Advances in Molecular Relaxation and Interaction Processes, 20 (1981) 215—231
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THE INTERMOLECULAR DIMER POTENTIAL OF NON-DIPOLAR LINEAR MOLECULES

AHMED A. HASANEIN*, MAURO FERRARIO and MYRON EVANS

Chemistry Department, University College of Wales, Aberystwyth. SY23 1NE, Gt. Britain

(Received 16 December 1980)

ABSTRACT

The intermolecular potentials of H_2, D_2, F_2, O_2, N_2 and CO_2 are examined using three independent estimates:

i) The Kihara/Koide method, involving core anisotropy, van der Waals dispersion, quadrupolar interaction and octopolar induction terms.

ii) The ab initio calculation for dimers of these molecules, using 4 - 31G and 6 - 31G basis sets.

iii) The atom-atom (R.I.S.M.) method.

While some consistent features emerge, there is qualitative disagreement in the majority of approach configurations which implies that the Kihara/Koide potential is overestimating the attractive part of the potential energy surface and underestimating the anisotropy of this surface in comparison with the ab initio method.

The atom-atom and Kihara/Koide potentials agree almost quantitatively in the majority of approach configurations, so that the extra electrostatic features considered by Kihara et al seem generally to have little effect on the atom-atom results.

INTRODUCTION

In the second of this series of papers[1] we aim to compare from different viewpoints some analytical potential forms for linear molecules. For non-dipolar polyatomic molecules, Kihara et al[2] have constructed an intermolecular potential function.

$$u(\rho) = u_0 \left[(\rho_0/\rho)^{12} - 2(\rho_0/\rho)^6 \right] \qquad (1)$$

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

which is similar to that of Lennard-Jones[3]. The variable ρ is set equal to the minimum distance between impenetrable molecular cores. The core may take any shape as long as it remains convex. If the cores are properly chosen the sizes and shapes of the molecules can be taken into account in a realistic way. In this representation a convex body is characterised by its three fundamental measures: the volume V, the surface area S, and the measure M, which is the mean curvature integrated over the surface of the convex body. These can be related to measured second virial co-efficient data.

Although this describes the size and shape of a molecule in a realistic way, the dependence of the potential depth on the molecular orientation is not accounted for by consideration of the core potential alone. The dependence of the potential depth on the molecular orientation is caused partly by the electrostatic multipole interactions between the molecules. According to Kihara et al[1,4] the quadrupolar interaction is negligible for oxygen and probably for fluorine, but is not negligible for nitrogen and hydrogen, and is quite strong for carbon dioxide. However these speculations are not borne out by far infra-red induced absorption spectra[5,6], especially in oxygen, where hexadecapolar forces seem to be as strong as the quadrupolar forces.

A scan of the core potential and the quadrupole interaction energy takes the form

$$u = u_0\left[\left(\frac{\rho_0}{\rho}\right)^{12} - 2\left(\frac{\rho_0}{\rho}\right)^{6}\right] + \frac{3}{4}\frac{Q^2}{r^5} f(\theta_1, \theta_2, \phi_1 - \phi_2) \qquad (2)$$

where

$$f(\theta_1, \theta_2, \phi_1 - \phi_2) = 1 - 5\cos^2\theta_1 - 5\cos^2\theta_2 - 15\cos^2\theta_1\cos^2\theta_2 + 2\left[4\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2)\right]^2$$

Here r is the distance between the molecular centres, θ_1 and ϕ_1 are the polar angles of the axis of one molecule with respect to the line connecting the two; θ_2 and ϕ_2 are those of the second.

Although this approximation to the intermolecular potential is simple and useful, a more accurate description has been developed[4] to cover the van der Waals attraction[7] and to substitute this for the second term of the core potential in eqn.(2). Taking into account the potential of the London dispersion force, the role of electrostatic polarisabilities[8] and the effects of octopolar induction[9], Kihara and Koide[4] have developed a potential form in nine typical orientations of the non-dipolar molecules, CO_2, D_2, N_2, O_2 and F_2.

A wide variety of basis sets has been used[10-14] in ab initio MO calculations of the intermolecular interaction potentials. The interaction

energy was found to be significantly sensitive to the type of basis set used[12-14], but no attempt was made to consider explicit changes in the potential energy parameters in increasingly sophisticated basis sets.

In this paper we use the 4 - 31G and 6 - 31G split valence basis sets to calculate the potential energy surface for the dimers of the above molecules and we wish to compare these ab initio calculations with the Kihara/Koide potential forms[4] which are among the most sophisticated in the literature. A further comparison is made with the atom-atom potential for these molecules.

COMPUTATIONAL METHOD

Calculations were carried out using the Gaussian 76 programme of Pople et al[15-17]. The configurations chosen by Kihara and Koide[4] were used with the monomer geometries kept at their experimental values[18]. The calculations were carried out on the Honeywell 6080 and CDC 7600 systems of Aberystwyth/UMRCC.

RESULTS AND DISCUSSION

The ab initio calculated monomer properties are given in the following table and the results are illustrated in Figs. (1) to (5) which we describe in turn.

TABLE

Monomer properties calculated by the ab initio method

Molecule[a]	Total energy (in a.u.)	
	4 - 31G	6 - 31G
H_2	- 1.1267	- 1.1267
N_2	- 108.7537	- 108.8678
O_2	- 149.3088	- 149.4614
F_2	- 198.4580	- 198.6457
CO_2[b]	- 187.3279	- 187.5149

a. The calculated dipole moment for all the molecules is zero.

b. The calculated charges are: O: - .4835;
C: + .9670 by 4 - 31G and O: - .4317;
C: + 0.8634 by 6 - 31G.
Atomic charges for other molecules are zero.

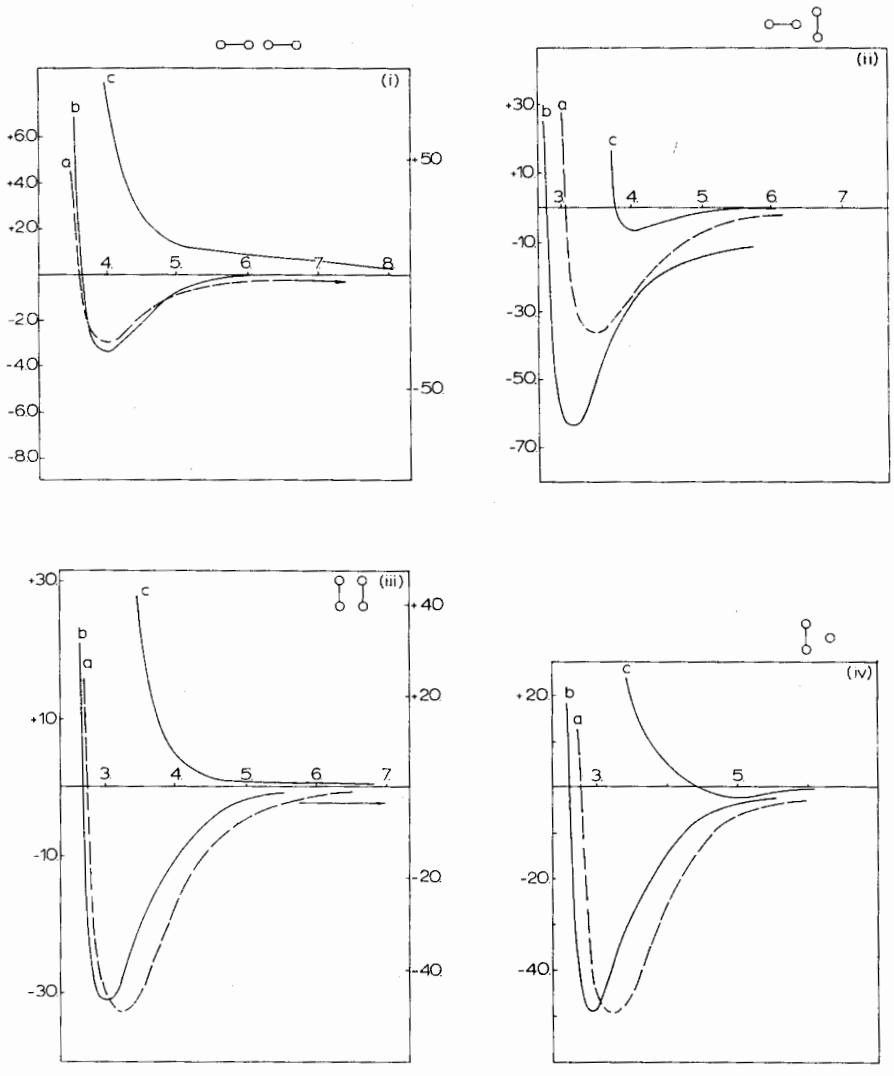


Fig. 1. Hydrogen and Deuterium:

(i) (zz) configuration

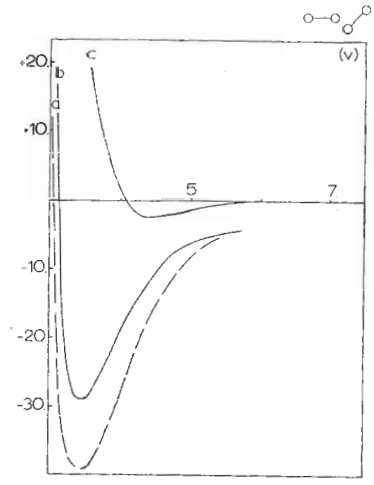
(a) atom-atom potential (σ(H) = 2.8 Å; ϵ/K (H) = 15.0 K).

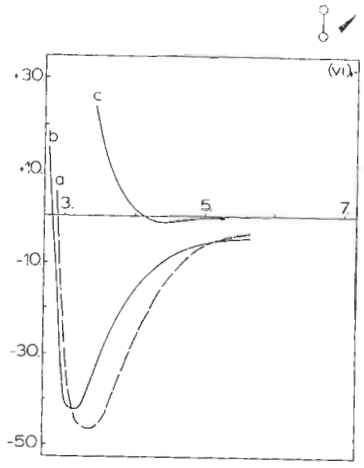
(b) Kihara/Koide potential.

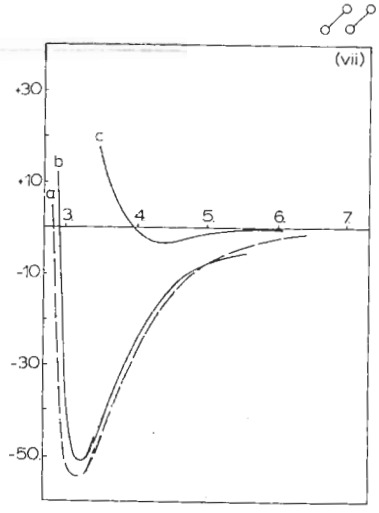
(c) 6 - 31G ab initio calculations.

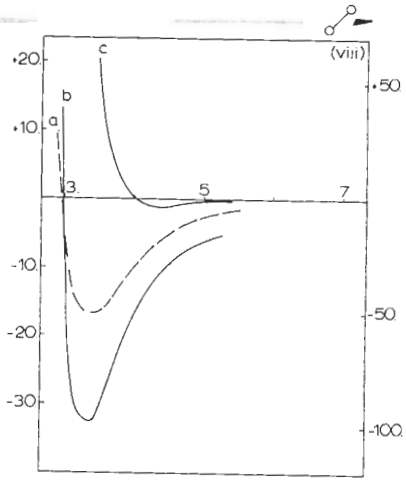
(ii) (zx); (iii) (xx); (iv) (xy); (v) (zd); (vi) (xd); (vii) (dd); (viii) (dd′) and (ix) (dd″).

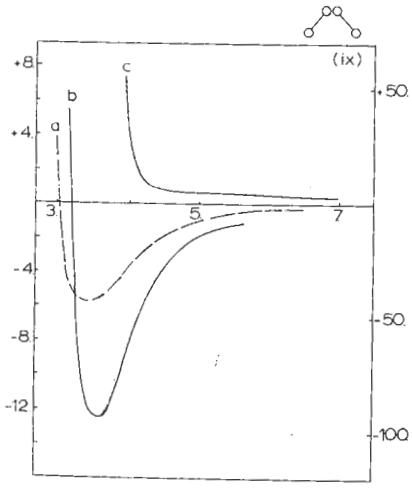
Ordinate: Kelvin; Abscissa Å.


(v)
+20
+10
-10
-20
-30
a
b
c
5
7

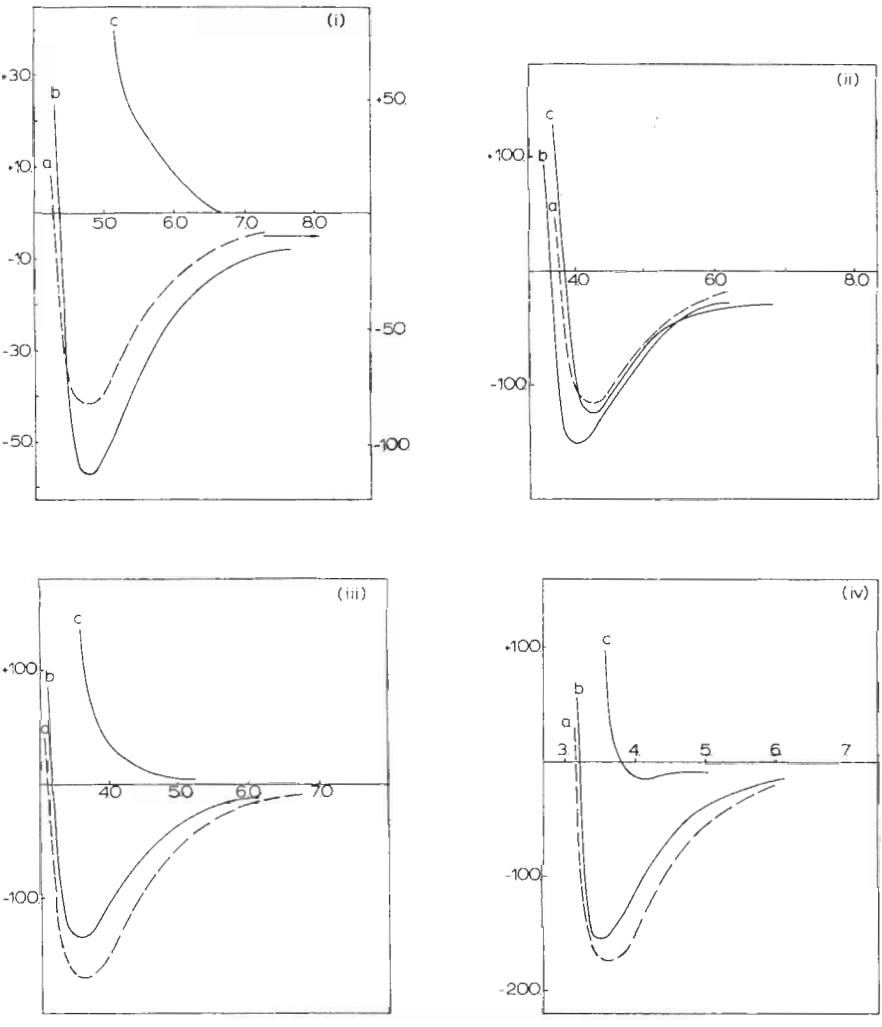

(vi)
+30
+10
-10
-30
-50
a
b
c
3
5
7


(vii)
+30
+10
-10
-30
-50
a
b
c
3
4
5
6
7

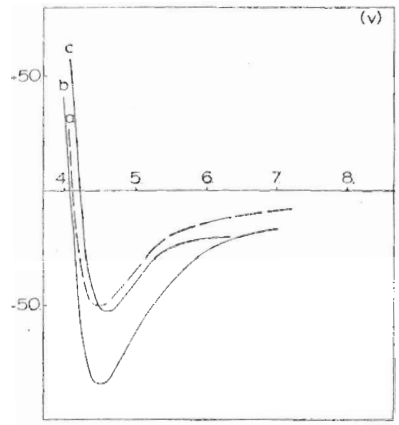

(viii)
+20
+10
-10
-20
-30
+50
-50
-100
a
b
c
3
5
7

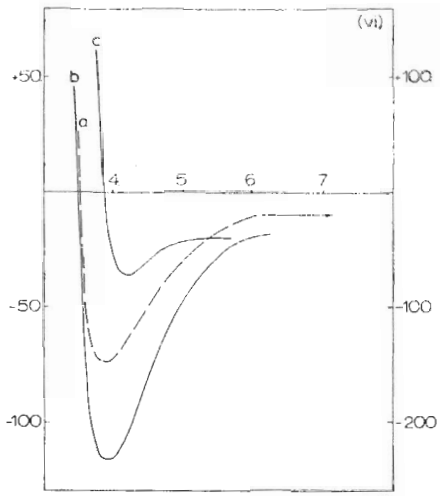

(ix)
+8
+4
-4
-8
-12
+50
-50
-100
a
b
c
3
5
7

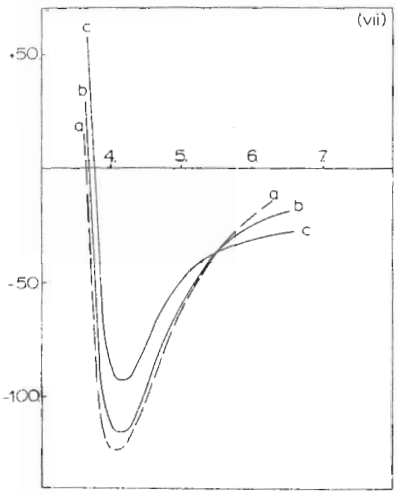
20

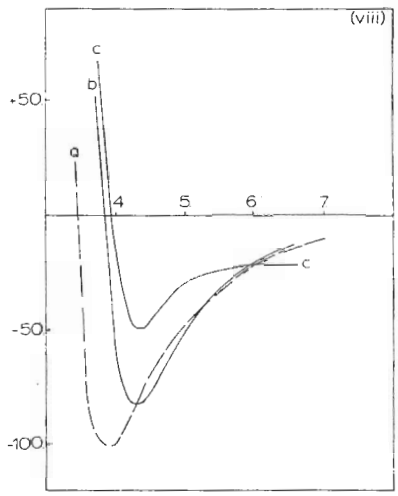


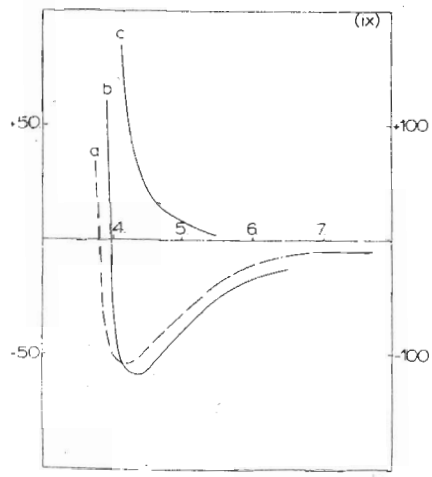
ig. 2. Nitrogen:
tom-atom parameters: (σ(N) = 3.341 Å; ϵ/k(N) = 44.0 K).


(v)
+50
-50
c
b
a
4
5
6
7
8


(vi)
+50
-50
-100
+100
-100
-200
c
b
a
4
5
6
7


(vii)
+50
-50
-100
c
b
a
4
5
6
7


(viii)
+50
-50
-100
c
b
a
4
5
6
7


(ix)
+50
-50
+100
-100
c
b
a
4
5
6
7

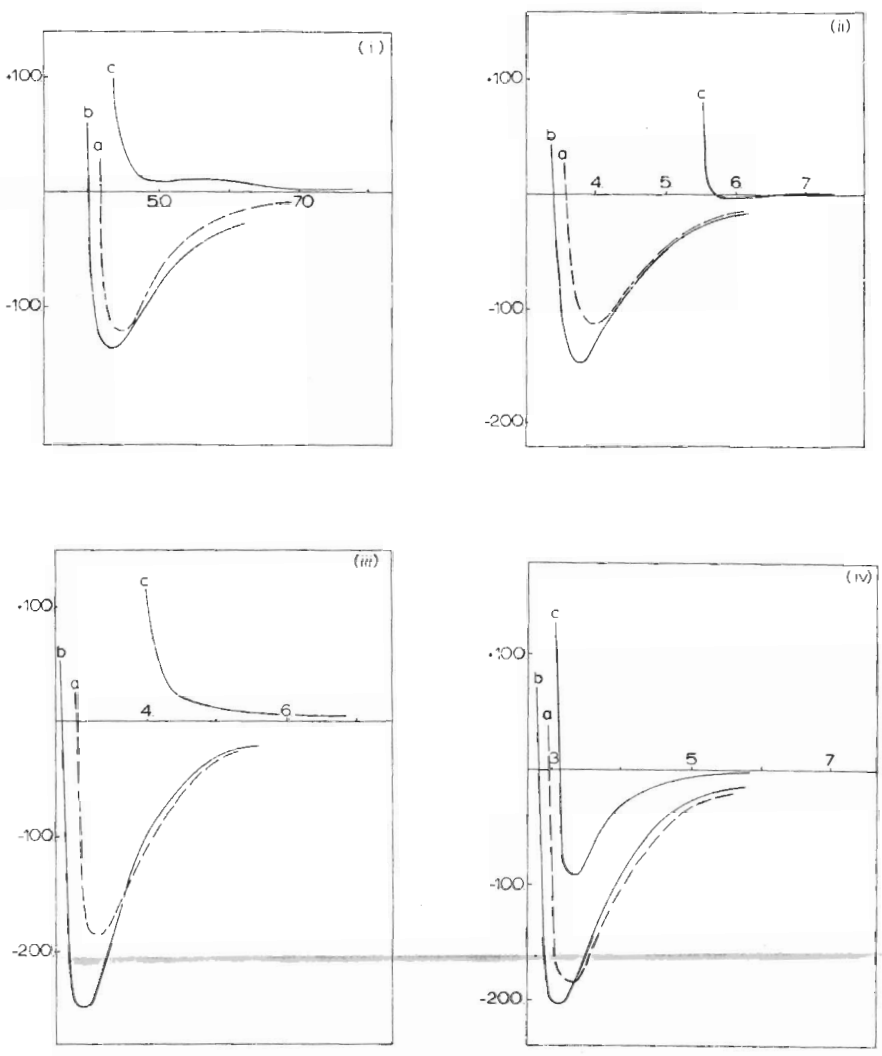
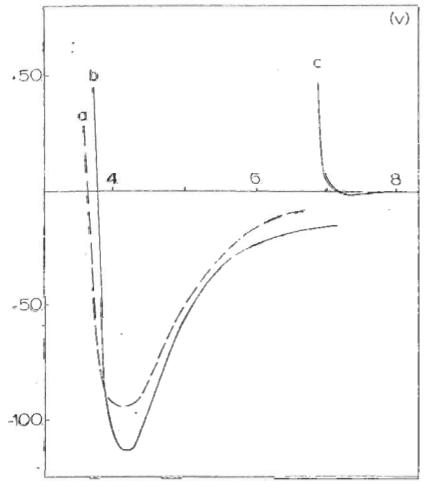
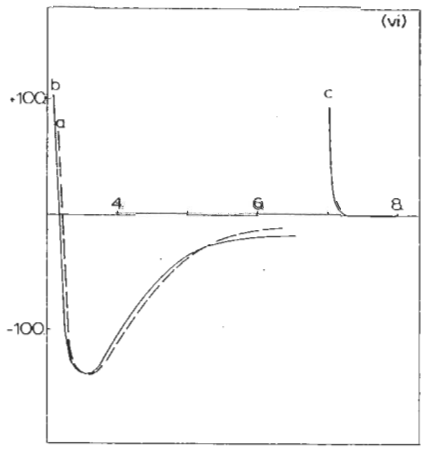
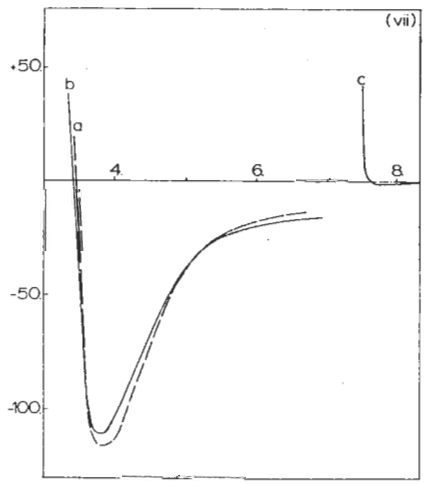
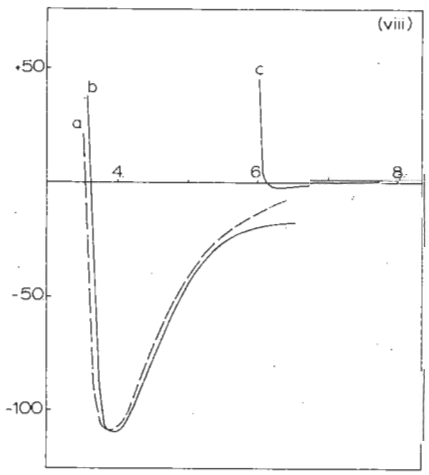


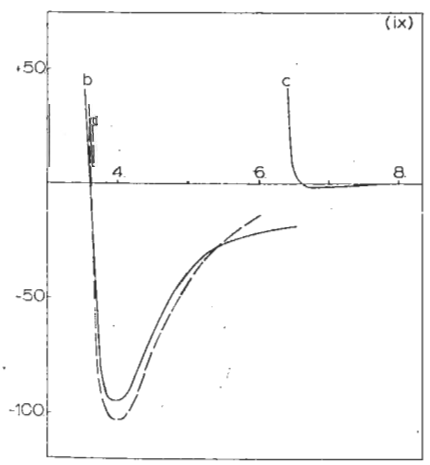
Fig. 3. Oxygen:
Atom-atom parameters ($\sigma(0)$ = 3.09 Å; $\epsilon/k(0)$ = 44.6 K).


(v)
+50
-50
-100
a
b
c
4
6
8


(vi)
+100
-100
a
b
c
4
6
8


(vii)
+50
-50
-100
a
b
c
4
6
8


(viii)
+50
-50
-100
a
b
c
4
6
8


(ix)
+50
-50
-100
a
b
c
4
6
8

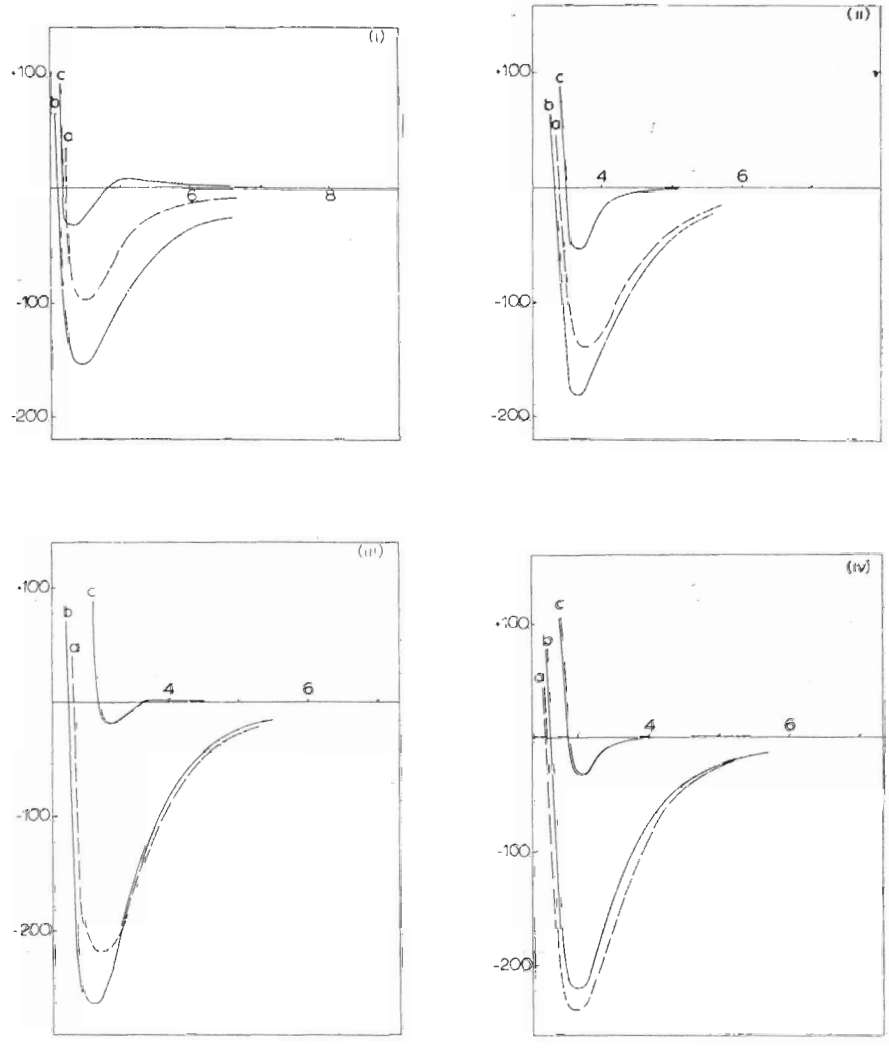
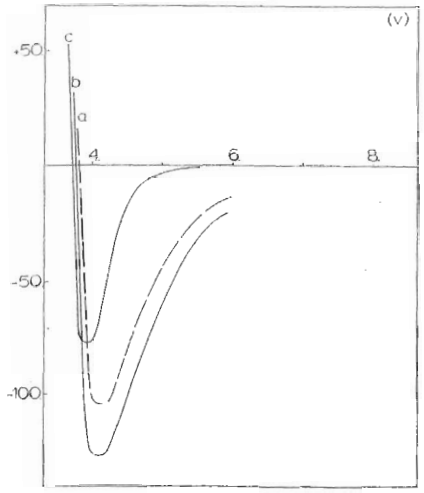
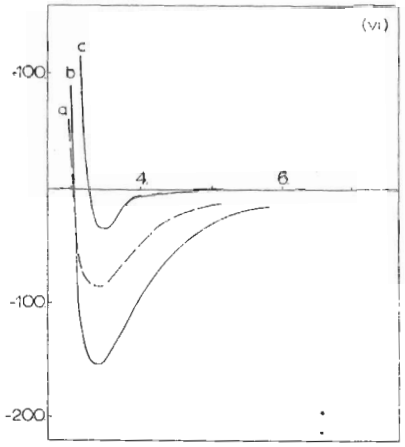
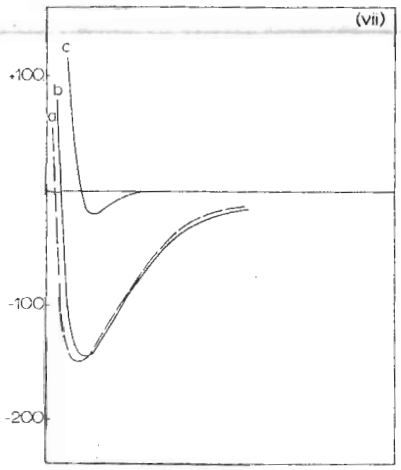
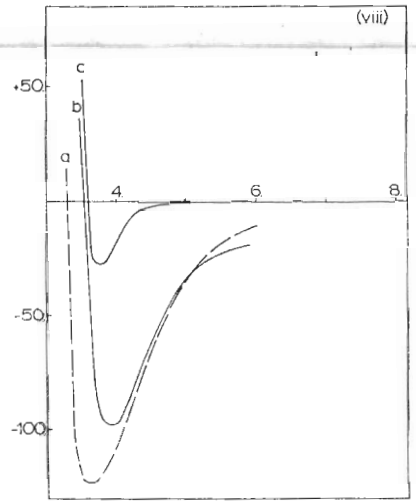


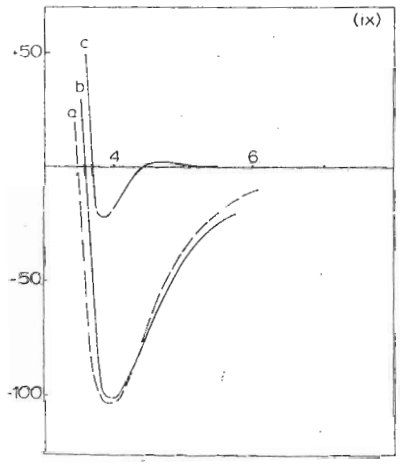
Fig. 4. Fluorine:
Atom-atom paramters (σ(F) = 2.8 Å; ϵ/k(F) = 60 K).


(v)
+50
-50
-100
c
b
a
4
6
8


(vi)
+100
-100
-200
c
b
a
4
6


(vii)
+100
-100
-200
c
b
a


(viii)
+50
-50
-100
c
b
a
4
6
8


(ix)
+50
-50
-100
c
b
a
4
6

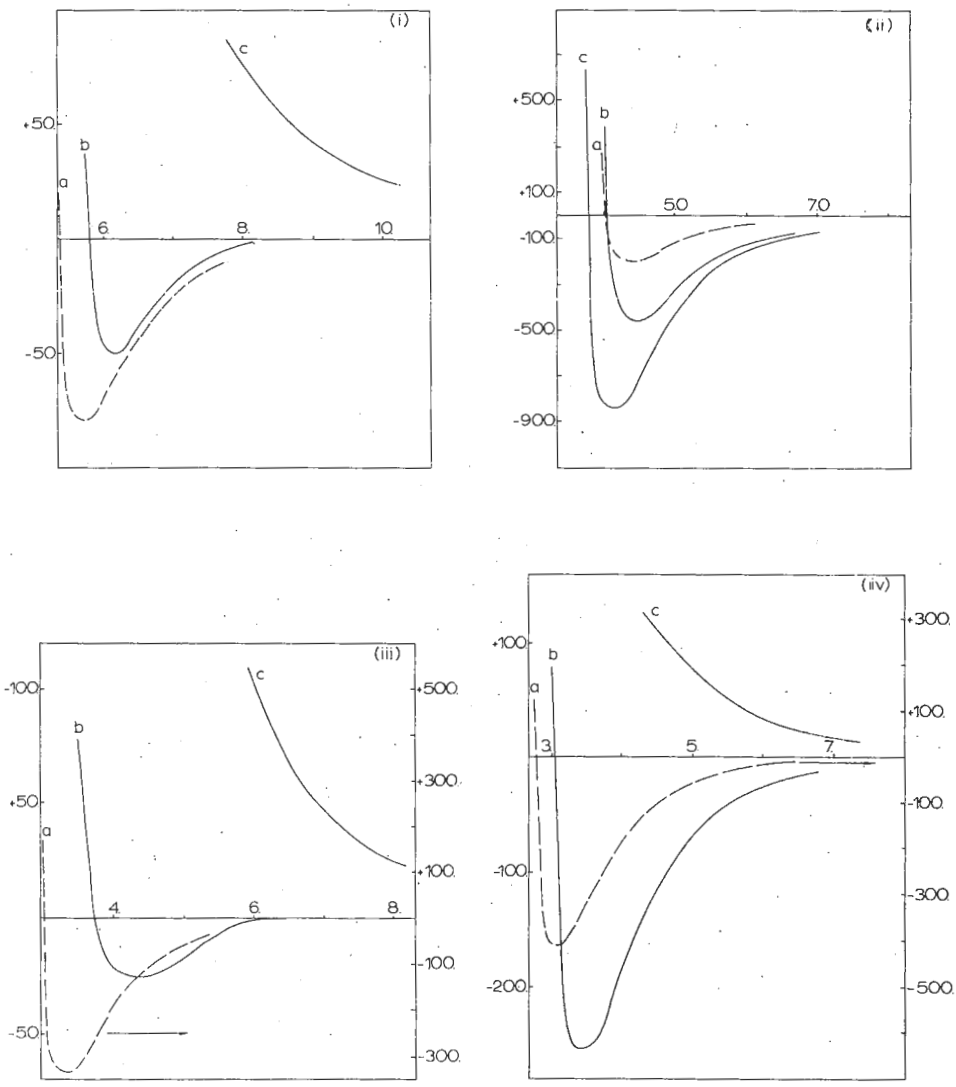
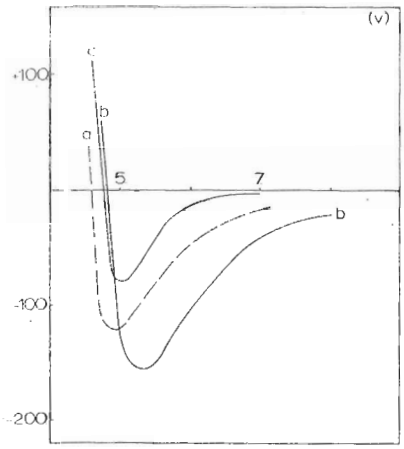
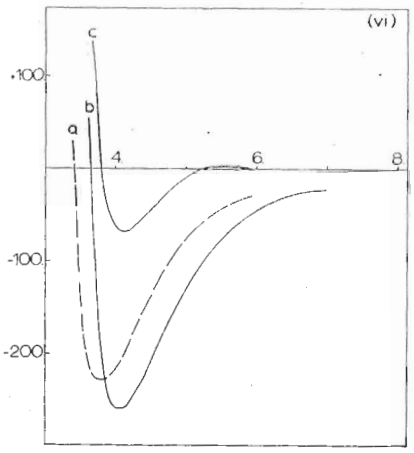
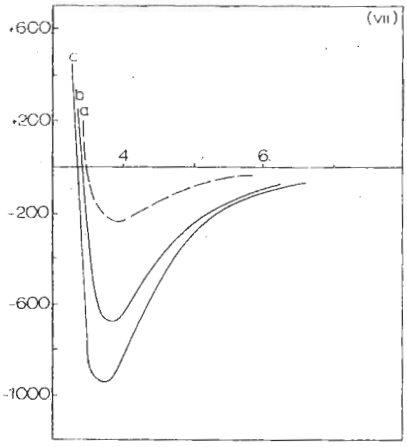
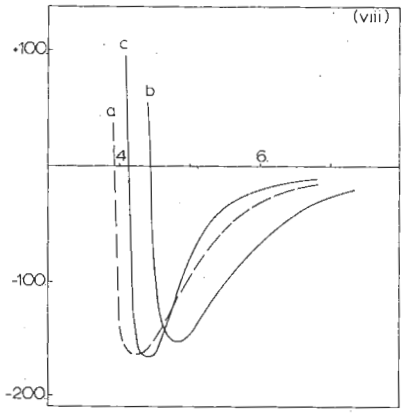


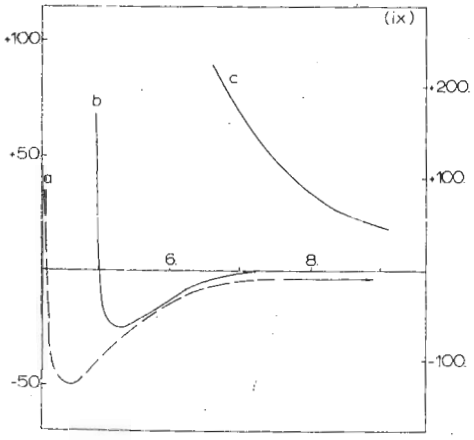
Fig. 5. Carbon Dioxide:
Atom-atom paramters (σ(C) = 2.8 Å; ϵ/k(C) = 50 K); σ(c...O) = 2.945 Å; ϵ/k (c...O) = 47.3 K).


(v)
+100
-100
-200
5
7
a
b
c


(vi)
+100
-100
-200
4
6
8
a
b
c


(vii)
+600
+200
-200
-600
-1000
4
6
a
b
c


(viii)
+100
-100
-200
4
6
a
b
c


(ix)
+100
+50
-50
+200
+100
-100
6
8
a
b
c

Hydrogen

Configurations are shown schematically in Fig. 1: (a) on each panel is the atom-atom potential; (b) is the Kihara/Koide estimate for deuterium; and (c) is the ab initio estimate for hydrogen. It is obvious that both the atom-atom and Kihara/Koide potentials overestimate the attractive part of the potential compared with the ab initio estimates. In paper 1 of this series the former was thoroughly tested against the most comprehensive experimental data available for CH_3F, agreement being much better with these than with the atom-atom estimate. There are instances in the case of H_2/D_2 where the Kihara/Koide and atom-atom potentials are in qualitative disagreement with the ab initio results, the latter being purely positive and the former being megative. Despite a large qualitative discrepancy, the minimum energy configuration is the same one in both Kihara/Koide and the ab initio result.

Nitrogen

Nitrogen has a much bigger quadrupole moment. In three configurations (Fig.2) the three potentials agree almost perfectly. These are low energy configurations. In other instants where the ab initio potential is non-negative it seems that the others are overestimating the effect of dispersion. Again in the parallel approach (panel (iii)) there is qualitative disagreement.

Oxygen

In this case there is pronounced disagreement between the model and ab initio results (Fig.3) in every configuration except the perpendicular one of panel (iv). This crosswise configuration is that where the quadrupolar attraction is strongest, and presumably also the hexadecapolar. This is interesting because the far infra-red induced absorption of a compressed oxygen has an anomalously broad band, stretching out to much higher frequencies than that of nitrogen and is explicable in terms of $J \longrightarrow J + 4$ (hexadecapolar induced) dipole transitions. Again there is qualitative disagreement in panel (iii), the parallel approach which is the minimum energy configuration of the Kihara/Koide potential and is repulsive in the ab initio calculation. For O_2 Kihara and Koide do not take into consideration quadrupolar interaction, which in some instants, including that of panel (iii) is repulsive. In some cases (e.g. panel (v)) the ab initio result is an

immensely strong repulsion field at no less than 7 Å intermolecular separating while the Kihara/Koide estimate allows an approach distance of less than 4 Å. This may be attributed to the existence of O_2 in a triplet state, thus increasing the intermolecular repulsion.

Fluorine

In the fluorine molecule (Fig.4) the potential curves are always negative (with both ab initio and model potentials) although the latter are deeper. The distances at which the potential curves cut the axis are similar in almost all cases and there is no strong disagreement as in the case of oxygen. The minimum energy configuration from the ab initio calculation is (v) and (iii) in the Kihara/Koide representation, which is similar to the atom-atom behaviour.

Carbon Dioxide

In Fig.5, configuration (ii) (vii) and (viii) there is an inversion of the trend of Figures (1) to (4) where the model potential wells are always deeper than the ab initio. In these cases the three estimates agree fairly well in position and depth. However in configurations (i), (iii), (iv) and (ix) there is qualitative disagreement once more, the ab initio results remaining non-negative throughout. Both the ab initio and Kihara/Koide potentials indicate that the configuration (vii) is the one of least energy, closely followed in the ab initio representation by configuration (ii). However, configuration (iv), which is the third deepest in the Kihara/Koide representation is entirely non-negative in the ab initio calculations which is also the case for configurations (i), (iii), (iv) and (ix). The characteristic features of the orientation dependence of the intermolecular model can be represented by Kihara's quadrupolar molecular models, made of two ferrite magnets with plastic or wooden spherical caps. An assembly of such molecular models simulates the crystal structure of carbon dioxide. It follows that the ab initio calculations are not dominated to the same extent by quadrupolar forces.

It is worth mentioning that the results obtained by both 4 - 31G and 6 - 31G basis sets are more or less the same. The crucial problem in the variational calculations of intermolecular interactions are[19] the coupling of inter- and intra-correlation effects as well as the variation of the intra-correlation energy with distance, and in view of the smallness of these forces, and due to overlap effects one may get a fully repulsive potential

curve, so the exchange and overlap effects must be accounted for. As previously noted[13] the interaction energies obtained by the SCF and CI method are very similar but improved values for the total energy and thus the interaction energy of a particular basis set are obtainable by optimization of the orbital exponents at each internuclear separation. Dixon et al[14] have carried out SCF calculations including configuration interaction for hexagonal H_6 with several basis sets. Adding polarization functions to the basis set was found to improve the calculated potential energy parameters. So some improvements may be made to the 4 - 31G and 6 - 31G results if we add P and/or D polarization functions or with still higher angular momentum; combined with minimization of orbital exponents at different intermolecular distances, and this may play different roles in such geometrical arrangements considered here in our study.

CONCLUSIONS

Intermolecular potential estimates have been compared from three sources: the atom-atom, the Kihara/Koide equation and ab initio calculations. In many configurations there is qualitative disagreement and it seems that the Kihara/Koide and atom-atom representations overestimate the attractive part in some configurations. The disagreement for oxygen is particularly acute.

ACKNOWLEDGEMENTS

The S.R.C. is thanked for support to M.W.E. and M.F., and the Royal Society for a bursary to A.A.H.

REFERENCES

1 A.A. Hasanein, M. Ferrario and M.W. Evans, Adv. Mol. Rel. Int. Proc., (1980) in press.

2 T. Kihara and M. Kotari, Proc. Phys.-Math. Soc. Japan, 25 (1943) 602; T. Kihara, Revs. Modern Phys., 25 (1953) 831; Adv. Chem. Phys., 5 (1963) 147; T. Kihara, Acta Crystallogr., 16 (1963) 1119; 21 (1966) 877; Adv. Chem. Phys., 20 (1971) 1.

3 J.E. Lennard-Jones, Proc. Roy. Soc. (London) A, 106 (1924) 463; Proc. Phys. Soc. London, 43 (1931) 461; Physica, 4 (1937) 941.

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

5 M.W. Evans, Mol. Phys., 29 (1975) 1345; J. Chem. Soc., Faraday Trans. II, 69 (1973) 763; Spectrochim. Acta, 30 (1974) 79.
6 M.W. Evans, A.R. Davies and G.J. Evans, Adv. Chem. Phys., 44 (1980) 235-481.
7 A. Koide and T. Kihara, Chem. Phys., 5 (1974) 34.
8 G.A. Victor and A. Dalgarno, J. Chem. Phys., 53 (1970) 1316.
9 W.B. Streett and D.J. Tildesley, Proc. Roy. Soc., 348A (1976) 485; 355A (1977) 239; W.B. Streett and K.E. Gubbins, Ann. Rev. Phys. Chem., 28 (1977) 373.
10 M. Krauss and F.H. Mies, J. Chem. Phys., 42 (1965) 2703.
11 T.L. Gilbert and A.C. Wahl, J. Chem. Phys., 47 (1967) 3425.
12 I. Shavitt, R.M. Stevens, F.L. Minn and M. Karplus, J. Chem. Phys., 48 (1968) 2700.
13 M.D. Gordon and D. Secrest, J. Chem. Phys., 52 (1970) 120.
14 D.A. Dixon, R.M. Stevens and D.R. Herschbach, Faraday Disc. Chem. Soc., 62 (1977) 110.
15 R. Ditchfield, W.J. Hehre and J.A. Pople, J. Chem. Phys., 54 (1971) 724.
16 J.S. Binkley, J.A. Pople and W.J. Hehre, J. Amer. Chem. Soc., 102 (1980) 939.
17 J.S. Binkley, R.A. Whiteside, P.C. Hriharan, R. Seeger, J.A. Pople, W.J. Hehre and M.D. Newton, Q.C.P.E. Program No. 368.
18 "Tables of interatomic distances" and "Supplement"; Chem. Soc. Spec. publ. (1965).
19 W. Kutzelnigg, Faraday Disc. Chem. Soc., 62 (1977) 185, 311.