Ion—water MIDI-1 pair potential for computer simulation

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Dedicated to Professor Ľ. Treindl, DrSc., in honour of his 60th birthday

The $F^-\cdots H_2O$ model system was used in the test of the MIDI-1 basis as a candidate for obtaining pair potential functions in an economic way. It is shown that MIDI-1 basis augmented by diffuse functions and corrected for basis set superposition error provides pair potential energies which lead to satisfactory structural and energetic results in Monte Carlo calculations.

Для модельной системы $F^-\cdots H_2O$ были методом Хартри—Фока рассчитаны парные потенциальные энергии в MIDI-1 базисе. Оказалось, что базис MIDI-1, дополненный диффузной функцией и откорректированный на отклонение суперпозиции (basis set superposition error) дает парный потенциал, подходящий для расчетов Монте Карло. В работе обсуждаются структурные и энергетические данные, полученные в рамках Монте Карло симуляции для модели раствора $F^-\cdots nH_2O$.

Monte Carlo (MC) and molecular dynamics (MD) computer simulations provide a powerful tool for the model studies of liquids, solutions and melts [1—3]. Their success or failure is determined to a considerable extent by the appropriate choice of potential energy functions which describe the interactions at the molecular level. Mostly, the pair potentials are used in these simulations, *i.e.* the total configurational potential energy is expressed as a sum of pair contributions

$$U = \sum_{i<j} u(i,j) \qquad (1)$$

where $u(i,j)$ is the potential energy between molecules i and j. There are basically three types of pair potentials:

a) empirical (determined from experimental data),
b) theoretical (derived from *ab initio* quantum-chemical calculations),
c) model (*e.g.* hard-cores, Lennard—Jones potential).

Quantum-chemical pair potentials for various types of molecular complexes were published in past years and have proved their usefulness for a wide range

of applications [4—7]. Moreover, they are the only choice when dealing with solvation of transition states and short-lived complexes which appear in chemical reactivity. The quality of pair potentials is influenced by the proper choice of the computational method and by the basis set used. The choice of the method in *ab initio* calculation is frequently dictated by the nature of the intermolecular interactions present in the system, *e.g.* in the case of the ion—water interaction (where the coulombic component of the interaction energy is dominant) the SCF approximation is quite satisfactory. The selection of the basis set is more delicate problem, especially in connection with the supermolecular approach of interaction energies calculation. Using SCF energies of the supersystem, ion, and water, *i.e.* E_{iw}, E_i, and E_w, the interaction energy is simply

$$\Delta E_{i,w} = E_{iw} - (E_i + E_w) \qquad (2)$$

We require the basis set which properly describes the properties of the subsystems and has the Basis Set Superposition Error (BSSE) as small as possible. BSSE is connected with the use of truncated basis sets and results in the overestimation of interaction energies [8]. Upper bound of this error can be easily estimated following the Boys—Bernardi procedure [9] in which both subsystems are calculated with the supersystem basis set yielding energies E_i^c and E_w^c. Then the BSSE corrected interaction energy is

$$\Delta E_{i,w}^c = E_{iw} - (E_i^c + E_w^c) \qquad (3)$$

Since we plan to perform computer simulations with various kinds of ions of different size and charge either in solution or in the melt we decided to examine medium sized basis set MIDI-1[10] which may presumably be applicable also to larger systems. As a model system we chose the complex $F^- \cdots H_2O$ (more sensitive to details of the basis set than positive systems) previously studied by several authors [11—16]. Our aim was to produce a pair potential function in the first step and use it subsequently in a mini MC calculation in order to verify the performance of the MIDI-1 basis set in similar applications.

Calculations

Five different attractive and repulsive configurations of molecular complexes $F^- \cdots H_2O$ which may be useful in MC calculations were chosen following the philosophy of *Kistenmacher et al.* [11]. The experimental geometry was adopted for the water molecule ($r(O—H) = 0.9572 \times 10^{-10}$ m, $a(H—O—H) = 104.9°$). The MIDI-1 basis set for the fluorine atom was augmented by diffuse p-function. Including diffuse function is necessary with negatively charged systems, but one should keep in mind that with unsaturated basis sets, as is our MIDI-1 basis, this leads to the increase of BSSE [8]. We may observe (Fig. 1) that BSSE

is inversely proportional to the exponent of the diffuse function. Thus, we optimized our exponent of p-functions with respect to the minimal total SCF energy of the complex with a particular emphasis on keeping BSSE as low as possible. The compromise between these two requirements led to the exponent 0.122 which is by about 0.02 larger than would correspond to the minimal SCF energy.
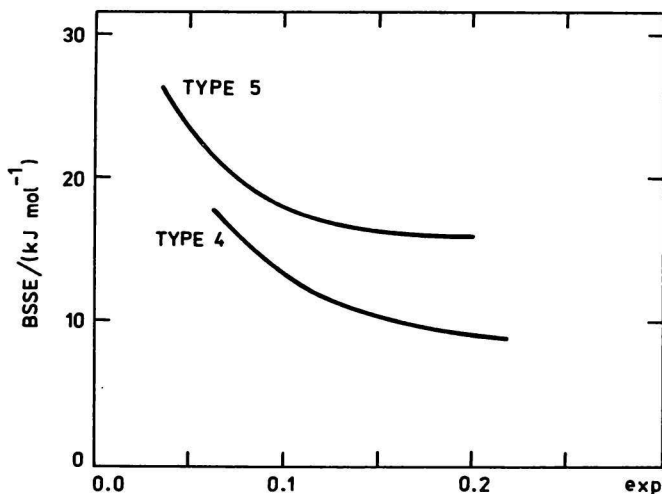

Fig. 1. Dependence of the Basis Set Superposition Error (BSSE) on the exponent of the diffuse p-function on the fluorine atom for geometry configurations 4 and 5. The F—O distance is 3×10^{-10} m.

The scan of $F^- \cdots H_2O$ surface for five different configurational types yields 34 SCF energies. Additional 38 energies for the fitting were obtained by the numerical interpolation of individual curves. These points were mostly located in the low-energy region to enhance the correct fitting of minima. The ion—water SCF interaction energies were corrected for BSSE using relation (3). Since the medium sized basis sets often overestimate the dipole moment of water molecule (and hence the coulombic part of the interaction energy) we decided to analyze the components of $\Delta E_{i,w}$ [17]. The coulombic part of the interaction energy was scaled by the ratio of experimental and MIDI-1 dipole moments ($p_{exp}/p_{MIDI-1} = 0.8956$). Our uncorrected SCF, BSSE corrected and dipole moment scaled interaction energies are compared to reference curves [11] obtained with a very extended basis (Fig. 2). We may observe that with MIDI-1 basis set the best results are obtained with BSSE corrected energies. These energies were used in the subsequent fitting. We also calculated correlation effects using the second-order perturbation energies [8]. Correlation corrections were much
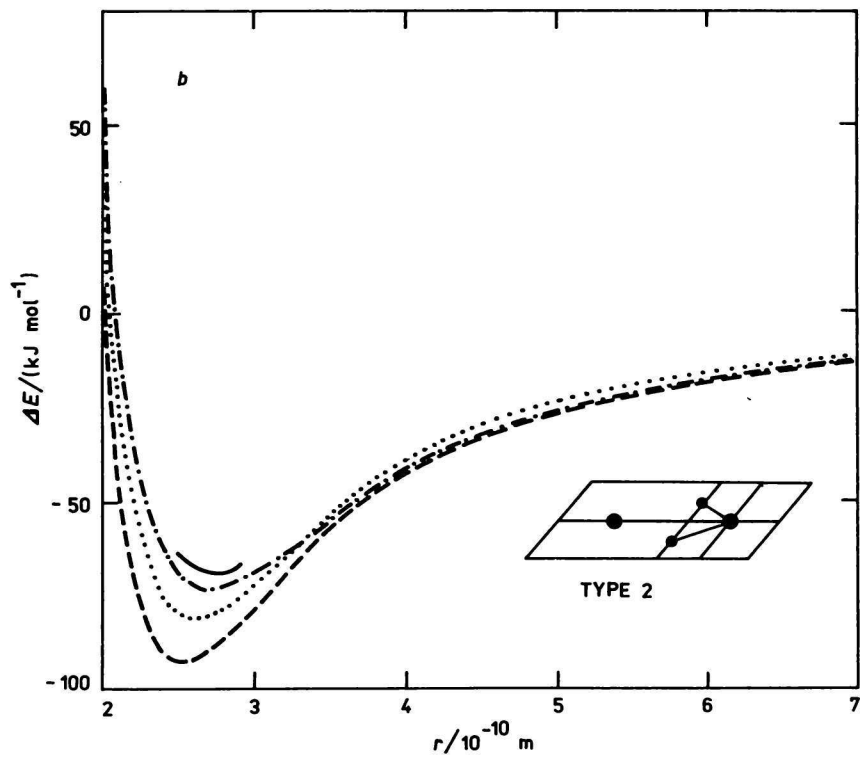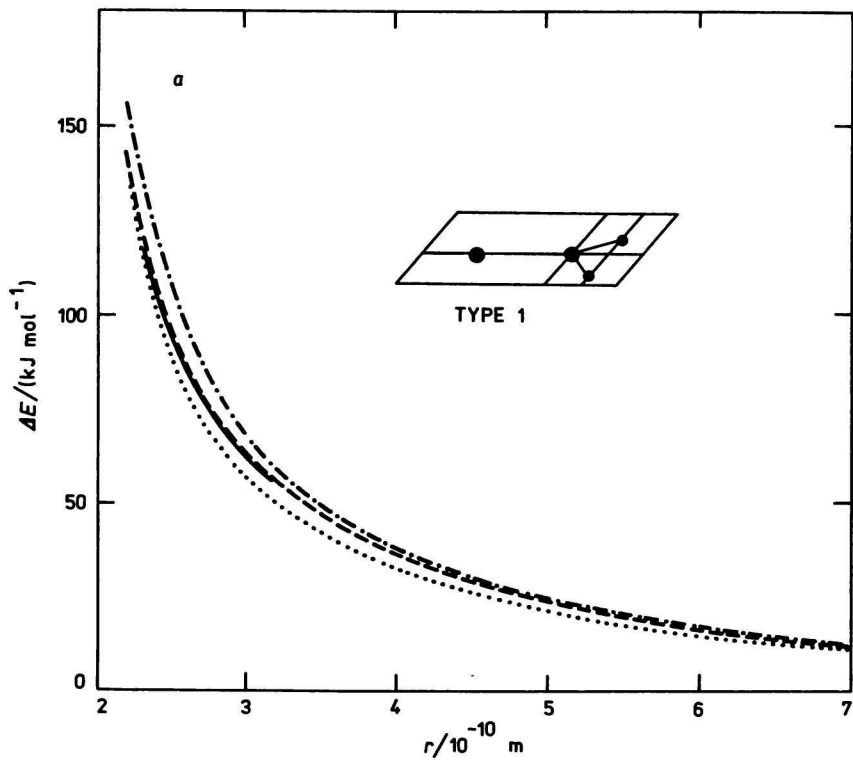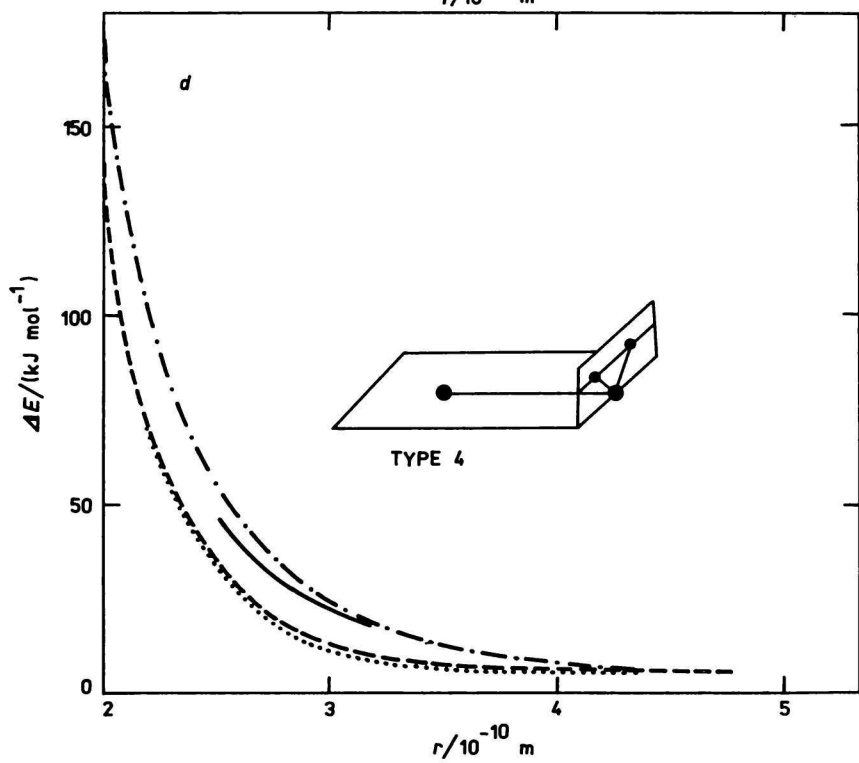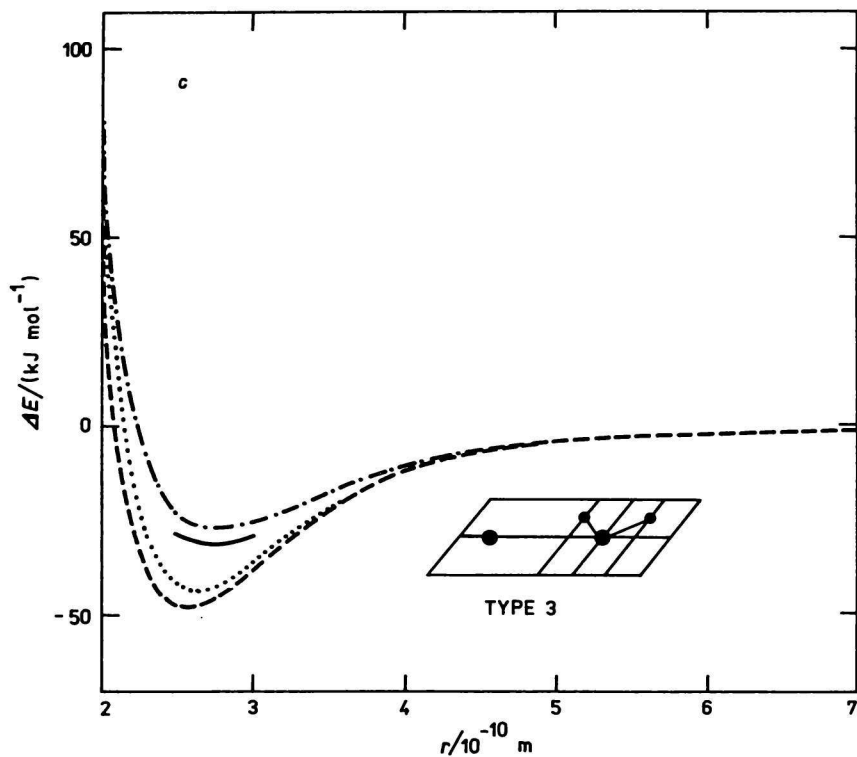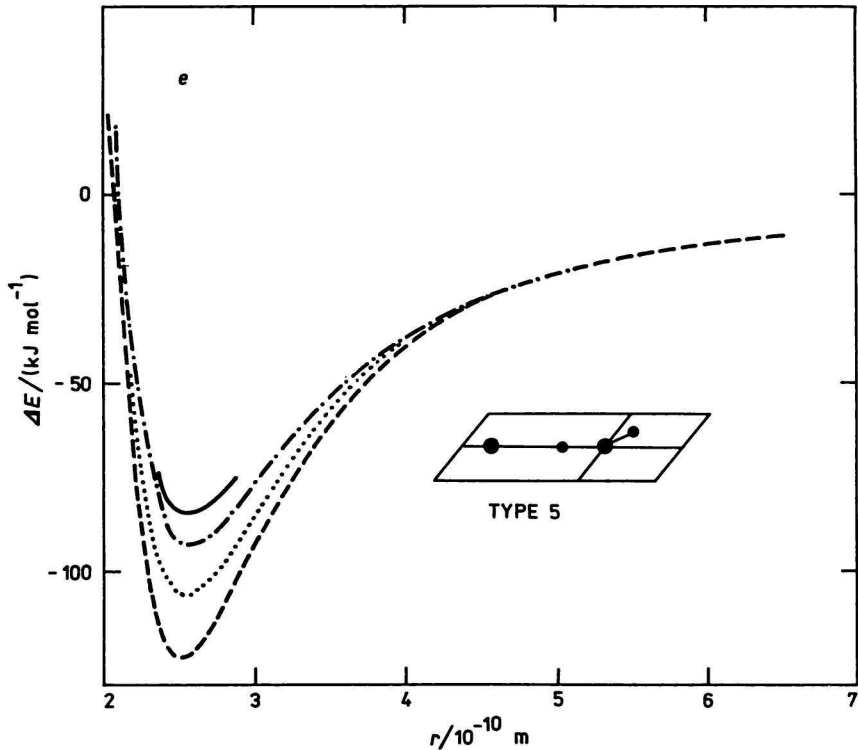
Fig. 2. Potential energy functions of the $F^- \cdots H_2O$. Interaction energy — — — ΔE_{SCF}, —·—·— ΔE_{SCF} BSSE corrected, ·············· ΔE_{SCF} with scaled dipole moment of the H_2O molecule, ———— reference curves [11].

smaller than inaccuracies that result from our limited basis set and were not further investigated.

Several forms for pair potential functions [6] were proposed and tested. After some experimentation we arrived at two alternatives — the "full" and the "economical" expressions. The explicit form of the "full" potential is

$$\Delta E = K[Q_{F-M}r_{F-M}^{-1} + Q_{F-H}(r_{F-H-1}^{-1} + r_{F-H-2}^{-1})] - A_{F-O}r_{F-O}^{-8} -$$
$$- A_{F-H}(r_{F-H-1}^{-8} + r_{F-H-2}^{-8}) + B_{F-O}r_{F-O}^{-12} - C_{F-M}r_{F-M}^{-2} -$$
$$- C_{F-H}(r_{F-H-1}^{-2} + r_{F-H-2}^{-2}) - G_{F-M}r_{F-M}^{-4} - G_{F-H}(r_{F-H-1}^{-4} + r_{F-H-2}^{-4}) - \quad (4)$$
$$- D_{F-M}\exp(-W_{F-M}r_{F-M}) - D_{F-H}[\exp(-W_{F-H}r_{F-H-1}) +$$
$$+ \exp(-W_{F-H}r_{F-H-2})]$$

Table 1

Parameters of the pair potential function (eqn (4))

Parameter unit	12-parameter function	8-parameter function
$A_{F-H}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^8)$	134.68	97.53
$A_{F-O}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^8)$	34093.91	34095.42
$B_{F-O}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^{12})$	396760.35	439989.44
$C_{F-H}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^2)$	805.09	686.22
$C_{F-M}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^2)$	-723.46	-1025.87
$G_{F-H}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^4)$	-904.00	-784.83
$G_{F-M}/(\text{kJ mol}^{-1}\,(10^{-10}\,\text{m})^4)$	-1822.34	-1851.29
$D_{F-M}/(\text{kJ mol}^{-1})$	61.76	0.0
$D_{F-H}/(\text{kJ mol}^{-1})$	4999.88	0.0
$W_{F-M}/(\text{kJ mol}^{-1}\,10^{10}\,\text{m}^{-1})$	0.29	0.0
$W_{F-H}/(\text{kJ mol}^{-1}\,10^{10}\,\text{m}^{-1})$	2.20	0.0
Root mean square deviation of the fit kJ mol^{-1}.	2.32	5.00

with resulting parameters presented in Table 1. r are interatomic distances of the elements given in the index, resp. M denotes the "fourth centre" [18] located 0.15×10^{-10} m apart from the oxygen in the direction of the C_2 axis of the water molecule and A, B, C, D, G, and W are optimized parameters. Q are products of partial atomic charges (-1.0, -0.7 and 0.35 for fluorine, oxygen and hydrogen atoms, respectively). The constant $K = 1389.38$ transforms the coulombic energy from atomic units (a.u.) to kJ mol^{-1}. In the "economical" pair potential we dropped the exponential terms, since they enhance the time needed for one potential energy evaluation in MC procedure considerably. The curve fitting was carried out by a multidimensional least-squares procedure, using gradient algorithm due to *Fletcher* and *Powell* [19]. In the initial stage we used all 34 (calculated) and 38 (interpolated) energies to obtain reasonable guess of the parameters. The interpolated points were dropped in the final fitting, but the resulting parameters did not change considerably. The use of the interpolated points led to better initial guess of the fit and improved the representation of the pair potential function in the minimum region. The final form of the potential without exponential terms was used in the MC simulations. For the water—water interaction MCY pair potential [18] was used.

The standard Metropolis—Monte Carlo [1] computer experiments were performed within the canonical (NVT) ensemble with the cubic periodic boun-

dary conditions by the minimum image method (number of water molecules $N_w = 26$, number of F^- ions $N_s = 1$, $T = 300$ K). Details of the simulation were identical with our previous calculation which utilized SCF/4-31G pair potential [14]. The simulations were run with modified version of CLAMPS program [20] updated for rigid water molecules. Our calculations included an equilibration phase which included 4×10^5 configurations followed by 7.8×10^5 averaging configurations. The configurations were stored on the production file in regular intervals and analyzed with the program ANAL written in our laboratory.

Discussion

The visual comparison of our MIDI-1 potential energy curves with the reference curves in Fig. 2 shows immediately that uncorrected SCF curves overestimate the attraction or underestimate the repulsion between F^- and H_2O. Much better results are obtained with BSSE corrected curves. Only for configuration 3 this correction overshoots reference results. Unfortunately, BSSE is rather large and amounts to 25, 50, and 25% of original SCF values for attractive configurations 2, 3, and 5 near their respective equilibrium distances. Consideration of the dipole moment scaling is less effective than the correction for BSSE and combination of both these corrections overshoots correct
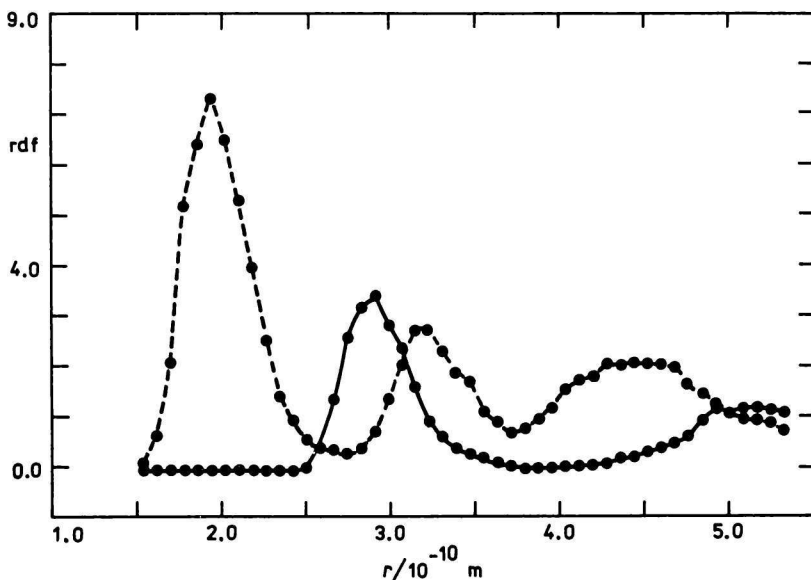

Fig. 3. Radial distribution functions (rdf). ———— for F—O and — — — — for F—H.

results considerably. The second-order perturbation interaction energies for F —O distances (1.46, 1.32, 1.32, 1.46, and 1.32) $\times 10^{-10}$ m of configurations 1 to 5 are -2.7, 4.9, 1.7, -1.4, and 9.7 kJ mol^{-1}, respectively, *i.e.* much smaller than BSSE.

More quantitative insight into the quality of pair potential energies (PPE) provide MC results. Structural characteristics in terms of maxima on radial distribution functions (rdf) (Fig. 3) and coordination number of the first solvation sphere are presented in Table 2. The position of the first maximum of rdf for fluorine—oxygen $g_{F—O}$ is at 2.9×10^{-10} m and that of rdf for fluorine—hydrogen $g_{F—H}$ at 1.94×10^{-10} m. The difference between these two maxima is 0.96×10^{-10} m, *i.e.* very close to the O—H bond distance in the water molecule. This suggests the preferred orientation of the water molecule to F$^-$ through the linear hydrogen bond. This structural characteristics is in accord with the literature data [13]. The second maximum appears at 4.9×10^{-10} m and 3.2×10^{-10} m for $g_{F—O}$ and $g_{F—H}$ rdf's, respectively. Positions of all maxima are slightly overestimated (by about 0.3×10^{-10} m) in comparison with literature data. The same also holds for the value of the coordination number.

Table 2

Structural characteristics for the first solvation sphere. A comparison with some available literature data

$\dfrac{g_{F—O}}{10^{-10}\,\text{m}}$	$\dfrac{g_{F—H}}{10^{-10}\,\text{m}}$	N^a	Ref.
2.60	1.65	6.20	[13]
2.50	1.68	5.00	[21]
2.60	1.70	4.09	[12]
2.20	1.20	6.30	[15]
2.67	1.73	5.80	[22]
2.7—2.8^b	—	—	[23]
2.9	1.94	7.0	

a) Coordination number; *b)* values obtained for small clusters.

Energy characteristics of MC calculations are collected in Table 3. The most important thermodynamic quantity [12, 21] is the partial molar internal energy of the transfer of one solute molecule from the dilute gas into a liquid ΔU_s. Simultaneously, this quantity is most sensitive to the quality of PPE. It is calculated [24] as a difference $\Delta U_s = U_{sw}(N_w, N_s) - U_w(N_w)$, where $U_{sw}(N_w, N_s)$ is total configurational potential energy for the sample with N_w solvent and N_s solute molecules and $U_w(N_w)$ is total configurational potential energy for pure

Table 3

Summary of Monte Carlo energy quantities

Quantity	Value			
$kJ\,mol^{-1}$	This paper	Other values		
$U_{sw}(N_w, N_s)$	-1828	-3344^a		
$U_w(N_w)$	-952	-952^a		
ΔU_s	-876	$-2392^a,$	$-597^b,$	$-464^c,$
		$-406^d,$	-452^e	
$U'_w(N_w)$	-821	-529^a		
U_{relax}	131	$422^a,$	$334^b,$	422^c

Ref.: *a*) [14], *b*) [12], *c*) [13], *d*) and *e*) experimental values, quoted in Ref. [12], resp. [13].

solvent with N_w molecules. Results in Table 3 show that our ΔU_s is considerably closer to other published data, than our previous ΔU_s obtained with the PPE based on the 4-31G SCF data. Both our results were obtained with the same sample of 26 water molecules, so that the difference reflects exclusively the much better quality of the MIDI-1 PPE in comparison to the 4-31G PPE. The relation of our present results to other literature data obtained with more sophisticated methods and basis sets for PPE is also influenced by the fact that other authors mostly used larger samples in MC calculations. Some information on the influence of N_w on thermodynamic quantities may be inferred from the discussion in *Jorgensen's* and *Beveridge's* papers [12, 13]. The final energy quantity presented in Table 3 is the relaxation energy $\Delta U_{relax} = U'_w(N_w) - U_w(N_w)$, where $U'_w(N_w)$ represents the configurational potential energy of N_w water molecules in the presence of the solute molecule.

We may conclude that MIDI-1 basis, augmented with diffuse functions when applied to negative systems, gives PPE which are in fair agreement with reference results. The correction for BSSE is necessary. Structural and energetic characteristics of MC calculations based on these pair potential functions represent considerable improvement over 4-31G data [14] and are in satisfactory agreement with the results obtained from more sophisticated potentials. Thus, our results suggest that MIDI-1 basis may be a good choice for calculations of PPE of extended systems.

The considerable difference between experimental and our value of ΔU_s for $N_w = 26$ prompted us to run additional MC simulation for $N_w = 124$ (other parameters were identical with those for $N_w = 26$). This calculation led to the following internal energies: $U_{sw}(N_w, N_s) = -1227.1$ kJ mol^{-1}, $U'_w(N_w) = -877.6$ kJ mol^{-1}, $U_w(N_w) = -885.8$ kJ mol^{-1}. The resulting internal

energy of transfer $\Delta U_s = -341.3 \text{ kJ mol}^{-1}$ which is substantially closer to both experimental and reference theoretical data.

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