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Transferable Intermolecular Potential Functions for Water, Alcohols, and Ethers. Application to Liquid Water[1]

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Abstract: Transferable intermolecular potential functions (TIPS) suitable for use in liquid simulations are reported for water, alcohols, and ethers. Interaction sites are located on oxygens, hydroxyl hydrogens, and the carbons in alkyl groups. Each type of site has Coulomb and Lennard-Jones parameters chosen to yield reasonable structural and energetic results for both gas-phase dimers and pure liquids. A Monte Carlo simulation of liquid water at 25 °C using the TIP potential compares favorably with experiment or results from Clementi's CI potential except that the OO radial distribution function is calculated to be too flat beyond the first solvent shell. Simulations of liquid methanol and ethanol have also been carried out as described in the accompanying papers. Overall, in view of the simplicity and transferability of the potentials, the initial results are most encouraging for the treatment of fluids with even more complex monomers and for extension to other types of interaction sites.

I. Introduction

The profound role of solvent effects in organic chemistry and biochemistry emphasizes the need to model theoretically complex liquids and solutions. Progress has been made on simple liquids and aqueous solutions of small solutes through molecular dynamics and Monte Carlo simulations.[4] A critical component in the research is intermolecular potential functions describing interactions between monomers in the fluids. The generation and suitability of the functions have been persistent problems whether they are obtained empirically by fitting to known properties of the dimers and liquids[5a] or quantum mechanically by fitting computed dimerization energies.[3,5b,6-8] A general hazard of using results for dimers is that the effective interactions in the condensed phase may not be well represented by a function applicable to the gas phase, while iterative fitting to data for liquids is laborious. The paucity of accurate experimental information on potential surfaces for dimers also hinders the empirical approach.

At the same time, the questions of basis set size and correlation energy corrections further complicate the quantum mechanical route. It is apparent that the results for a liquid are sensitive to the shape of the dimer potential which may necessitate the inclusion of correlation effects, e.g., by configuration interaction (CI), particularly to describe the dispersion interactions between polarizable groups.[8] Adding such corrections post facto has met with limited success.[14,15] However, extensively exploring potential surfaces at the CI level for systems with more than two nonhydrogen atoms is not practical at this time.

Table I. Standard Geometrical Parameters for Saturated Alcohols and Ethers[a]

alcohols		ethers		general	
r(OH)	0.945	r(CO)	1.410	r(CC)	1.535
r(CO)	1.430	r(CC$_O$)	1.516	∠CCC	109.47
r(CC$_O$)	1.512	∠COC	112.0		
∠COH	108.5				
∠CCO	107.8				

[a] Bond lengths in Å; bond angles in degrees.

What is clearly desirable is to have simple, effective intermolecular potential functions for dimers that yield reasonable results in fluid simulations. The potentials should also be transferable so that one set of parameters for atoms or groups of atoms can be used to construct potential functions for many different systems. Previous work along these lines has focused on potential functions for studying protein structure in water.[16] The potentials are often complex with many interaction sites, and some require special functions for hydrogen bonding. The recent work by Hagler and Lifson is a notable advancement since hydrogen bonding requires no extraordinary treatment and there is only one interaction site per atom located at the nucleus.[17] These functions are for carboxylic acids and amides and were derived primarily from experimental data on crystals.

With this encouragement, it seemed possible that transferable intermolecular potential functions (TIPS) could be derived for simulating organic liquids and solutions. The approach has been to keep the TIPS as simple as possible and to choose the necessary parameters to give reasonable structural and energetic results for some simple liquids and trends for series of dimers. Parameters are reported here for water, alkanes, alcohols, and ethers. Water and alochol dimers are analyzed extensively, and Monte Carlo results for liquid water using the TIP function are presented. The accompanying papers describe the results for liquid methanol and ethanol in detail.

II. Transferable Intermolecular Potential Functions

A. Form and Parameters. The computing time for a Monte Carlo simulation of a pure liquid is largely determined by the

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Table II. TIP Parameters for Alcohols and Ethers[a]

site	q	$10^{-3} A^2$	C^2
O in H_2O	−0.80	580	525
O in ROH	−0.685	515	600
O in ROR'	−0.58	500	625
H in H_2O	0.40	0	0
H in ROH	0.40	0	0
CH_4	0.00	8529	3167
CH_3	*b*	7950	2400
CH_2	*b*	7290	1825
CH	*b*	6800	1150
C	*b*	6100	800

[a] Units are for q (electrons), A^2 (kcal Å^{12}/mol), and C^2 (kcal Å^6/mol). e^2 in eq 1 is 332.17752 kcal Å/mol. [b] Charges chosen to achieve neutrality of monomers–see text.

Table III. TIP Results for Dimers[a]

dimer	r_{OO}	θ	TIP $-\Delta E$	6-31G* $-\Delta E^b$
HOH···OH_2	2.78	27	5.70	5.64
cyclic $(H_2O)_2$	2.82	41	4.31	
bifurcated $(H_2O)_2$	2.935		4.09	
HOH···OMe_2	2.80	32	5.70	5.73
HOH···OHMe	2.78	32	5.69	5.73
MeOH···OH_2	2.80	25	5.36	5.55
MeOH···OHMe	2.79	27	5.68	5.66
EtOH···OHEt	2.805	28	5.99	
i-PrOH···OH-*i*-Pr	2.81	30	6.33	
t-BuOH···OH-*t*-Bu	2.905	33	6.26	

[a] Distances in Å; angles in degrees; energies in kcal/mol. All results are for linear dimers except as indicated. [b] Data from ref 24.

number of interatomic distances that are evaluated for the dimer potential, which is proportional to the number of interaction sites for a monomer squared. Although Hagler and Lifson explicitly consider each atom, it is imperative for the present purposes to consider alkyl groups as single units centered on carbon. This approximation has been tested in the accompanying study of liquid methanol and is not found to have significant consequences.[15] Thus, ethanol would be represented by four interaction sites, the methyl and methylene groups, the oxygen, and hydroxyl hydrogen. As in the Hagler–Lifson potentials, pseudo lone pairs are not appended to the oxygen. Their addition was also not found to enhance the results for liquid water discussed below, and it is worth noting that they are not utilized in Clementi's CI potential for the water dimer.[5b] Even with the four-site model for ethanol the Monte Carlo run for the liquid required 13 h on a CDC/6600.[18] Roughly 40 h would be needed if all atoms were represented, and the many sites of an EPEN[16a] potential would require about 7 days.

Hagler and Lifson found 12–6–1 and 9–6–1 functions to describe the interactions between sites with about equal success. The 12–6–1 (Coulomb plus Lennard-Jones) form has been adopted here since it is consistent with earlier work.[3,6–9] Nevertheless, 12–6–1 and 9–6–1 functions were developed for water and were found to yield results of similar quality for the liquid. As indicated in eq 1, each type of site has three parameters, a charge in

$$\Delta E(12\text{–}6\text{–}1) = \sum_{a}^{\text{in } A} \sum_{b}^{\text{in } B} \left(\frac{q_a q_b e^2}{r_{ab}} + \frac{A_a A_b}{r_{ab}^{12}} - \frac{C_a C_b}{r_{ab}^{6}} \right) \quad (1)$$

electrons, q, and an A and C. Some of the charges must be chosen to preserve the neutrality of monomers. For simplicity, the charge on C_O in alcohols is taken to cancel the net charge on the hydroxyl group. In ethers the charge on oxygen is neutralized equally by the two adjacent alkyl carbons. More remote alkyl groups have no charge. Since standard geometries[19] are also employed for the functionalities as summarized in Table I, this imples that the dipole moments for alcohols will all be equal as will those for ethers. In reality, they vary over a range of roughly 0.2 D for alcohols and a range somewhat less for ethers.[20]

Lennard–Jones parameters have previously been derived for CH_4 and CH_3 or CH_2 groups in simulations of liquid methane,[21] butane, and decane.[9a] Considering the success of these works, similar parameters for alkyl groups should be adopted here. Although Ryckaert and Bellemans use the same values for methyl and methylene groups,[9a] it is more appropriate to have different parameters for the various CH_n. For n = 0–4, the number of valence electrons increases from 4 to 8, so substantial changes in the size and polarizabilities of the groups must exist. The previous parameters were incorporated in the following manner. Reported Lennard–Jones parameters for several series were analyzed including the noble gases, molecular halogens, atomic carbon to neon, and CH_4, NH_3, H_2O, HF, and Ne.[22] Roughly linear correlations are found for the A and C parameters (eq 1) with increasing numbers of electrons or polarizability. This is not surprising for C in view of the London equation.[22] With use of these relations and the parameters for methane and the Ryckaert–Bellemans parameters as an average for CH_3 and CH_2, parameters for the complete CH_n series were estimated. Only minor modifications were made to the C parameters for n = 1 and 2 after trends in dimerization energies for alcohols (vide infra) were considered. The final parameters for alkyl groups are recorded in Table II.

The parameters for oxygen and hydrogen were considered next. For water, values were sought that gave both reasonable structural and energetic results for the water dimer and liquid water. Consequently, many short (ca. 100K configurations) Monte Carlo runs were executed with different parameters and three- and four-point charge models for the monomer. As Hagler and Lifson found previously,[17] the Lennard-Jones parameters for hydrogen could just as well be set to zero. This leaves only three parameters, A_O, C_O, and q_O, in the simple three-site TIP model for water since $q_H = -q_O/2$. The final value for C_O^2 (Table II) is close to Meath's estimate of 625.[22] The charge for oxygen, −0.80 e, yields a dipole moment of 2.25 D for the monomer in the experimental geometry (r(OH) = 0.9572 Å, ∠HOH = 104.52°)[23] which is adopted throughout this study. The experimental number is 1.85 D for the gas phase,[20] while Clementi's CI potential has 2.19 D.[5b] As discussed previously, enhancement of a monomer's polarity on dimer formation and in condensed phases is observed.[3a,20]

The parameters for oxygen in alcohols and ethers were adjusted to yield reasonable potential surfaces for dimers as discussed in the next section. The lessening of charge on oxygen in going from water to alcohol to ether (Table II) is qualitatively consistent with ab initio calculations by Tse, Newton, and Allen on water, methanol, and dimethyl ether using STO-3G, 4-31G, and 6-31G* basis sets.[24] The dipole moments for alcohols and ethers using the TIP model and the standard geometries are 2.21 and 2.20 D, respectively, which are again significantly larger than experimental data for isolated molecules.[20]

B. Results for Dimers. Optimizations were carried out for the linear forms of a variety of dimers involving water, methanol, ethanol, isopropyl alcohol, *tert*-butyl alcohol, and dimethyl ether in deriving the TIPS. The variables r_{OO} and θ were optimized in each case assuming a linear hydrogen bond, staggered or anti geometries for the monomers, and that the ROH plane is perpendicular to and bisects the R'OR'' plane as shown in I. Some results using the final TIP parameters are summarized in Table

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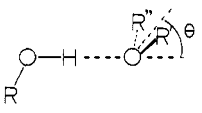

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III. Also shown are the recently calculated 6-31G* dimerization energies for five of the dimers.[24] These are the most sophisticated ab initio results obtained so far for this series. Unfortunately, accurate experimental data are not available for the structures and energies of these dimers in the gas phase except for water. For example, estimates of the dimerization enthalpies of methanol and ethanol from *PVT* and spectroscopic data range from 3 to 7 kcal/mol.[25] For the water dimer, the experimental values for r_{OO}, θ, and $-\Delta E$ are 2.98 Å, 60°, and 5.44 ± 0.7 kcal/mol[26] which are in accord with ab initio calculations using large basis sets and CI.[5b,27]

6-31G* computations yield dimerization energies for second-row hydrides in agreement with the best estimates.[27] Of course, this is fortuitous since correlation effects are not included. Dispersion becomes increasingly important in the present context as the alkyl groups are elaborated. In Table III it is seen that the 6-31G* dimerization energies for the five dimers vary little except the $MeOH\cdots OH_2$ dimer is somewhat less bound. The TIP parameters were adjusted to reproduce this *pattern* and also to be appropriate in the simulation of liquid water. The quantitative similarity of the 6-31G* and TIP dimerization energies was not sought deliberately.

Some rationale for the progression of dimerization energies for the alcohols can be sought in heats of vaporization of the liquids going to the ideal gases. The experimental data are 8.5, 9.5, 9.7, and 9.6 kcal/mol at the boiling points and 9.1, 10.2, 10.9 and 11.2 kcal/mol at 25 °C for methanol, ethanol, isopropyl alcohol and *tert*-butyl alcohol, respectively.[25] The TIP dimerization energies exhibit roughly the same trends.

The OO separations in the linear dimers are all about 2.80 Å with the TIPS except for *tert*-butyl alcohol dimer where a steric effect is apparent. The 6-31G* results of Tse et al. show the same pattern; however, the bond length is longer at 2.96 ± 0.02 Å.[24] The shorter distance for the water dimer was found to be needed in order to yield the proper location for the first peak in the liquid's OO radial distribution function (g_{OO}).

Besides the minima, the shapes of the potential surfaces for dimers must be carefully considered. The dimerization energy for the linear water dimer is plotted against OO separation for three potential functions in Figure 1. In each case, θ has been fixed at its optimum value for the minimum. The well shape for the TIP (12-6-1) function is similar to Clementi's CI potential though the latter function has its minimum at 2.88 Å and a bit deeper well, −5.84 kcal/mol.[3a,5b] In contrast, the STO-3G-based potential has a substantially deeper and narrower well which leads to an overly sharp first peak in g_{OO}.[3a] As illustrated in Figure 2 and summarized in Table III, the order of stabilities for water dimers from the TIP function is linear > cyclic > bifurcated. The same prediction is made with the CI potential.[3a]

At this point, it might be asked why not just fit the TIP function to the CI potential? This was done by using the energy-distributed random geometries procedure.[3a,6-8] The resultant coefficient for the r^{-6} term ($C_O{}^2$) was 2–3 times larger than the value in Table II, and the linear well was deepened too much. This led to too low an energy for liquid water and too high a first peak in g_{OO}. Scheraga et al. also had disappointing results in fitting the EPEN potential to the CI function.[16a] Apparently, the exact form for the CI potential is critical to its success. The ΔE vs. r_{OO} plots for the alcohol dimers are shown in Figure 3. Since the contributions from electrostatics are the same, the gradual deepening and broadening of the well are due to increased dispersion effects as the dimers get larger. The dependence of the TIP dimerization energies for water and the alcohols on θ is displayed in Figure 4. In this case, the OO separations have been fixed at their optimum values for the linear minima. The curves are very flat

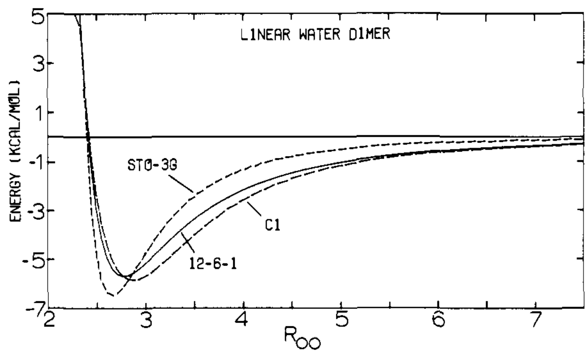

Figure 1. Variation of the dimerization energy for the linear water dimer with OO separation (Å) from the TIP (12-6-1), STO-3G, and CI potential functions.

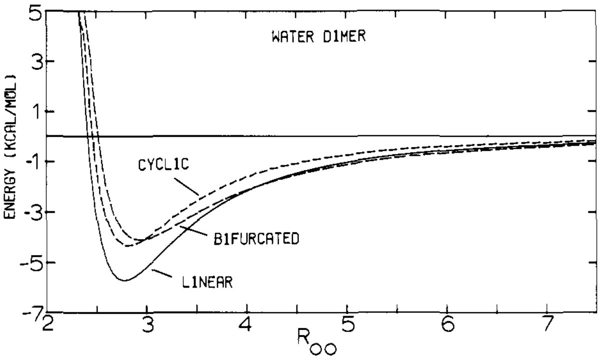

Figure 2. Variation of the dimerization energy for three geometries of the water dimer from the TIP function. Angular variables have been fixed at their optimal values for the minima.

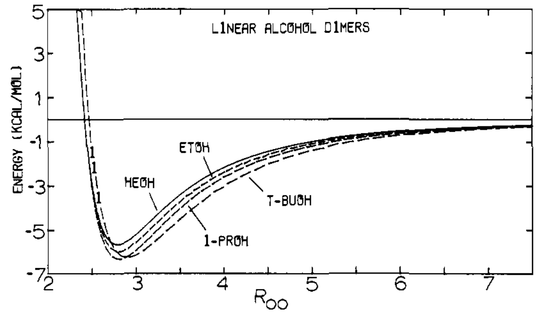

Figure 3. Variation of the dimerization energies for linear alcohol dimers with OO separation (Å) from the TIP functions. The bending angle θ has been fixed at its optimum value for the minimum in each case.

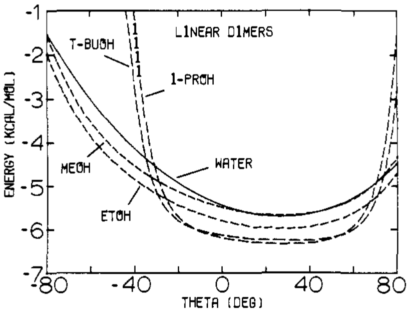

Figure 4. Variation of the dimerization energies for the linear dimers with angle θ. R_{OO} has been fixed at its optimum value for the minimum in each case.

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Table IV. Computed and Experimental Properties of Liquids at 25 °C[a]

water	TIP	exptl[b]	CI[c]
$\Delta H_V°$	8.9	10.7	9.2
C_V	15.0	17.9	20.1
methanol	TIP[e]	exptl[d,e]	MHL[e]
$\Delta H_V°$	7.8	9.1	8.0
C_V	16.3	15.9	20.1
ethanol	TIP[f]	exptl[d,f]	
$\Delta H_V°$	8.6	10.2	
C_V	20.4	22.0	

[a] $\Delta H_V°$ in kcal/mol; C_V in cal/(mol deg). [b] See ref 3. [c] Reference 5. [d] Reference 25. [e] Reference 15. [f] Reference 18.

near the minima which all occur at ca. 30°. The 6-31G* values for the five dimers in Table III are 42–55°.[24] The CI potential gives 30° for the water dimer and nearly the same dependence as the TIP results in Figure 4.[3a] Apparently, three-point charge potentials underestimate the bending while four-point charge models including pseudo lone pairs overly structure the ΔE vs. θ curve.[3a] It should also be noted that steric effects narrow the wells in Figure 4 for the isopropyl alcohol and *tert*-butyl alcohol dimers, particularly for negative θ where the alkyl group of the hydrogen bond acceptor swings toward the alkyl group of the donor.

Overall, the TIP description of dimers seems acceptable in comparison with available experimental and ab initio results on dimerization energies, geometries, and the shapes of the potential surfaces. The remarkably simple form of the TIP function (eq 1) must be kept in mind. Naturally, the true test comes with the liquid simulations.

III. Monte Carlo Simulation of Liquid Water

A. Procedure. The Monte Carlo simulations of liquid water with the TIPS model were carried out under the same conditions and in the same manner as the earlier work with the STO-3G potential.[3] Some key details are that a cubic sample of 125 water monomers was employed at 25 °C and with the experimental density (1 g-cm^3). Periodic boundary conditions, Metropolis sampling, and a spherical cut off for the potential at an OO separation of half the length of an edge of the cube were used. One molecule was picked and displaced randomly on each move. An acceptance rate of ca. 50% for new configurations was achieved by using ranges of ±0.15 Å for the translations and ±15° for the rotation about a randomly chosen axis. The calculations were initiated with a configuration from an earlier run. Although numerous short runs were executed in generating the potential function, the results using the final parameters (Table II) are focused on here. The system was thoroughly equilibrated by using several hundred thousand configurations. Averaging for the reported properties occurred over an additional 350K configurations. A 500K run with 216 monomers verified that the structural and energetic results were not dependent on system size.

The energy of a configuration was obtained from the pairwise sum of the dimerization energies for each monomer as usual. The assumptions in such Monte Carlo calculations including the neglect of three-body and higher order interactions have been discussed previously.[3,5–8] The present concern is how the TIPS function fares for liquid water in comparison with experiment and other dimer potentials. Naturally, such a simple function was not anticipated to yield results of as high quality as from the more elaborate, nontransferable potentials for water such as ST2 or CI.[5] However, it was hoped that an adequate description of this unusally complex liquid could be obtained and that the TIP functions would be particularly successful for modeling organic liquids and solutions in which cooperative effects are less profound.

B. Thermodynamics and Energy Distributions. The computed heat of vaporization for the liquid going to the ideal gas, ΔH_V^0, and the heat capacity, C_V, are compared with the results from the CI potential[3b,c] and experiment in Table IV. The theoretical $\Delta H_V°$'s were obtained from the configurational potential energy, E_i, which is calculated directly in the simulations, in the standard manner summarized by eq 2 and 3.[7,8] For water, $P\Delta V°$ is essentially the same as RT since the gas is relatively ideal. The theoretical C_V's are obtained from eq 4, where C_V^i is computed

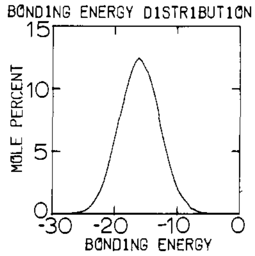

Figure 5. The distribution of bonding energies for monomers in liquid water from the Monte Carlo simulation with the TIP function. The units for the ordinate are mol %/kcal mol^{-1}.

$$\Delta H_V° = \Delta E_V° + P\Delta V° \tag{2}$$

$$\Delta H_V° \approx -E_i + P\Delta V° \tag{3}$$

$$C_V \approx C_V^i + C_V° \tag{4}$$

from the fluctuation of the intermolecular energy in the Monte Carlo calculations and $C_V°$ is the heat capacity of the ideal gas.[28] The addition of $C_V°$ attempts to correct for the contributions from the intramolecular vibrations, internal rotations, and the kinetic energy for complete rotation and translation of the monomers. The assumption of the same intramolecular contributions to C_V in the liquid and in the ideal gas is a first approximation. Quantum effects on the thermodynamic results may also be considered.[29] It is not clear that such refinements can be made with enough certainty to yield significant improvement over eq 3 and 4.

Table IV contains a preview of the thermodynamic results for methanol and ethanol.[15,18] For methanol, a second potential function was constructed that explicitly includes the methyl hydrogens.[15] It is referred to as MHL for modified Hagler–Lifson. The computed E_i's and $-\Delta H_V°$'s include cutoff corrections of −0.08, −0.23, and −0.40 kcal/mol for water, methanol, and ethanol. The corrections are calculated from eq 5, and it is assumed that $g(r) = 1$ beyond the cutoff. Futhermore, only the Lennard–Jones terms are retained in the potential, $u(r)$; the Coulomb terms are assumed to average to zero.

$$\Delta E_{\text{corr}} = \sum_{i}^{\text{on } A} \sum_{j}^{\text{on } B} 2\pi\rho_j \int_{r_c}^{\infty} r^2 g_{ij}(r) u_{ij}(r)\, \mathrm{d}r \tag{5}$$

The $\Delta H_V°$'s from the TIPS are uniformly underestimated by 14–17% which is expected owing to the neglect of three-body effects.[3,5–8] Consequently, the $\Delta H_V°$'s are predicted in the right order: water > ethanol > methanol. The C_V's are large in view of the hydrogen bonding, and the TIP values are in good agreement with experiment. It should be noted that the standard deviations (σ) for the C_V's from the statistical fluctuations in the Monte Carlo calculations are ca. ±1–2 cal/(mol deg). The standard deviations for the configurational energies were also obtained from control functions and are less than ±0.05 kcal/mol.[30] The results for water from the CI potential are modestly better than from the TIP function. For methanol, the effects of including the methyl hydrogens in the MHL potential are not substantial. It should be reiterated that the TIP parameters were fixed prior to the simulations of the alcohols. Further results for the alcohols are deferred to the accompanying papers. As will be presented elsewhere,[31] Monte Carlo simulations have also been carried out

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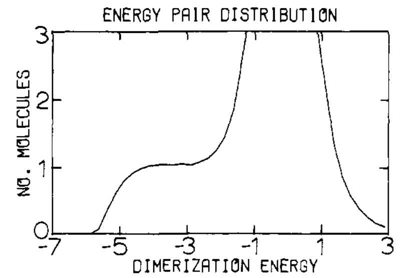

Figure 6. TIP results for the distribution of dimerization energies for a monomer in liquid water. The units for the y axis are molecules/kcal mol^{-1}.

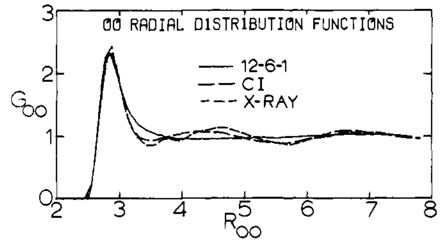

Figure 7. OO radial distribution functions for liquid water at 25 °C from X-ray data (ref 33) and the TIP and CI potential functions.

for liquid n-butane and 1,2-dichloroethane by using TIPS including the CH_n parameters given here. In these cases the computed ΔH_V and C_V are in exact agreement with experiment.

The distribution of bonding energies for monomers in liquid water from the TIP model is plotted in Figure 5. The monomers experience a continuum of energetic environments covering a 20-kcal/mol range. The unimodal nature, shape, and range of the distribution are now familiar since they concur with results from the CI and STO-3G potentials.[3,5c]

The energy pair distribution from the TIP simulation is shown in Figure 6. The ordinate gives the average number of molecules that are bound to a monomer with the dimerization energy shown on the abscissa. The minimum in the TIP function restricts the dimerization energies to be above −5.8 kcal/mol. Most interactions involve distant molecules and fall between ±1 kcal/mol. The distribution has previously been reported in simulations with the ST2[5a] and STO-3G[3] potentials and with the recent multipole model for water which incorporates three-body effects.[32] The ST2 and STO-3G results show a distinct minimum at −2.0 to −2.5 kcal/mol, clearly separating the hydrogen-bonded neighbors from the bulk. Although the distributions from the TIP and multipole models do not show the minimum, the simulation with the latter potential involved such a short Monte Carlo run (40K) that it must be considered incomplete at this time.[32] A reasonable cutoff for hydrogen bonding in Figure 6 is about −2 kcal/mol. Integrating to this point yields an average of 3.4 hydrogen bonds per monomer. The same figure was obtained from the STO-3G potential.[3] Further analysis of the hydrogen bonding is made in a following section.

Overall, the thermodynamic results and energy distributions from the TIP functions compare well with experimental data or the results of simulations with the best available dimer potentials. This is particularly encouraging in view of the simple form and transferability of the TIPS.

C. Radial Distribution Functions. Radial distribution functions (RDFS) represent the deviations in the distributions of atoms in the liquid from the bulk values expected if the liquid were structureless. The density of y atoms about atoms of type x is $\rho_{xy}(r) = \rho_y{}^{\circ} g_{xy}(r)$, where r is the xy separation, $\rho_y{}^{\circ}$ is the bulk density of y atoms (N_y/V), and $g_{xy}(r)$ is the xy RDF.

The OO RDFS for water at 25 °C from the TIP and CI potentials and from Narten's X-ray diffraction experiments[33] are shown in Figure 7. The results from the CI potential are in the best agreement with Narten's data for any potential function known to date. Both the TIP and CI simulations reproduce the observed height and location of the first peak in g_{OO}. In contrast, most other potentials including two of the better ones, ST2 and STO-3G,[3,5a] predict heights of 3–4 for the first peak in g_{OO}.

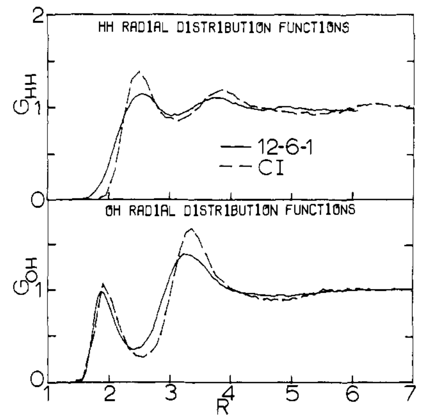

Figure 8. OH and HH radial distribution functions for liquid water at 25 °C from the simulations with the TIP and CI functions.

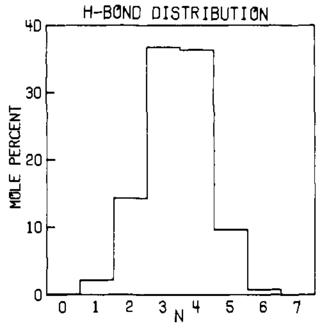

Figure 9. Distribution of coordination numbers for hydrogen-bonded neighbors from the simulation with the TIP function. A hydrogen bond is defined by a dimerization energy below −2.0 kcal/mol.

The major deficiency of the TIP results is that g_{OO} is flat beyond the first peak, whereas second and third solvent shells are indicated clearly in the X-ray data. Attempts to remedy this problem resulted in a battle of give and take. The outer peaks can be obtained at the expense of the first peak becoming too high and the energy too low by employing a narrower and deeper hydrogen-bonding well. Analogously, both the ST2 and STO-3G potentials yield the outer peaks; however, the first peak is seriously exaggerated. All things considered, it seemed better to obtain a more accurate distribution for the nearest neighbors than the details in farther regions. The first peak in the TIP results is also a little too broad so its integral to 3.5 Å reveals 5.5 neighbors which overestimates the experimental value of ca. 5.[33] Therefore, although the number of hydrogen bonds is about right, the TIP model is not distinguishing first and second nearest neighbors as sharply as it should.

The OH and HH RDF's from the simulations with the TIP and CI potentials are compared in Figure 8. The experimental data are not as well established as for g_{OO} due to difficulties in unravelling the necessary neutron diffraction data.[3,5,33] The TIP results are again not as structured as the CI curves; however, the overall agreement is reasonable especially for the peak locations. The first peak in g_{OH} is for the hydrogen bonds. It integrates to 1.7 which implies ca. 3.4 hydrogen bonds per monomer in accord with the estimate from the energy pair distribution.

D. Hydrogen-Bonding Analysis. Configurations were stored every 2000 attempted moves during the Monte Carlo run for water

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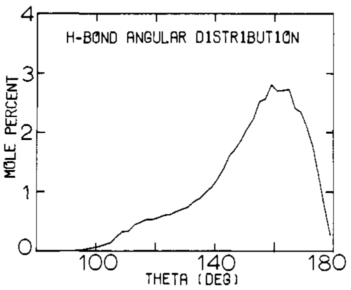

Figure 10. Distribution for the hydrogen bond angle, θ (O···H–O), between monomers with dimerization energies below –2.0 kcal/mol (TIP results).

with the TIP potential. With use of the hydrogen-bonding limit of –2.0 kcal/mol suggested by the energy pair distribution, the saved configurations could be analyzed to obtain some details on the hydrogen bonding.

The distributions for the hydrogen bond numbers and for the hydrogen bond angle, θ (O···HO), are shown in Figures 9 and 10. Analogous plots have previously been obtained for water with the STO-3G potential,[3b] hydrogen fluoride,[6] methanol,[7] and ammonia,[8] The percentage of monomers in 1–6 hydrogen bonds from the TIP calculation is 2, 14, 37, 36, 10, and 1%. No free monomer is found in agreement with infrared data.[34] The distribution from the STO-3G potential also predicts the predominance of monomers in 3 or 4 hydrogen bonds to the extent of 86%. The combined figure is 73% from the TIP results; the difference largely comes from the STO-3G potential finding only 2% of the monomers in more than 4 hydrogen bonds vs. 11% for TIP. Again the TIP potential indicates less well-defined structure, though the differences are not great. The distributions from the TIP and STO-3G potentials are both consistent with the available infrared data which have been discussed previously.[3b,34] The symmetry of the distribution is mirrored in the symmetry of the bonding energy distribution (Figure 5).

The distributions for the hydrogen bond angle, θ, are very similar from the TIP and STO-3G simulations.[3b] A continuous spectrum of bond bending covering an 80° range is indicated. The average hydrogen bond is bent ca. 20° as predicted by Pople.[35] The distribution precludes the significant occurrence of cyclic dimers in the liquid since they would be represented by values of θ near 115°.

IV. Conclusion

Transferable intermolecular potential functions for water, alkanes, alcohols, and ethers have been created, and their predictions for properties of gas-phase dimers and five liquids have been analyzed. The principal problem to arise is the predicted flatness of the OO radial distribution function for water beyond the first peak. The results should be considered in the context of the unusual complexity of the structure of liquid water, the performance of the numerous other potential functions for water, and the simplicity of the TIP model. The TIPS appear particularly appropriate for use in simulating organic liquids and solutions,[15,18,31] while the suitability of such a simple functional form for describing liquid water and aqueous solutions will require further study. Overall, the results presented here and in the following paper are promising in view of the simplicity and transferability of the potentials. Future work will include simulations of dipolar aprotic solvents, dilute solutions with organic solutes, and the development of TIP parameters for other functionalities. More in depth study of the fluids is also desirable including computation of other properties such as density and variation of conditions, particularly temeperature.

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