-multipole repulsion or alternatively the Copeland-Cole equation is failing to appreciate the strong repulsion between hydrogen at short inter-molecular distances. This situation is apparent in reverse in fig. 1(f), the antiparallel ''fish-bone''.

In fig. 1(d) there is again a very close similarity between the ab initio and Copeland/Cole representations, leaving the atom-atom representation adrift in the sense that the dispersive energy well is too shallow. The agreement probably has something to do with the fact that the hydrogen hydrogen interaction in this T-shape approach is weak.

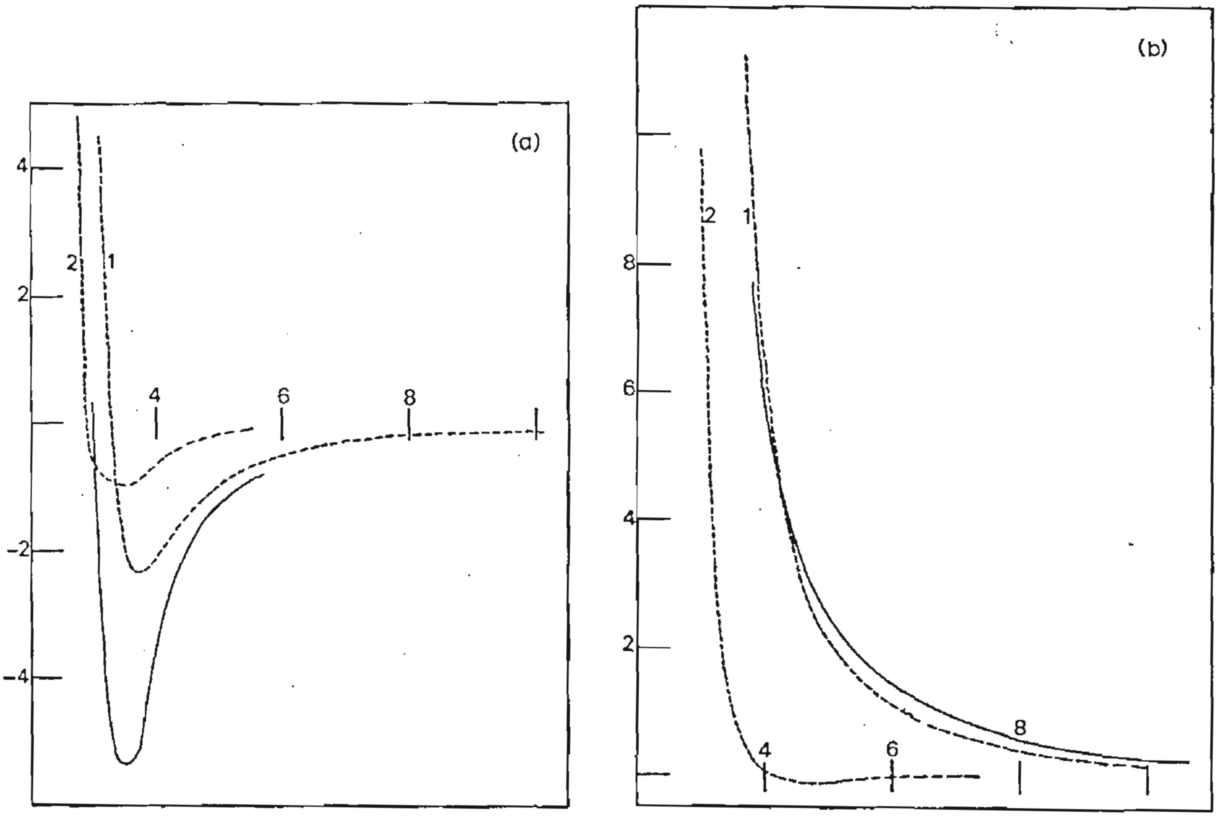
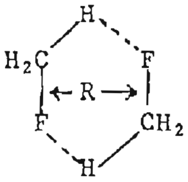


Fig. 1.

(a) Pair interaction energy of two CH_3F molecules. The antiparallel approach:



where the dotted lines indicate the possible existence of weak hydrogen bonding in the plane of the paper (Approach 6 in Table 1)

________ ab initio 631G basis set.

- - - - (1) Copeland Cole potential

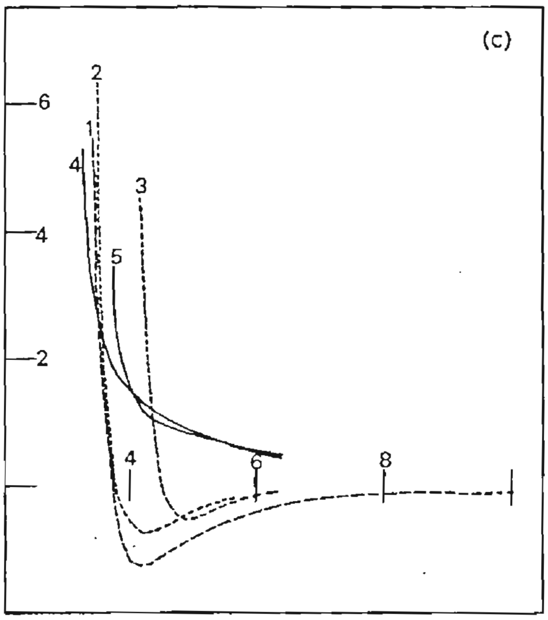
(2) 5 x 5 atom-atom potential.

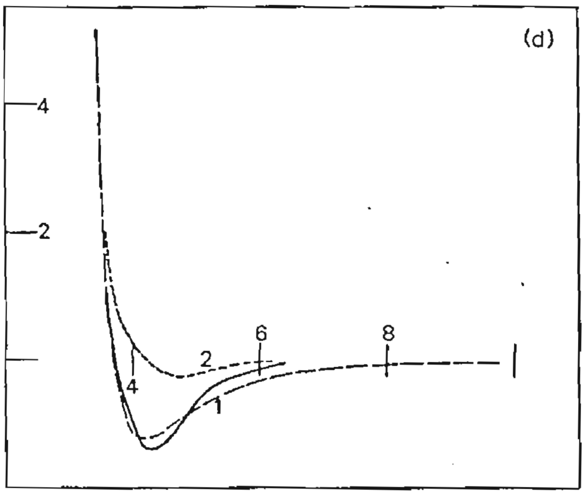
Ordinate: 10^3 x atomic energy units (Hartree/Fock)

Abscissa: R/Å

(b) As for fig 1(a), with the approach

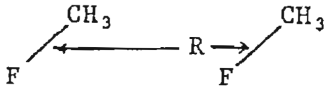
$$CH_3 - F \quad F - CH_3$$
$$\longleftarrow R \longrightarrow$$





For hydrogen positions see table (1), Approach 1

(c) As for fig 1(a), parallel ''fishbone'' approach: (Approaches 11 and 12)



∠45°

(1) Copeland-Cole potential

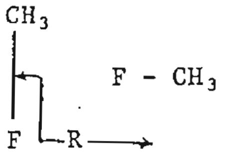
(2) H staggered, atom-atom

(3) H eclipsed, atom-atom

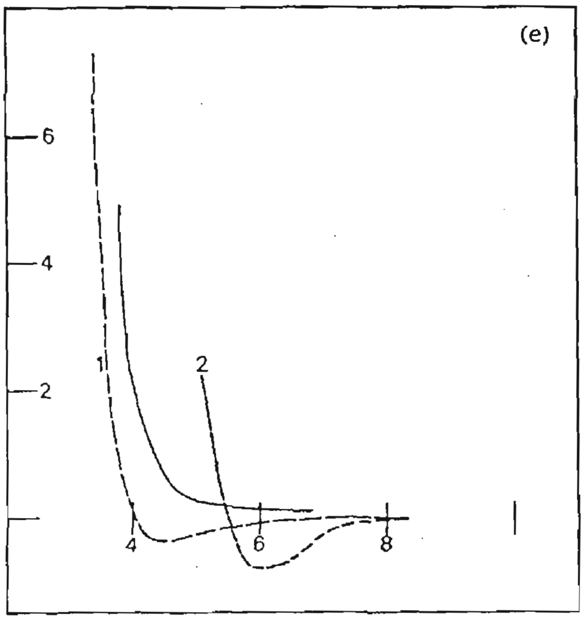
(4) H staggered, ab initio

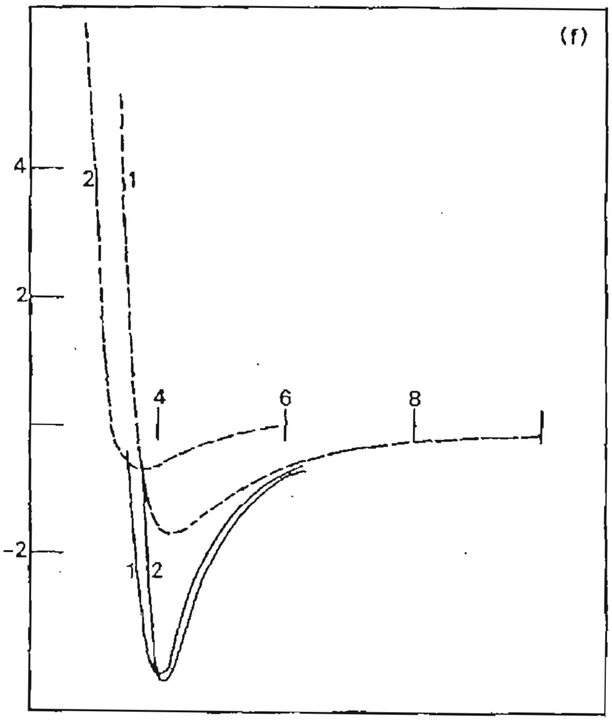
(5) H eclipsed, ab initio

(d) As for fig 1(a), perpendicular approach:

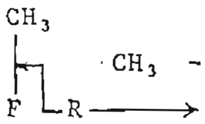


For hydrogen positions see table (1) Approach 7

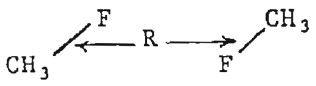




(e) As for fig 1(a), the perpendicular approach: Approach 8.



(f) As fig 1(a), the antiparallel ''fishbone'' (Approaches 13 and 14)

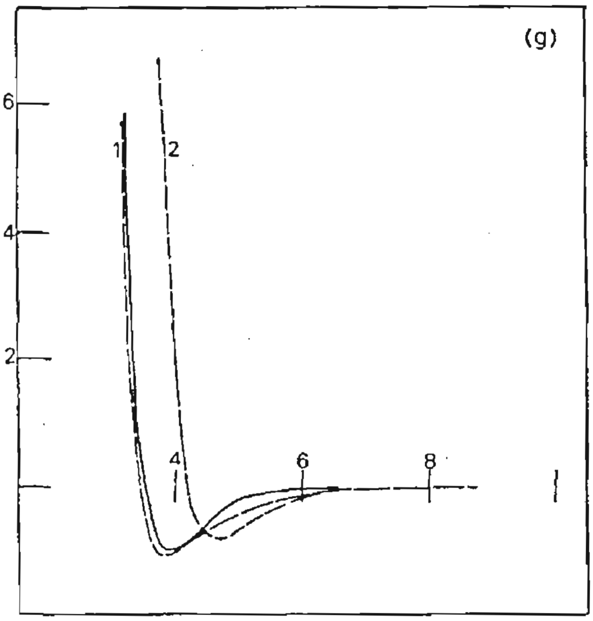


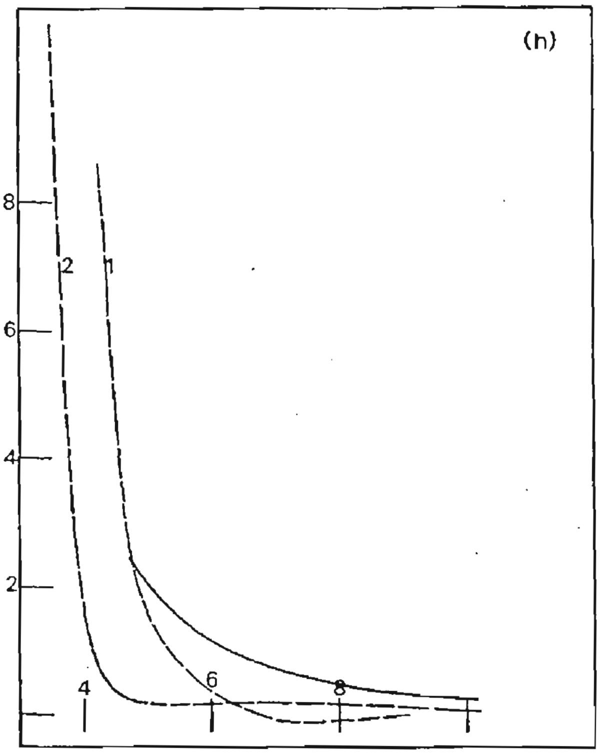
\- - - - (1) Copeland/Cole potential

(2) Atom-atom potential

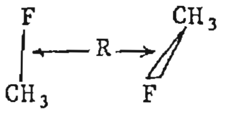
________ (1) Eclipsed H's ab initio

(2) Staggered H's ab initio





(g) As for 1(a), perpendicular approach: (Approaches 9 and 10)



(h) As for fig 1(a), the approach: (Approach,2)

$$\mathrm{F-CH_3} \quad \mathrm{CH_3-F}$$
$$\longleftarrow R \longrightarrow$$

In contrast in fig. 1(e) the three representations are more separated in detail, although the Copeland/Cole is closer once again to the ab initio result. The hydrogen-hydrogen interaction again is probably the cause of loss of realism in the Copeland Cole representation, which does not treat each H as a separate entity.

In fig. 1(f) the antiparallel fishbone, the position of the minimum of the Copeland-Cole and ab initio calculations is identical, but the depth is widely different.

In the crossed 90° approach of fig. 1(g) these two representations again agree remarkably well, in both position and depth, while the atom-atom is again in disagreement, probably because of the latter's inability to account for the adhesive effect of polarisability.

Finally in fig. 1(h) there is a rare instance of better positioning by the atom-atom potential but again the Copeland-Cole seems to be more in agreement with the ab initio estimate because of the elimination of the negative part exhibited by the atom-atom.

We remark finally in this section that the ''experimental'' Copeland/Cole potential and ab initio estimate are often in agreement with each other than the non-electrodynamic, ''purely shape anisotropic'' atom-atom interaction. However there are some discrepancies which obviously remain to be considered by some independent source such as how well spectral features can be reproduced using some representation of these potential surfaces in a molecular dynamics simulation. It is unlikely that variation of the parameters of the atom-atom potential will remove the discrepancies typified in figs 1(b) and 1(h), i.e. an unrealistic negative part to the overall profile. It is more likely that either a parameterisation of the ab initio surface or a direct use of the Copeland-Cole result will produce more realistic results from a molecular dynamics simulation.

Results of Trimer Calculation

The purpose of this exercise is to lend support to the thesis of Finney and co-workers [5] that non pair additivity is an important factor to take into consideration when structuring a molecular dynamics algorithm for polar liquids, the most important example being water, for which calculations by del Bene and Pople [15] show clearly the influence of non-pair-additivity in trimer, tetramer, pentamer and hexamer clusters. If non-pair-additivity is significant in a polar liquid such as CH_3F then an algorithm should be used for molecular dynamics simulations which avoids the assumption of pairwise energy interaction. Such a program is under development by Finney and co-workers [20].

An ab initio calculation of the trimer interaction energy of CH_3F can give only a rough idea of the non-pair-additivity because of the size of the cluster (three fluorine atoms). However the table below summarizes a calculation in both the 4-31G and 6-31G basis sets.

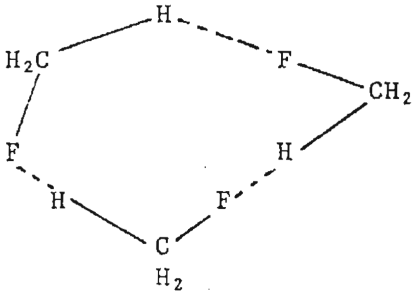
Cyclic Trimer Study

	4 - 31 G	6 - 31 G
ΔH_T	- 8.1 k cal mole^{-1}	- 7.3 k cal mole^{-1}
$3\Delta H_D$	- 7.5 ''	- 6.6 '' ''
ΔH_{ABC}	- 0.6(4) ''	- 0.6(9) '' ''

In the notation of this table

$$\Delta H_T = 3\Delta H_D + \Delta H_{ABC}$$

H_D being the dimer interaction energy and ΔH_{ABC} the non pair-additivity term. The cluster chosen for this calculation is the cyclic trimer:



While the non-pair-additivity term is smaller than in the water trimer it is significant at about 10% of ΔH_T. As the size of the multimer increases it is expected that the non-additivity term will increase in a non-linear fashion (McQuarrie [21]), and in consequence there will be a need to take this into account in a future molecular dynamics simulation.

APPENDIX

Description of the Copeland-Cole Potential

The potential is made up of a central Lennard-Jones component with the usual ε/k and σ; an electrostatic energy U(ES) described by a permanent dipole moment μ, quadrupole moment Θ, and average polarisability α and anisotropy of repulsive forces characterised by the Buckingham and Pople expression [2] U (shape) with shape factor D. We have

$$U(\text{total}) = U(LJ) + U(ES) + U(\text{shape}) \tag{A1}$$

where

$$U(LJ) = 4\varepsilon\left[(\sigma/R)^{12} - (\sigma/R)^{6}\right]$$

where R is the distance between the centres of the C - F bonds of a pair of CH_3F molecules. The values of ε and σ used were taken from the analysis of Casparian and Cole [22] using the transport theory of Monchick and Mason [4]. The electrostatic energy is the sum of five terms:

$$U(ES) = U(\mu,\mu) + U(\mu,\Theta) + U(\Theta,\Theta) + U(\mu,\text{ ind }\mu) + U(\Theta,\text{ ind }\mu) \tag{A2}$$

Define the angle θ_1 as that between dipole $\underset{\sim}{\mu_1}$ and the vector $\underset{\sim}{R}$ and θ_2 that between $\underset{\sim}{\mu_2}$ and $\underset{\sim}{R}$. Further define the angle ϕ as that generated between $\underset{\sim}{\mu_1}$ and $\underset{\sim}{\mu_2}$ by the clockwise rotation of $\underset{\sim}{\mu_2}$ with respect to $\underset{\sim}{\mu_1}$ (Mason and Spurling [23]). In the notation $C_1 = \cos\theta_1$, $C_2 = \cos\theta_2$, $S_1 = \sin\theta_1$, $S_2 = \sin\theta_2$, $C = \cos\phi$, we have:

$$U(\mu,\mu) = -(\mu^2/R^3)(2C_1C_2 - S_1S_2C)$$

$$U(\mu,\theta) = (3\mu\theta/2R^4)(C_2 - C_1)(3C_1C_2 - 2S_1S_2C + 1)$$

$$U(\theta,\theta) = (3\theta^2/4R^5)(1 - 5C_1^2 - 5C_2^2 - 15C_1^2C_2^2$$

$$+ 2(4C_1C_2 - S_1S_2C)^2)$$

$$U(\mu,\ \mathrm{ind}\mu) = -(\alpha\mu^2/2R^6)(3C_1^2 + 3C_2^2 - 2)$$

$$U(\theta,\ \mathrm{ind}\mu) = -(9\alpha\theta^2/8R^8)(4C_1^4 + 4C_2^4 + S_1^4 + S_2^4)$$

$$U(\mathrm{shape}) = 4D(\sigma/r)^{12}\varepsilon(3C_1^2 + 3C_2^2 - 2)$$

D is a factor which Buckingham and Pople [2] have proposed as a description of molecular shape anisotropy. D = o for spherical molecules and must lie between the limits of -0.25 for a flat "platelike" molecule and +0.5 for an infinitely thin "rodlike" molecule, with the dipole along the $\theta = 0$ axis.

U(shape) is most negative for antiparallel alignment of rodlike molecules.

The six parameters ε, σ, μ, θ, α and D were determined by Copeland and Cole by reproducing the second pressure virial coefficient B_p and dielectric virial coefficient B_ε to within 5% with ε and σ previously calculated from a fit of viscosity data. The agreement to within 5% for both B_p and B_ε over a wide temperature range was obtained only by adding to the central force potential U(LJ) the permanent dipole energy U(μ,μ), induced dipole energy, U(μ, indμ) + U(θ, indμ), dipole-quadrupole energy U(μ,θ), quadrupole-quadrupole energy U(θ,θ) and shape anisotropy U(shape). The dipole-dipole and dipole-quadrupole energies have the major effect on B_p, but the values of B_ε are primarily determined by induced dipole and shape interactions, with lesser contribution from the other term. The shape effect on B_ε is large and negative. To determine ε and σ, viscosity data accurate to 1% over a >100K range of temperature were used for CH_3F.

Two of the three electrostatic molecular parameters, μ and α, the mean molecular polarisability, are independentley established in the literature. However θ, the quadrupole moment of CH_3F is not established with accuracy. The e.s.u. Copeland-Cole value is 2.3×10^{-26}, obtained by attributing differences of measured B_p values from values calculated using viscosity based U(LJ) and dipole energies to dipole-quadrupole and quadrupole-quadrupole interaction energy.

The parameters finally determined by Copeland and Cole are: $\sigma = 3.80$Å; $\varepsilon/k = 199$K; $\mu = 1.85$D; $\alpha = 2.97 \times 10^{-24}\mathrm{cm}^3$; $\theta = 2.3 \times 10^{-26}$ e.s.u.; D = +0.25. Consideration of the dipole-octopole energy for CH_3F resulted in a change of less than 1% in B_ε.

REFERENCES

1 T. Kihara and A. Koide, Adv. Chem. Phys., 33 (1975) 51.

2 A.D. Buckingham and J.A. Pople, Trans. Faraday Soc., 51 (1955) 1173, 1180.

3 T.G. Copeland and R.H. Cole, J.Chem.Phys., 64 (1976) 1741.

4 E.A. Mason and L. Monchick, J.Chem.Phys., 35 (1961 1676; Adv.Chem.Phys., 12 (1967) 329.

5 J. Finney, Faraday Disc. No.66, 1978.

6 S. Singh and Y. Singk, J.Phys.B, 5 (1972) 2039; S. Singh, Physica, 89A (1977) 219

7 C.R. Brundle, M.B. Robin, H. Basch, J.Chem.Phys., 53 (1970) 2196.

8 Tal-Kyu Ha, J.Mol. Struct. 11 (1972) 179.

9 C.A. Naleway and M.E. Schwartz, TCA 30 (1973) 347.

10 H.B. Schlegel and S. Wolfe J.C.P. 67 (1977) 4194.

11 T.B. Lakdar, M. Suard, E. Taillandier and G. Berthier, Mol.Phys., 36 (1978) 509.

12 K.B. Wiberg, J.A.C.S. 101 (1979) 1718.

13 M.W. Evans, A.P. Davies and G.J. Evans, Adv. Chem.Phys., 44 (1980)

14 J.S. Binkley, R.A. Whiteside, P.C. Hariharan, R. Seeger, J.A. Pople, W.J. Hehre and M.D. Newton, Q.C.P.E. program No.368.

15 E. Del Bene and J.A. Pople, J.Chem.Phys. 58 (1973) 3605.

16 R. Ditchfield, W.J. Hehre and J.A. Pople, J.Chem.Phys. 54 (1971) 724.

17 J.S. Binkley, J.A. Pople and W.J. Hehre, J.A.C.S., 102 (1980) 939.

18 ''Tables of interatomic distances'' and ''supplement'', Chem.Soc. Spec. Publ. 1965.

19 G. Cramer, Mol.Phys., 31 (1976) 1833.

20 J. Finney et al, communication.

21 D.A. McQuarrie, ''Statistical Mechanics'', Harper and Row, 1975.

22 A.S. Casparian and R.H. Cole, J.Chem.Phys., 60 (1974) 1106.

23 E.A. Mason and T.H. Spurling, The Virial Equation of State, Pergamon, Oxford, 1969.