J. Am. Chem. Soc. 1983, 105, 355-360

Interaction of Methane and Methanol with Water

G. Bolis,[1a] **E. Clementi,***[1a] **D. H. Wertz,**[1b] **H. A. Scheraga,**[1b] **and C. Tosi**[1c]

Contribution from IBM Corporation, Poughkeepsie, New York 12602, Cornell University, Baker Laboratory of Chemistry, Ithaca, New York 14853, and Istituto G. Donegani, S.P.A., Novara, Italy 28100. *Received December 21, 1981*

Abstract: Intermolecular interaction energies of methane and methanol with a water molecule are computed in the SCF approximation with a minimal basis set and with the counterpoise correction; the value for the dispersion correction is estimated by a perturbation method. The computed interaction energies for a water molecule at a large number of different positions and orientations relative to either CH_4 or CH_3OH (the latter in three different conformations) are used to derive simple analytical atom–atom pair potentials. These potentials are used elsewhere in Monte Carlo studies of the hydration of CH_4 and CH_3OH.

Introduction

The interaction energy between water (H_2O) and methane (CH_4) and methanol (CH_3OH), respectively, is of interest because aqueous solutions of CH_4 and CH_3OH can be considered as models for studying hydrophobic and hydrophobic-plus-hydrophilic interactions. For this reason these two solutes have been considered by numerous investigators.[2-8] A crucial aspect in these studies is the availability of reliable intermolecular potentials. Therefore, the problem of $CH_4\cdots H_2O$ and $CH_3OH\cdots H_2O$ potentials is addressed in this paper.

It is well known[9] that reasonable interaction energies can be obtained from ab initio computations provided that a proper basis set and proper theoretical models are selected. In particular, a relatively small basis set, with inclusion of dispersion and induction corrections, provides reliable potentials.[10] In a step-by-step procedure, we can idealize the derivation of intermolecular potentials by considering, *first*, an atom–atom *two-body* potential at the Hartree–Fock level, *then* an atom–atom two-body potential at the CI level (addition of the dispersion correction), and *next* a three-body potential at the Hartree–Fock level; the difference between two- and three-body potentials at the Hartree–Fock level, i.e., the nonadditivity of the two-body potential, arises mainly from induction corrections and three-body short-range corrections.

For simulations of aqueous solutions it is desirable to have an "effective" two-body potential, which is pairwise additive. Such an effective two-body potential is obtainable from ab initio computations by the following argument. In general, for an *n*-body system, the exact potential $W(1,...,n)$ can be written as

$$W(1,...,n) = \sum V(i,j) + \sum V(i,j,k) + \ldots + V(1,...,n) \quad (1)$$

or approximated as

$$W(1,...,n) = \sum V(i,j)_{\text{effective}} \quad (2)$$

It should be noted that there are many and vastly different ways to define an effective potential. In eq 2, the effective potential is cast into the form of an atom–atom two-body potential; very generalized effective potentials can describe the interaction between atoms *i* and *j* where a given atom can belong to different "classes" according to its molecular environment.[9] In this work we have used

$$V(i,j) = V(i,j;\text{ Hartree–Fock}) + V(i,j;\text{ dispersion}) \quad (3)$$

as an approximation to the potential

$$V(i,j) = V(i,j;\text{ Hartree–Fock}) + V(i,j;\text{ full CI corrections}) \quad (4)$$

Computation of the Intermolecular Interaction Energies

We have not tried to obtain a *very* accurate interaction energy for a *few* conformations of the $CH_4\cdots H_2O$ (or $CH_3OH\cdots H_2O$) systems, but rather to derive reasonable potentials of equivalent validity for *all possible* conformations in the above systems. By "reasonable", we mean that the $CH_4\cdots H_2O$ and the $CH_3OH\cdots H_2O$ potentials should be about as accurate (namely with differences not longer than 10–20%) as the available two-body water–water CI potentials.[11] Indeed, the systems of final interest are neither $CH_4\cdots H_2O$ nor $CH_3\ OH\cdots H_2O$ but $CH_4\cdots(H_2O)_n$ and $CH_3OH\cdots(H_2O)_n$, where *n* is a larger number.

On the basis of previous studies of the interaction of H_2O with $(H_2O)_2$,[12], with Ar,[13] and with glycine,[10] or of the interaction of CH_4 with CH_4,[14] we have reason to assume that a reasonable two-body potential can be obtained from theoretical methods (1) by selecting a minimal, but well-optimized and balanced, basis set, (2) by correcting for the basis set superposition error with the counterpoise method,[15] and (3) by including dispersion corrections. The background for some of these steps can be found, for example, in a number of extensive review papers.[9,16,17]

The minimal basis set selected here is the one derived for first-row atoms.[18] It consists of a set of 16 primitive Gaussian functions (seven s type and three each of type $2p_x$, $2p_y$, $2p_z$) for both C and O atoms, in which five s-type primitive functions are contracted to one 1s, two s-type primitive functions are contracted to one 2s, and each of the three p-type primitive functions is contracted to one each of the type $2p_x$, $2p_y$, $2p_z$; four s-type primitive functions are contracted into a 1s function for the H

---

(1) (a) IBM Corporation, P.O. Box 390, Poughkeepsie, NY 12602; (b) Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853; (c) Istituto Ricerche G. Donegani, S.P.A., Via del Lavoro 4, Novara, Italy.

(2) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257 (1972).

(3) S. R. Ungemach and H. F. Schaefer III, *J. Am. Chem. Soc.*, **96**, 7898 (1974).

(4) J. C. Owicki and H. A. Scheraga, *J. Am. Chem. Soc.*, **99**, 7403 (1977).

(5) S. Swaminathan, S. W. Harrison, and D. L. Beveridge, *J. Am. Chem. Soc.*, **100**, 5705 (1978).

(6) H. A. Scheraga, *Acc. Chem. Res.* **12**, 7 (1979).

(7) G. Bolis and E. Clementi, *Chem. Phys. Lett.*, **82**, 147 (1981).

(8) G. Bolis, G. Corongiu, and E. Clementi, *Chem. Phys. Lett.*, **86**, 299 (1982).

(9) E. Clementi, "Computational Aspects for Large Chemical Systems", Lecture Notes in Chemistry, Vol. 19, Springer-Verlag, New York, 1980.

(10) W. Kolos, *Theor. Chim. Acta*, **51**, 219 (1979).

(11) O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 1351 (1976).

(12) E. Clementi, W. Kolos, G. C. Lie, and G. Ranghino, *Int. J. Quantum Chem.*, **17**, 377 (1980).

(13) W. Kolos, G. Corongiu, and E. Clementi, *Int. J. Quantum Chem.*, **17**, 775 (1980).

(14) W. Kolos, G. Ranghino, E. Clementi, and O. Novaro, *Int. J. Quantum Chem.*, **17**, 429 (1980).

(15) S. F. Boys and F. Bernardi, *Mol. Phys.*, 19, 553 (1970).

(16) P. Claverie, In "From Diatomics to Biopolymers", B. Pullman, Ed., Wiley, New York, 1978.

(17) A. D. Buckingham, *Adv. Chem. Phys.*, **12**, 107 (1967).

(18) L. Gianolio, R. Pavani, and E. Clementi, *Gazz. Chim. Ital.*, **108**, 181 (1978).

0002-7863/83/1505-0355$01.50/0

Table I. Cartesian Coordinates (in au), Net Charges (in electron), and Molecular Orbital Valency State Energies (in au) for CH_3OH and CH

name	X	Y	Z	net charge	MOVS energies
		Methanol S[a]			
C	0.00	0.00	0.00	−0.4305	1.0584
O	0.1570	0.0000	2.6924	−0.5422	0.3663
HC1	1.9469	0.0000	−0.7062	0.2215	0.2936
HC2	−0.9734	−1.6860	−0.7062	0.1907	0.2760
HC3	−0.9734	1.6860	−0.7062	0.1907	0.2760
HO	−1.5160	0.0000	3.3751	0.3700	0.3038
		Methanol P[a]			
C	0.00	0.0000	0.0000	−0.4310	1.0583
O	0.0000	−0.1570	2.6924	−0.5431	0.3664
HC1	1.9469	0.0000	−0.7062	0.1975	0.2790
HC2	−0.9734	−1.6860	−0.7062	0.3176	0.2910
HC3	−0.9734	1.6860	−0.7062	0.1879	0.2754
HO	0.0000	1.5160	3.3751	0.3711	0.3040
		Methanol E[a]			
C	0.00	0.00	0.00	−0.4315	1.0583
O	−0.1570	0.00	2.6924	−0.5440	0.3666
HC1	1.9469	0.00	−0.7062	0.1874	0.2755
HC2	−0.9734	−1.6860	−0.7062	0.2079	0.2848
HC3	−0.9734	1.6860	−0.7062	0.2079	0.2848
HO	1.5160	0.00	3.3751	0.3722	0.3042
		Methane			
C	0.00	0.0000	0.0000	−0.8502	0.9446
H1	2.0665	0.0000	0.0000	0.2125	0.2896
H2	−0.6888	1.9483	0.0000	0.2125	0.2896
H3	−0.6888	−0.9741	1.6872	0.2125	0.2896
H4	−0.6888	−0.9741	−1.6872	0.2125	0.2896
		Water			
O	0.0000	0.0000	0.0000	−0.6802	0.3528
H1	1.1072	1.4305	0.0000	0.3401	0.2935
H2	1.1072	−1.4305	0.0000	0.3401	0.2935

[a] S, P, and E refer to the staggered perpendicular and eclipsed conformations discussed in the text.

atoms. In this basis set, the contraction coefficients are not those derived directly from atomic computations with uncontracted basis sets, as is usually done, but are obtained from contracted functions, with the contraction coefficients variationally optimized.[18] For the separated atoms, this basis set (except for H) is energetically somewhat better than a Slater single-ζ and not too different from a Slater double-ζ basis set.[19]

For CH_4 we have used the equilibrium geometry reported by Herzberg,[20] for H_2O the one of Benedict et al.,[21] and for CH_3OH the one discussed by Fink and Allen.[22] The Cartesian coordinates (and the geometry) for CH_4, CH_3OH, and H_2O are given in Table I (where the first letter of the code name for the atoms is the atomic symbol, and the following one designates the neighboring atom). For CH_3OH, three different conformations were considered: the staggered (S) (the most stable one in the gas phase), the eclipsed (E), and an intermediate one referred to as perpendicular (P). With our minimal basis set (and in the self-consistent-field approximation) the energy of internal rotation (relative to 0 for S) is computed as 2.20 and 1.39 kcal/mol for E and P, respectively. These values are higher than those obtained with an extended basis set with added polarization functions,[23] where the computed energies were 1.93 and 1.27 kcal/mol for the E and P conformations, respectively. However, the experimental barrier to internal rotation is 1.07 kcal/mol.[24-26] It should be noted that in our computation we have simply rotated the OH bond without reoptimizing the bond lengths and bond angles of the methyl group.

The interaction energy surface between H_2O and CH_4 or CH_3OH has been scanned at a number of points corresponding to different positions and relative orientations of the partners in the $CH_4\cdots H_2O$ and $CH_3OH\cdots H_2O$ complexes; 220 points were used for CH_4, 45 points for CH_3OH(E), 115 points for CH_3OH(P), and 70 points for CH_3OH(S).

As has been noted often, for example, recently by Clementi et al.,[27] the use of the counterpoise method[15] (CP) to correct for the basis set superposition error is more important for complexes in which the two molecules overlap strongly (generally a repulsive situation) than for those in which the overlap is weak or very weak. This statement is basis set dependent: small basis sets and/or relatively large basis sets with a poor energy description in the inner shell orbitals have larger basis set superposition error than relatively large basis sets with a good energetic description of the inner-shell orbitals. With our basis set and for $CH_4\cdots H_2O$ repulsive interactions, energies obtained without CP in the range of 17 to 20 kcal/mol increase to 20 to 25 kcal/mol upon basis superposition correction. Near the minimum, interaction energies of about −0.4 kcal/mol with CP would yield about −0.7 kcal/mol without CP (but larger differences have been encountered). The same pattern holds for methanol, where energies of about −8.5 kcal/mol without CP are corrected to −5.9 kcal/mol with CP, near the minimum. The larger superposition error near equilibrium in the methanol complexes relative to methane is due to the closer internuclear approach in $CH_3OH\cdots H_2O$ relative to $CH_4\cdots H_2O$. As noted above, we have used CP for all the complexes considered in this work.

From these remarks, one can appreciate that weak interactions computed without the CP correction can yield seriously spurious energies, grossly different from those obtained either with CP or with appropriately extended basis sets. *Fortuitously*, the basis set superposition error can yield interaction energies in agreement with experimental data, however, for internuclear distances that generally disagree with the experimental data; i.e., this relation is not unique in that different internuclear distances give the same energies when corrected by the superposition error. To use the superposition error as a device to correct (a) for dispersion and other correlation corrections and (b) for omission of three- and many-body interaction seems to be a questionable procedure; the superposition correction accounts for only a *part* of effects a and b. Studies supporting a different point of view have been published.[28]

The dispersion energy has been computed with a relation in which the total dispersion interaction is split into interactions between individual bonds; a London-type formula is then applied to each bond–bond interaction, assuming that the interaction center of each bond coincides with the midpoint of the bond. The dispersion correction assumes the form[10]

$$E_{\mathrm{disp}} = -(1/4)(U_{\mathrm{A}}U_{\mathrm{B}})/(U_{\mathrm{A}} + U_{\mathrm{B}})R_{ij}^{-6}\ \mathrm{Tr}[\mathrm{T}_{ij}\mathbf{A}_i\mathrm{T}_{ij}\mathbf{A}_j] \quad (5)$$

where U_{A} and U_{B} are the average excitation energy of molecules A or B, respectively, $R_{ij} = |\boldsymbol{R}_{ij}|$ is the vector joining the midpoints of bond j in molecule B and bond i in molecule A, $\mathbf{A}_i$ and $\mathbf{A}_j$ are the polarizability tensors of the two bonds, $\mathrm{T}_{ij} = 3(r_{ij} \otimes r_{ij}) - \mathbf{1}$ where, $\mathbf{1}$ is the unit matrix, and r_{ij} is the unit vector

$$\mathbf{r}_{ij} = \mathbf{R}_{ij}/R_{ij}$$

---

(19) E. Clementi and C. Roetti, "Atomic Data and Nuclear Data Tables", Vol. 14 Academic Press, New York, 1974, p 177.

(20) G. Herzberg, "Electronic Spectra of Diatomic Molecules", Van Nostrand-Raynolds, New York, 1966.

(21) W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, **24**, 1139 (1956). The OH internuclear distance is 0.957 Å; the HOH bond angle is 104.52°.

(22) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2661 (1967).

(23) The extended basis set is the one reported in H. Popkie and E. Clementi, *J. Chem. Phys.* for CH_4; the basis set for the oxygen atom is equivalently expanded.

(24) R. M. Lees, F. J. Lovas, W. H. Kirckhoff and D. R. Johnson, *J. Phys. Chem. Ref. Data*, **2**, 205 (1973).

(25) The total energies for methanol (gas phase) in the *S* conformation are −114.9355 au with an intermediate basis set (ref 22), −113.90217 with a subminimal basis set (ref 26), −114.59528 au with a minimal basis set (used here), and −115.08396 au with an extended basis set.[23] The computationally correct value, however, is the one closest to the Hartree–Fock limit and not far from the one reported here (−115.084 au) with the extended basis set.

(26) L. Pederson and K. Morokuma, *J. Chem. Phys.*, **46**, 3941 (1967).

(27) E. Clementi, G. Corongiu, and G. Ranghino, *J. Chem. Phys.*, **74**, 578 (1981).

(28) W. L. Jorgensen, *J. Am. Chem. Soc.*, **102**, 543 (1980).

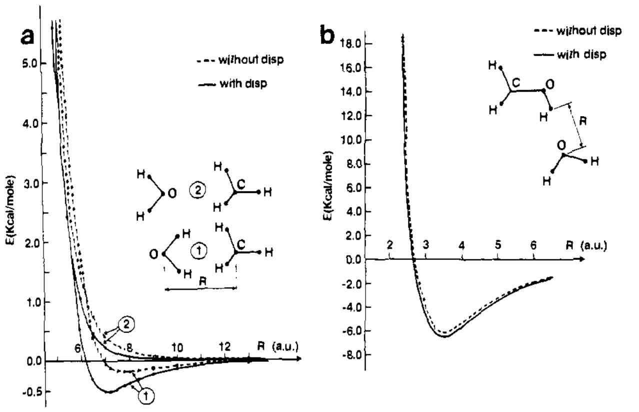

Figure 1. Ab initio computations for two conformations of $CH_4\cdots H_2O$ (a) and for one conformation of CH_3OH-H_2O (b), with and without dispersion correction.

For a discussion of eq 5 see ref 10 and 16. The average excitation energy for the $CH_4\cdots H_2O$ system is $U = 0.65$ au,[10] and for the $CH_3-OH\cdots H_2O$[29] system it is $U = 0.80$ au (using twice the value of Watanabe's ionization potential[29]).

The values of the transverse polarizabilities (needed for the polarizability tensors) are: 3.9,[30] 2.93,[31] and 5.129[32] for the CH, CO, and OH bonds, respectively. The values of the anisotropy terms (the difference between the longitudinal and transverse polarizabilities) are: 1.42,[30] 2.739,[31] and −1.012[32] for the same bonds, respectively. All of the above values are given in atomic units. The SCF computations and the basis set superposition corrections have been obtained with the IBMOL program.[33]

In Figure 1, the interaction energies are reported for two orientations of methane (a) and for one orientation of methanol (b) interacting with water at different internuclear distances but with the same relative orientations. The dispersion corrections in methane and methanol are nearly comparable in value; however, in the system $CH_4\cdots H_2O$ the *most important* fraction of the attraction is due to the *dispersion* correction; conversely, in $CH_3\cdots H_2O$ the dispersion correction is rather *unimportant*, since the Hartree–Fock interaction is large.

In Figure 2, we report a second conformation (the first one being given in Figure 1) for $CH_4\cdots H_2O$, yielding an attractive interaction. In this case, at the minimum, the Hartree–Fock attraction is larger than the dispersion attraction (both, however, adding up to only about −0.6 kcal/mol). This conformation is more reminiscent of a hydrogen bond than the one in Figure 1; equivalently, at the minimum the ratio (Hartree–Fock attraction/dispersion attraction) is not far from that for $(H_2O)_2$ (see, for example, ref 14).

The basis set superposition error does not follow the variation pattern of the dispersion correction; indeed, there is no physical ground for such an assumption. The superposition error reaches a maximum value when the oxygen atom (insufficiently described by the basis set in the very energetic 1s electrons) overlaps an atom with an energetically more reasonable basis set description (for example, a hydrogen atom). In this case, the oxygen atom makes partial use of the hydrogen atom basis set, regaining part of the energy of the 1s electron. Since the 1s orbital energy is about −20.5 au, compared with a value of −0.5 au for hydrogen, it is not difficult to "create" fictitious interactions with an appropriate basis set superposition error (in principle even as large as hundreds of kcal/mol).

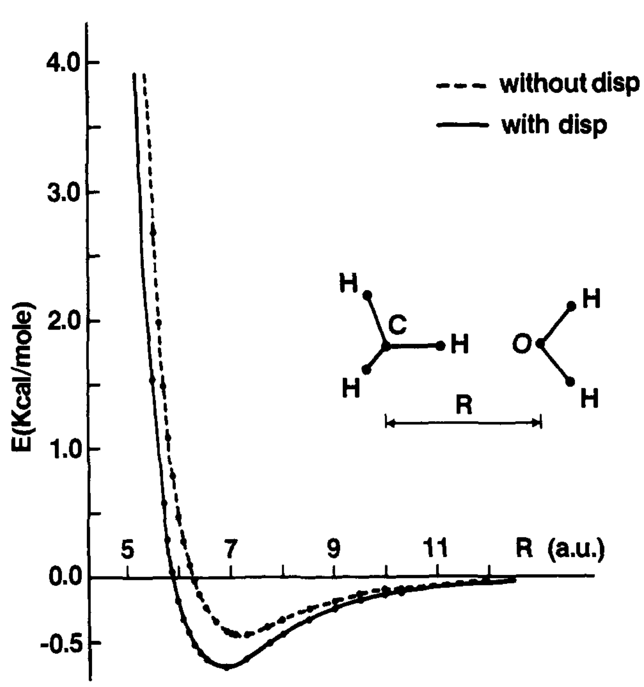

Figure 2. Lowest energy conformation for $CH_4\cdots H_2O$ (ab initio with and without dispersion correction).

Derivation of the Intermolecular Potentials

Table I gives the atomic coordinates (in au), the net charges, NC (in electrons), and the molecular orbital valency state (MOVS) energies (in au) for methane, for the three conformations of methanol, and for water. These data are sufficient to determine the *classes*[27] for the carbon, hydrogen, and oxygen atoms of CH_4 and CH_3OH. In CH_4, there is one class of carbon atom and four equivalent hydrogens, according to the NC and MOVS energy. In CH_3OH, there are two classes of hydrogens, i.e., those of the CH_3 and OH groups, which differ both in NC and in MOVS energy. The carbons of CH_4 and CH_3OH differe both in NC and in MOVS energy (i.e., belong to different classes), but the hydrogens of CH_4 and CH_3- have similar NC's and MOVS energies (i.e., belong to the same class).

The computed interaction energies for the $CH_4\cdots H_2O$ complex were fitted by two potentials of the form of eq 6, described previously,[9,27] viz.

$$V(i,j) = -\frac{A(a,b)}{R_{ij}^{6}} + \frac{B(a,b)}{R_{ij}^{12}} + \frac{C(a,b)q_iq_j}{R_{ij}} \qquad (6)$$

where a and b are indexes denoting a class, as defined above, and q_i and q_j are the charges in Table I. One potential (3TA) describes more optimally the interactions in the attractive region, while the second (3TR) is optimal in the repulsive region. For this reason, in fitting eq 6, we have divided the computed interaction energies into two groups, those that are repulsive (by more than 0.6 kcal/mol) and the remaining ones (that are mainly attractive). The two groups of interaction energies are fitted independently. The two corresponding sets of A, B, and C coefficients are given in Table II; note that the value for C is about one. [We shall refer to this potential as a 3T potential (three terms).] In computing the interaction energy for $CH_4\cdots H_2O$, one switches from one potential to the next at the threshold value, 0.6 kcal/mol. More specifically, the interactions are computed with the 3TA potential and the computed value is accepted if it is equal to or smaller than 0.6 kcal/mol. If the computed value is larger than 0.6 kcal/mol, the interaction is recomputed with the 3TR potential and the resulting value is accepted if it is greater than 0.6 kcal/mol; if it is equal to or smaller than 0.6 kcal/mol, the accepted value is the average of the 3TA and 3TR values. In this procedure, a discontinuity remains between the 3TA and 3TR potentials; thus, these cannot be used for problems requiring derivatives of the potentials. In the 3TR potentials the A coefficients are smaller

---

[29] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[30] J. O. Hirschfelder, C. F. Curtis, and B. B. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1954.

[31] J. W. Smith, "Electric Dipole Moments", Butterworths, London, 1955.

[32] M. J. Huron and P. Claverie, *Chem. Phys. Lett.*, **4**, 429 (1969).

[33] IBMOL Version 7. The latest documentation is available from L. Gianolio, Istituto G. Donegani, S.P.A., Via del Lavoro 4, Novara, Italy 28100. See also E. Ortoleva, G. Castiglione, and E. Clementi, *Comput. Phys. Commun.*, **19**, 337 (1980).

Table II. Fitting Constants for CH_3OH and CH_4 Interacting with Water

$i-j$[a]	A[b]	B	C	D
		Methanol[c]		
O − O	735.5900	488 046.0114	0.9648	
O − C	−856.9602	246 014.0518	1.0186	
O − HC	−121.5038	149.5940	0.9757	
O − HO	139.7382	1 227.5124	1.1038	
H − O	11.3076	451.3174	0.9500	
H − C	0.0000	0.0000	1.0394	
H − HC	142.4907	12 302.4940	0.9853	
H − HO	−116.4495	2.5719	1.0834	
		Methane (3T) Attractive Part		
O − H	−5.8154	0.0009	1.0016	
O − C	893.8261	1 869 731.2672	0.9937	
H − H	46.4619	9 485.5824	1.0003	
H − C	0.0000	265.6061	0.9918	
		Methane (3T) Repulsive Part		
O − H	−115.3361	21.8084	1.0266	
O − C	776.9197	532 145.6352	0.9907	
H − H	0.0000	469.9326	1.0232	
H − C	−297.6928	5 650.0176	0.9916	
		Methane (4T)		
O − H	0.051 294	23.7888	0.9964	0.0000
O − C	1 794.555 316	264 115.5775	0.9961	0.0000
H − H	3.248 324	1 057.8340	0.9897	0.0000
H − C	0.000 376	1 159.3906	0.9881	−14.7589

[a] The atoms under i refer to water; those under j refer either to CH_4 or CH_3OH. [b] The units of A, B, C and D are such as to give $V(i,j)$ of eq 6 and 7 in kcal when R_{ij} is in angstrom units and q_i and q_j are given in electronic charge units. [c] The parameters of methanol are averages over the S, P, and E conformations.

relative to the corresponding B coefficients or appear with a negative sign, thus representing a repulsion.

We also fitted a four-term (4T) form (eq 7) to obtain an atom–atom potential for $CH_4\cdots H_2O$.

$$V(i,j) = -\frac{A(a,b)}{R_{ij}^6} + \frac{B(a,b)}{R_{ij}^{12}} + \frac{D(a,b)}{R_{ij}^4} + \frac{C(a,b)q_iq_j}{R_{ij}} \qquad (7)$$

The fitting constants A, B, C, and D are given in Table II.

The mean standard deviations between the ab initio and fitted energies (for the 4T potential) are ±0.83, ±0.12, and ±0.04 kcal/mol by excluding repulsive energies greater than 5.0, 2.0, and 0.6 kcal/mol, respectively. The lowest ab initio energy is −0.69 kcal/mol, which the 4T potential simulates as −0.65 kcal/mol. Thus, the fitting is very good in the attractive region but less so in the repulsive region, especially at high-energy values. The mean standard deviation for the 3TA potential is ±0.05 kcal/mol. The lowest ab initio energy of −0.69 kcal/mol is simulated as −0.65 kcal/mol by the 3T potential.

The two potentials (4T and 3T) are not too dissimilar. *Their combined use in a given problem is useful because it enabled us to estimate how trends in the data depend on the specific form selected to describe the same set of ab initio interaction energies.* Monte Carlo simulations performed with both the 3T and 4T potentials yield comparable data at a simulated temperature of 300 K.[7,8]

For $CH_3OH\cdots H_2O$, we used[8] only one potential obtained with an equation of the form of eq 6. The mean standard deviation between the ab initio and fitted energies (including those $CH_3\cdots H_2O$ complexes that are repulsive by more than 5.0 kcal/mol) is ±0.346 kcal/mol considering the entire set of values for the three conformations. The mean standard deviations for the complexes with the S, P, and E conformations are ±0.41, ±0.33, and ±0.32 kcal/mol, respectively. The lowest ab initio energies (and fitted energies in parentheses) are −6.08 (−5.67), −6.88 (−7.30), and −7.08 (−7.32) kcal/mol for the S, P, and E conformations, respectively. The A, B, and C coefficients for $CH_3OH\cdots H_2O$ are given in Table II.

In Figure 3, we compare the fitted and ab initio data (SCF + CP + dispersion) for $CH_3OH\cdots H_2O$ and for $CH_4\cdots H_2O$ (3T and 4T potentials). From this figure, it can be seen that the 3T potential is somewhat less steep than the 4T potential in the repulsive region, and that the 3T potential approaches zero (at infinite distance) somewhat faster than the 4T potential. While the 3T and 4T potentials at first might appear to be essentially equivalent, a more definitive assessment can be obtained using both potentials for a given problem (see ref 7 and 8).

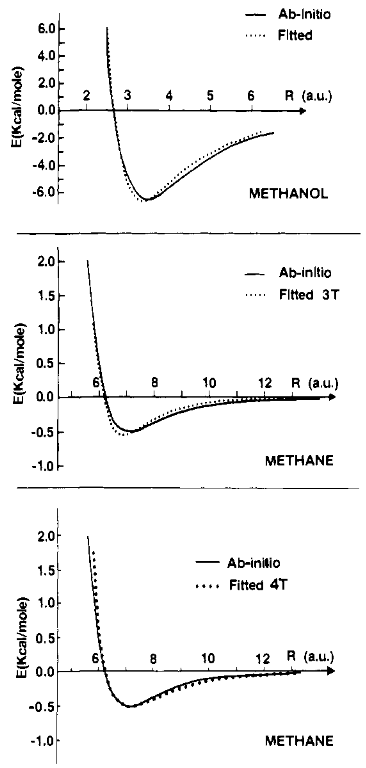

Figure 3. Comparison of computed (ab initio) and fitted potentials. For methanol the orientation is the same as in Figure 1b; for methane the orientation is the same as in Figure 1a, conformation 1.

Table III. Comparison of Interaction Energies Using Eq 3 or CI

R(C–O)[a]	SCF energy[a]	CI energy[a]	E(CI)[b]	eq 3[b]
6.4	−116.26578	−116.63366	−0.366	−0.572
7.1	−116.26679	−116.63444	−0.852	−0.675
7.7	−116.26688	−116.63418	−0.689	−0.528
98.0	−116.26630	−116.63308	0.000	−0.000

[a] In au. [b] In kcal/mol.

Let us consider once again[9-14] a comparison between the interaction energies computed either by the above relatively simple method or with CI, namely, a comparison between eq 3 and eq 4. We have selected $CH_4\cdots H_2O$ as a test case rather than $CH_3OH\cdots H_2O$ because, in the latter case, the largest contribution to the interaction energy (at the most stable conformation) comes from the Hartree–Fock term; the opposite is true for $CH_4\cdots H_2O$. We have performed four computatiaons for CH_4 + H_2O using a large basis set with polarization functions both at the SCF level and at the CI level. For the carbon and the oxygen atoms, the basis set[23] is an 11-s, 7-p, 1-d set contracted to (4, 3, 1); for the hydrogen atoms there are 6-s and 1-p functions contracted to (2, 1). In the CI computation, we have omitted excitation from the $1s^2$ of the carbon and oxygen atoms,; double and single excitations are constructred from the reference ground state considering the 8500 most important configurations and correcting for the remaining. The $CH_4\cdots H_2O$ geometries are selected from the most stable conformation (see Figure 2) with R(O–C) distances of 6.4, 7.1, 7.7, and 98.0 au. The computed total energies of $CH_4\cdots H_2O$ from the CI and from the SCF computations are given in Table III. Since the last distance corresponds to noninteracting CH_4 and H_2O, its total energy corresponds to *the zero* for the interaction energy. Therefore, the CI interaction energies at 6.4, 7.1, and

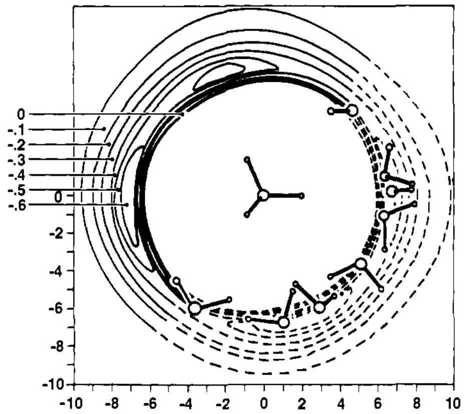

Figure 4. Isoenergy contour map for $CH_4 \cdots H_2O$. The plane contains the carbon and two hydrogen atoms of methane. The solid and dashed contours are symmetrical about the diagonal. Several orientations of the water molecule are shown, as examples. The axes are interatomic distances (in au) and the contours are energies (in kcal).

7.7 au are −0.368, −0.852, and −0.689 kcal/mol, respectively. The CI energies obtained have lowered the SCF by about 0.367 au, about 1.25 eV for each one of the eight electron pairs for the valence electrons (or about 70% of the total valence correlation). With the very simple technique of eq 3 (minimal basis set, CP and approximated dispersion corrections), the corresponding total interaction energies are as reported in Table III. The agreement between the CI interaction energies and those obtained from eq 3 justifies the use of the latter as a reasonable approximation. It is worth noting that the computer time needed in the CI computation is about a factor of 500 times larger than in the simple method given by eq 3.

It is noted that, in selecting $C \neq 1$, the system composed of the two molecules (CH_4 and H_2O, or CH_3OH and H_2O) has a very small residual charge. The residual charge will bring about a negligibly small error in MC computations of CH_4 or CH_3OH desolved in liquid water. Indeed, considering CH_4 and CH_3OH surrounded by 198 and 196 water molecules, respectively (see ref 7 and 8), the average interaction energies for water–methane and water–methanol differ by only 0.03 and 0.07 kcal/mol, respectively, by either excluding ($C = 1$) or retaining (C values as in Table II) the small residual charges. This error is smaller than the average deviation reported for the Monte Carlo simulations performed with the potentials given in Table II.[7,8] Note that the C parameters can be constrained in such a way that, even for $C \neq 1$, there is no residual charge.

From eq 1 it is evident that in this work we have not included three-body and higher term interactions. For a discussion of these corrections we refer to other papers.[9-14] We note, however, that one needs a reasonable idea of the two-body interactions before discussing three-body interactions. We recall that the three-body correction, due mainly to the induction energy,[9-14] can be obtained in the Hartree–Fock approximation, *provided that the two-body correction is known.* Equivalently, in solution studies, availability of simulations at the two-body level seems to be an obvious starting point for more accurate simulations.

Isoenergy Contour Maps

In Figure 4, we report an *isoenergy* contour map for $CH_4 \cdots H_2O$ obtained with the 3T potential. The plane considered in the map contains the carbon and two hydrogen atoms of CH_4. In Figures 5 and 6, we report isoenergy controur maps for $CH_3OH \cdots H_2O$ (in the S conformation); the plane either contains the C–OH group of atoms (Figure 5) or is parallel to it but displaced by 3 au (Figure 6). We recall that the isoenergy map represents the interaction energy between *one* water molelcule and the solute. These maps are obtained by placing the oxygen atom of the water molecule at grid points and by optimizing the orientations of the hydrogen atoms relative to the solute by energy minimization. Therefore, these maps should not be confused with *isopotential* electrostatic maps, where one simply computes the electrostatic potential of the wave function (at grid points) seen by one or more point charges (i.e., the electrostatic interaction between the charges and the molecule, described with some basis set). As is well known, the isopotential maps are basis-set dependent and often break down totally at equilibrium separations. In Figure 4, we report a few orientations of water molecule to show the variation of the orientation of the water molecules at different positions for its oxygen atom.

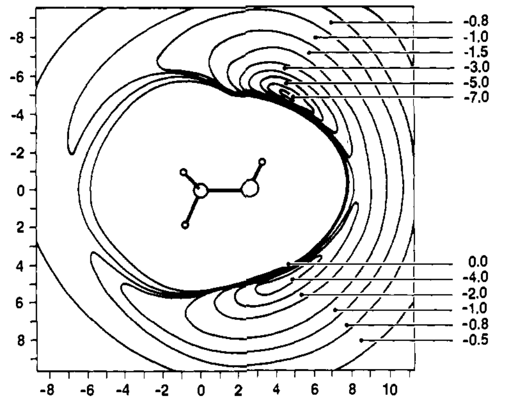

Figure 5. Isoenergy contour map for the staggered $CH_3OH \cdots H_2O$. The plane contains the C–O–H group. The units of the axes and of the contours are the same as in Figure 4. Various orientations of H_2O occur at various positions.

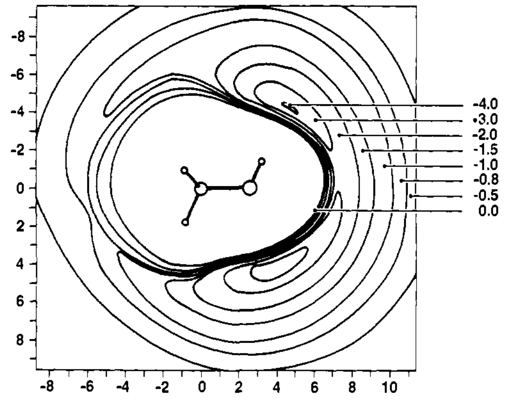

Figure 6. Isoenergy contour map for the staggered $CH_3OH \cdots H_2O$. The plane is parallel to the one of Figure 5 and displaced by 3 au (being symmetric above and below the plane). The units of the axes and contours are the same as in Figure 4.

Four shallow minima can be recognized in Figure 4. A water molecule placed in the shallow minimum *at the left of methane* (see Figure 4) is oriented with its oxygen atom nearer than its hydrogen atoms to CH_4. A water molecule placed in the minimum reported *at the top of methane* (see Figure 4) is oriented with its hydrogen atoms pointing toward methane and its oxygen atom farther away from methane. There is a symmetry plane bisecting the figure, through its diagonal. The isoenergetic contours are drawn as full lines in the top-left half of the figure and as dashed lines in the symmetric bottom-right half. The orientations of the water molecules are shown only in the bottom-right half. It seems reasonable to expect that clathrate-type structure of water molecules will enclose methane. Indeed, (1) the $CH_4 \cdots H_2O$ attraction is small compared to the $H_2O \cdots H_2O$ interaction, (2) water molecules in the two different minima (left and top, respectively) are related by a rotation (see above), and (3) there is a total of eight minima on a sphere of about 4 Å radius enclosing CH_4 and centered on its carbon atom. This well-known expectation is borne out in Monte Carlo calculations[7] with this potential; the point we wish to emphasize here, however, is that the *existence* of a clathrate-type structure can be inferred or rationalized from the isoenergy contour map. Since the $H_2O \cdots H_2O$ interaction is much larger than the $CH_4 \cdots H_2O$ interaction, the former will dominate in determining the structure of water around a methane molecule.

Thus, the *number* of H_2O molecules in the clathrate structure would not be expected to be equal to the number of minima; i.e., we would not expect to find only *eight* molecules of water surrounding CH_4 as a consequence of the existence of *eight* shallow minima.

In CH_3OH, the interaction between its OH group and H_2O is the dominant feature in the attractive region of the isoenergy map (see Figures 5 and 6). The figures show two regions of pronounced minima, one corresponding to a standard hydrogen bond between an H_2O molecule and the methanol OH group, and the other in the direction of the lone pairs of the oxygen atom. The two minima persist out of the plane, as shown in Figure 6. On this basis, we might expect that the OH of CH_3OH will take the place of an OH of H_2O when CH_3OH is in solution. Since the OH of CH_3OH assumes a different orientation for each conformation (for example, S, P, E), the $H_2O\cdots H_2O$ network is expected to be different for each conformation. These differences might alter the relative stabilities for the S, P, and E conformations.[22] However, it might be difficult for a Monte Carlo simulation to settle this small energetic detail (the barrier is only about 1 kcal/mol) with present-day water–water potentials for studies of solutions. The strength of the interaction between the OH group of methanol and H_2O is larger enough to perturb the water molecules in the CH_3 region of methanol (see Figures 5 and 6). On this basis, water molecules solvating the CH_3 group of CH_3OH might resemble the solvation of CH_4 around the methyl group but not around the hydroxyl group. However, the isoenergy contour maps alone are *not sufficient* to allow a more precise prediction of the organization of H_2O molecules about the methyl group of methanol in aqueous solution.

These $CH_4\cdots H_2O$ and $CH_3\cdots H_2O$ potentials have been used, together with an $H_2O\cdots H_2O$ potential,[11] in Monte Carlo studies of the hydration of methane and methanol; for details, see ref 7 and 8.

A number of points on the water–methanol potential surface have been computed with a larger basis set, (11s, 7p, 1d) for C and O atoms and (6s, 1p) for H atoms; as above, the CP and the dispersion corrections were added.[34] As expected these data confirm the potential reported in Table II; the largest difference is a decreased attraction for the first minimum (the one shown in the upper half of Figures 5 and 6) which now becomes as deep as the second minimum (the one shown in the lower half of Figures 5 and 6).

Acknowledgment. This work was supported in part by research grants from the National Science Foundation (PCM79-20279) and from the National Institute of General Medical Sciences of the Institutes of Health, U.S. Public Health Service (GM-14312).

Registry No. Water, 7732-18-5; methane, 74-82-8; methanol, 67-56-1.

Supplementary Material Available: Tables IV–VII giving the geometries for the $CH_4\cdots H_2O$ and CH_3—$OH\cdots H_2O$ systems and the corresponding interaction energies (SCF, SCF + CP, and SCP + CP + E_{disp}) (30 pages). Ordering information is given on any current masthead page.

---

(34) G. Corongiu, private communications.

Microwave Spectrum, Dipole Moment, and Substitution Structure of Peroxyformic Acid

M. Oldani, T.-K. Ha, and A. Bauder*

Contribution from the Laboratory for Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zurich, Switzerland. *Received July 29, 1982*

Abstract: The microwave spectra of peroxyformic acid (HCOOOH) and seven isotopic species have been investigated from 12 to 40 GHz. Rotational constants and all quartic centrifugal distortion constants have been adjusted from measured transition frequencies for the parent species. Measurements of the Stark splittings of three transitions have yielded the components of the permanent electric dipole moment μ_a = 0.922 (1) D, μ_b = 1.050 (2) D, and μ_{total} = 1.398 (2) D. From the inertia defect and the absence of any μ_c dipole component, we concluded the molecule to be planar. A complete substitution structure resulted from the analysis of all singly and one doubly substituted isotopic species. The stable conformation is characterized by an intramolecular hydrogen bond. No other conformer with an estimated energy difference of less than 700 cm^{-1} could be found. Ab initio SCF calculations with full geometry optimization were performed in a search of possible conformers. Three stable conformers were found which all feature a planar structure and which are higher in energy by 700 to 5000 cm^{-1} than the conformer measured.

1. Introduction

The structures and conformations of peroxy acids have been inferred in the past mostly from theoretical calculations. The microwave spectrum is known only for peroxyacetic acid.[1] From the microwave spectroscopic data of the parent species and the CH_3COOOD species, it was concluded that the peroxy acid moiety is planar, featuring an intramolecular hydrogen-bonded conformation. Infrared spectra have been recorded previously for peroxyformic acid[2,3] and partially assigned. The vibrational spectrum provided the first evidence of an intramolecular hydrogen bond. The interpretation of the vibrational spectrum was consistent with a planar structure.[4]

The first attempt to elucidate the conformation of peroxy acids was based on dipole moment considerations from measurements of the dielectric constant in solution.[5] A conformation with a dihedral angle of 72° for the peroxy group was suggested.

---

(1) Cugley, J. A.; Bossert, W.; Bauder, A.; Günthard, Hs. H. *Chem. Phys.* **1976**, *16*, 229.

(2) Giguere, P. A.; Weingartshofer Olmos, A. *Can. J. Chem.* **1952**, *30*, 821.

(3) Maker, P. D.; Niki, H.; Savage, C. M.; Breitenbach, L. P. *Anal. Chem.* **1977**, *49*, 1346.

(4) Brooks, W. V. F.; Haas, C. M. *J. Phys. Chem.* **1967**, *71*, 650.

(5) Rittenhouse, J. R.; Lobunez, W.; Swern, D.; Miller, J. G. *J. Am. Chem. Soc.* **1958**, *80*, 4850. "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, 1970; Vol. I, p 456.

0002-7863/83/1505-0360$01.50/0