

## AN IMPROVED POTENTIAL FOR NON-RIGID WATER MOLECULES IN THE LIQUID PHASE

P. BOPP, G. JANCsó\* and K. HEINZINGER

*Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz, Federal Republic of Germany*

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A modification of the central-force model for liquid water is proposed; a spectroscopic potential is adapted to describe the intramolecular interactions. Gas-liquid shifts of internal vibrational frequencies obtained from MD simulations are in good agreement with available spectroscopic data.

## 1. Introduction

Almost all of the interaction potentials employed in molecular dynamics (MD) simulation and Monte Carlo calculations on liquid water have treated the molecules as rigid systems [1-5] and thus did not allow investigation of the changes in molecular geometry and internal vibrational motions brought about by the gas-liquid transition.

The first potential which permitted internal vibrations was developed by Lemberg and Stillinger [6]. This so-called central-force (CF) model of liquid water describes all atom-pair interactions in the system in terms of three central potentials [ $V_{HH}(r)$ ,  $V_{OH}(r)$  and  $V_{OO}(r)$ ] independently of whether the atoms belong to the same molecule or not. The initial version of the CF model has later been modified by Rahman et al. [7] (CF1) and Stillinger and Rahman [8] (CF2) and subsequently also used in MD calculations on aqueous electrolyte solutions [9,10]. The results indicated that the CF2 potential represents one of the best available models of liquid water as far as the description of the structural and certain dynamic properties is concerned. Yet the vibrational frequencies and the gas-liquid shifts obtained from it are in serious disagreement with experiment; the reason for this limitation has been discussed in a previous publication [11]. The potential developed by Watts [12] for deformable water mole-

cules proved to be insufficient with respect to structural properties [13] and normal-mode calculations using force constants obtained for small clusters predicted gas-liquid shifts that are too low [14]. In a recent paper Reimers and Watts [15] presented a method for calculating the infrared spectrum of liquid water but no explicit form for the internal potential energy surface was given.

The purpose of this communication is to present a modification of the CF2 potential which is capable of producing liquid-phase vibrational frequencies in agreement with those obtained by spectroscopic investigations and at the same time maintains its good representation of the structural and dynamical properties of real water. This improved set of potentials can then be expected to give more realistic results than earlier models when being used in MD simulations to study the effects of pressure or various ions on the internal vibrational modes of water.

## 2. Determination of intramolecular potential

In the central-force approach [6-8] no distinction is made between inter- and intra-molecular oxygen-hydrogen and hydrogen-hydrogen interactions. The corresponding potential energy functions were constructed in such a way as to be representative of the intramolecular interactions in the distances  $r_{O-H} < 1.3 \text{ \AA}$  and  $r_{H-H} < 2.0 \text{ \AA}$ , and of the intermolecular interactions elsewhere. This approach leads to intrinsically

\* Permanent address: Central Research Institute for Physics of the Hungarian Academy of Sciences, Budapest, Hungary.

simple programs for MD simulations and allows the calculation of certain thermodynamic quantities through analytic techniques. However, several shortcomings of these central-force models must be noted:

(a) The vibrational motions in the gas phase within the harmonic approximation cannot be adequately described with only two independent quadratic force constants, as yielded by a central force field approximation.

(b) The experimentally observed gas-liquid frequency shifts are not well reproduced due to inadequate anharmonicities in these models [11].

(c) The insufficient height of the barrier to molecular dissociation or to unphysical deformation of the molecule prohibits the simulation of water and aqueous systems at elevated temperature or pressure.

A convenient way to overcome these shortcomings is the separation of the potential into an intramolecular part, which can no longer be of central-force type — i.e. depending only on the distance between two interacting centres — and an intermolecular part. Under ordinary circumstances only two out of  $10^9$  water molecules dissociate; if on the other hand the water molecules do dissociate under the conditions studied in a MD simulation, special procedures can be introduced in the simulation routine to take care of these infrequent events.

Because of its well-established high quality, the intermolecular parts of the interaction potential were taken from the CF2 potential without any modification.

For the intramolecular potential we have chosen to use the three internal coordinates usually employed in the analytic formulation of potentials obtained from perturbation-theory treatment of spectroscopic data, viz. the two oxygen-hydrogen distances and the hydrogen-oxygen-hydrogen angle. Several quite accurate sets of potential parameters have been reported in the literature [16–18] and have been thoroughly studied [18–20].

Because of its intrinsically correct behaviour for large oxygen-hydrogen separations, we chose to use a potential in the formulation of Carney, Curtiss and Langhoff (CCL) [18]:

$$V_{\text{intra}} = \sum L_{ij} \rho_i \rho_j + \sum L_{ijk} \rho_i \rho_j \rho_k + \sum L_{ijkl} \rho_i \rho_j \rho_k \rho_l \quad (1)$$

In this equation  $\rho_1 = (r_1 - r_e)/r_1$ ,  $\rho_2 = (r_2 - r_e)/r_2$  and

$\rho_3 = \alpha - \alpha_e = \Delta\alpha$ , where  $r_1, r_2$  and  $\alpha$  are the instantaneous O-H bond lengths and H-O-H angle; the quantities  $r_e$  and  $\alpha_e$  are the corresponding equilibrium values ( $r_e = 0.9572$  Å,  $\alpha_e = 104.52^\circ$ ). The force constants of the CCL potential are given in table 1.

The vibrational frequencies obtained from MD simulations (vide infra) using the CCL potential [18] for the intramolecular water interactions are given in table 2.

A comparison between the values obtained with and without external CF2 interactions ("gas-phase" values) shows that while the stretching frequencies are not sufficiently red-shifted in the liquid, the bending vibration has too high a blue-shift. It has been shown previously that the magnitude of the red-shifts of the stretching vibrational frequencies depends mainly on the principal

Table 1  
Potential constants of the intramolecular potential energy ( $V_{\text{intra}}$ ) (in units of  $10^{-12}$  erg)

Expansion term <sup>a)</sup>	Potential constants <sup>b)</sup>	
	gas phase [18]	liquid phase (this work)
$(\rho_1^2 + \rho_2^2)$	38.7291	38.7291
$\rho_1 \rho_2$	-0.925394	-0.925394
$(\rho_1 + \rho_2) \Delta\alpha$	2.09634	2.09634
$(\Delta\alpha)^2$	3.48489	3.48489
$(\rho_1^3 + \rho_2^3)$	-9.31625	-75.1000
$\rho_1 \rho_2 (\rho_1 + \rho_2)$	0.184163	-0.925394
$(\rho_1^2 + \rho_2^2) \Delta\alpha$	3.94713	3.94713
$\rho_1 \rho_2 \Delta\alpha$	-3.68325	0.0
$(\rho_1 + \rho_2) (\Delta\alpha)^2$	-1.07657	0.0
$(\Delta\alpha)^3$	-1.46139	0.0
$(\rho_1^4 + \rho_2^4)$	-9.78902	89.4000
$\rho_1 \rho_2 (\rho_1^2 + \rho_2^2)$	-5.64582	-0.925394
$\rho_1^2 \rho_2^2$	2.48940	0.0
$(\rho_1^3 + \rho_2^3) \Delta\alpha$	5.79792	5.79792
$(\rho_1 + \rho_2) \rho_1 \rho_2 \Delta\alpha$	-3.68325	0.0
$(\rho_1^2 + \rho_2^2) (\Delta\alpha)^2$	-4.30629	0.0
$\rho_1 \rho_2 (\Delta\alpha)^2$	2.79451	0.0
$(\rho_1 + \rho_2) (\Delta\alpha)^3$	0.0	0.0
$(\Delta\alpha)^4$	-0.029136	0.0

<sup>a)</sup> See eq. (1).

<sup>b)</sup> The large number of significant figures is required to permit replication of the computed results.

Table 2  
Internal vibrational frequencies of water (in  $\text{cm}^{-1}$ )

Vibrational mode	Spectroscopic data		Harmonic frequencies, gas		MD simulation, liquid <sup>b,c)</sup>		
	gas	liquid <sup>a)</sup>	CF2	CCL	CF2	CCL	this work
bend	1595	1645[21]	1369	1649	1593	1749	1709
sym. stretch	3657[21]	3345[22] 3340[23,24]	4266[7]	3832[18]	4573[11]		
asym. stretch	3756	3455[22] 3440[23]	3805	3943	4164	3714	3510

a) The stretching frequencies are assigned to the vibrations of strongly hydrogen-bonded water molecules giving the largest gas-liquid shifts [22,23].

b) The frequencies obtained from MD simulations without intermolecular interactions, under the conditions studied here, differ by less than  $20 \text{ cm}^{-1}$  for the stretches and less than  $10 \text{ cm}^{-1}$  for the bend from the harmonic values. It is thus appropriate to compare the values reported here with harmonic gas-phase values.

c) The error limit for the liquid frequencies is estimated as  $\pm 10 \text{ cm}^{-1}$ .

cubic and quartic force constants [11]. By a proper selection of such constants, satisfactory agreement can be achieved with experimentally observed shifts. As far as the bending vibration is concerned, a harmonic potential (in the angle-bending variable) already reproduces the experimental gas-liquid frequency shift [11], thus the cubic and quartic potential constants ( $L\rho_3\rho_3\rho_3$  and  $L\rho_3\rho_3\rho_3\rho_3$ ) can be neglected. It might be noted in this context that such adjustments of the potential constants also give rise to slight changes in the average molecular geometry in the liquid phase. For the intramolecular potentials studied here, the average O-H bond length ranges from 0.972 to 0.975 Å and the average H-O-H angle from 100.9 to 101.4°.

In addition, a further constraint was imposed on the choice of a suitable combination of higher-order potential constants, namely the requirement to reproduce approximately the dissociation energy ( $\text{H}_2\text{O} = \text{HO} + \text{H}$ , 118 kcal/mole [21]) when the O-H distance increases to a value of  $\approx 2.2 \text{ Å}$  [25].

The potential parameters of an intramolecular potential fulfilling these requirements are also given in table 1; a contour plot in  $r_{\text{O-H}_1}-r_{\text{O-H}_2}$  space of this potential surface together with the CCL potential surface is presented in fig. 1. Inspection of table 1 shows that the quadratic parts of the gas- and the liquid-phase potential are identical and that the large increase in the cubic stretching force constant ( $L_{iii}$ ) is partly compensated by changes in the quartic constant ( $L_{iiii}$ ). In an

effort to reduce the number of force constants, almost all of the cubic and quartic interaction constants (in terms of internal coordinates) have been omitted [20]. This simplification has very little influence on the gas-liquid internal vibrational shifts and is thus appropriate in the approach presented here. As can be seen from fig. 1, the overall shape of the liquid-phase potential is quite similar to the gas-phase potential surface.

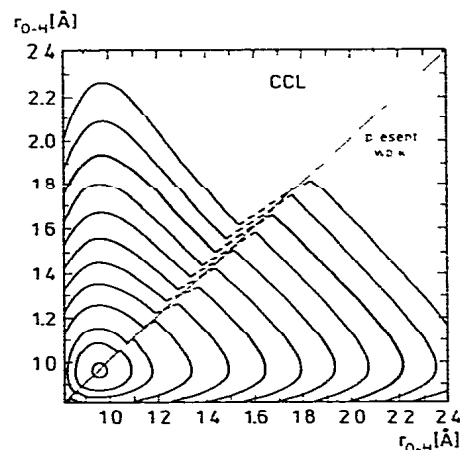


Fig. 1. Contour plot in  $r_{\text{O-H}_1}-r_{\text{O-H}_2}$  space (angle =  $104.52^\circ$ ) of the potential surface of Carney et al. [18] (top left) and of the potential surface for the intramolecular interactions in MD simulations of liquid water (lower right). Contour lines are (in units of  $10^{-12}$  erg) at 0.05, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 (fat), 9.0 and 10.0.

### 3. MD simulations

A suitably modified version of the MD program used in previous work with central-force water reported from this laboratory [9,10] was used for these investigations. The inclusion of intramolecular three-body interactions into the simulation leads to only a very limited increase in the computer time requirement. The system studied consisted of 200 water molecules at a density of  $0.998 \text{ g/cm}^3$  leading to a sidelength of  $18.171 \text{ \AA}$  for the periodic box. The average temperature for all the runs reported here was  $302 \pm 5 \text{ K}$ .

In order to test the gas-liquid frequency shifts generated by various intramolecular potentials, MD simulations of  $\approx 1000$  time steps, equivalent to a total elapsed time of  $\approx 0.25 \text{ ps}$ , were carried out and the autocorrelation functions of the hydrogen velocities and their Fourier transforms were calculated. As the fast oscillatory motions visible in these correlation functions dampen out after  $\approx 10$  oscillations, correlation lengths of  $0.08\text{--}0.12 \text{ ps}$  were used, thus allowing for a sufficient number of averaging processes. The reliability of the velocity autocorrelation functions was further tested by computing separately this function for the first 200 and for the second 200 hydrogens of the ensemble. The deviation in the positions of the maxima in the Fourier transforms (power spectra) of these runs from the ones using all hydrogens was found not to exceed  $\pm 10 \text{ cm}^{-1}$ .

The power spectra from an MD simulation over 2000 time steps using the intramolecular potential described in section 2 is compared in fig. 2 with the one obtained from a run using the original CF2 potential. Table 2 gives the positions of the maxima of these two functions, used here to identify the various modes of interest. Because of the limited length of the correlation functions, the peak centered at  $\approx 440 \text{ cm}^{-1}$  and representing the hindered translations and the librations is not resolved. The other peaks are identified with the H-O-H bending motion and with the O-H stretching motions.

The H-O-H bending peak does not call for any special comment. It is seen to be shifted by about the right amount with respect to the gas-phase value in the case of the new potential, while in the CF2 case the shift is too large (see table 2). The shape of the peak connected with the O-H vibrations is different in both models. A double peak is observed in the CF2 case, in

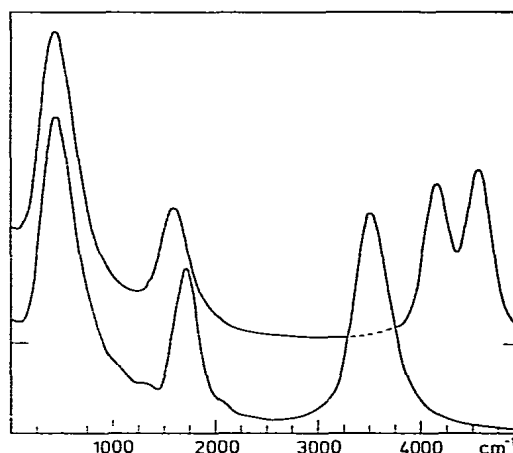


Fig. 2. Fourier transform (power spectrum) of the hydrogen velocity autocorrelation function, in arbitrary units. Top: CF2 potential; bottom: intramolecular interactions from table 2, intermolecular interactions from CF2.

analogy to the large separation between the symmetric and asymmetric O-H harmonic vibrational gas-phase modes in this model (cf. refs. [7,11]). Only a single band appears in the case of the new potential; it is centered at  $\approx 3500 \text{ cm}^{-1}$ , in reasonable agreement with experiment. An explanation for the blue-shift of the O-H peaks in the CF2 case was given in a previous paper [11].

### 4. Conclusion

We think that a potential surface capable of reproducing the internal vibrational behaviour of liquid water in molecular dynamics simulations may be a useful tool for further studies of the *changes* in the vibrational frequencies brought about by different solutes, in spite of the fact that such motions have wavenumbers  $\omega$  such that  $hc\omega > kT$ . (In other words, quantum effects may be expected to cancel in this case.) Within this approach, a potential as simple as possible has been developed which attempts to combine the advantages of the well-known central-force model with a more adequate anharmonic potential for the internal vibrations. Gas-phase harmonic force constants [18] were used, in keeping with re. [11], and the higher-order potential constants were adjusted to yield the proper gas-liquid frequency shifts in the MD simulation. We expect such a potential

to be capable of predicting vibrational frequency shifts in various aqueous systems, such as electrolyte solutions, and thus allow the analysis of measured spectroscopic properties on a molecular level.

The implementation of the potential into existing MD simulation programs requires only minor changes and the increase in the computational time is insignificant. In accordance with earlier conclusions [11,26], the present work clearly shows the importance of the vibrational anharmonicity in governing the gas-liquid vibrational frequency shifts. Preliminary simulations indicate that the structural properties are not changed by the modifications applied here to the original CF2 model. We realize that this potential is a simplified description of the very complex spectral behaviour of liquid water and there is ample opportunity for future improvements.

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