

## Water Pair and Three-Body Potential of Spectroscopic Quality from *Ab Initio* Calculations

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We present the first pair plus three-body potential of water from *ab initio* calculations that quantitatively reproduces the experimental far-infrared spectra of the water dimer and trimer. The dimer spectrum was obtained from the pair potential through rigorous six-dimensional quantum calculations of the vibration-rotation-tunneling levels. The three-body interactions, together with the pair potential, produce an accurate representation of the hydrogen bond torsional levels of the water trimer.

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Thirty years of classical Monte Carlo (MC) and molecular dynamics (MD) simulations with many different intermolecular potentials have still not yielded a potential that provides a quantitative description of all the (anomalous) properties of water and ice. Recently, a new source of information about the pair and many-body interactions in water has become available: the (far-)infrared spectra of small water clusters, from the dimer to the hexamer, prepared in supersonic molecular beams [1–8]. The high-resolution spectra of these very cold clusters correspond directly to the transitions between their quantum levels, without the statistical-thermodynamical averaging that complicates the interpretation of experimental data for the condensed phases. It was evident from the vibration-rotation-tunneling (VRT) level patterns observed in the spectra that the dynamical processes occurring in liquid water, which involve the breaking and reconstruction of hydrogen bonds, are also found in these clusters. Moreover, it was found that the dimer and trimer VRT level splittings are extremely sensitive to the detailed shape of the potential surfaces. They provide the most critical test of the water pair and three-body potential, especially in the physically important attractive region. All the *ab initio* and empirical water potentials that have been tested thus far produced VRT transition frequencies which deviate from experiment by factors of 2 or 3, or even by an order of magnitude; cf. Figs. 4–6 in Ref. [6], Fig. 12 in Ref. [9], and Fig. 6 in Ref. [10]. Although these potentials had been selected because they are believed to be the most accurate ones available, none of them passed this spectroscopic test. The only exception is the recent pair potential of Fellers *et al.* [11], which, however, was *fit* to the dimer spectrum.

This Letter presents a new pair and three-body potential for water obtained from *ab initio* electronic structure calculations, and its application in rigorous quantum calculations of the VRT levels and high-resolution spectra of the water dimer and trimer. Symmetry-adapted perturbation theory (SAPT) [12] has been employed to compute the pair potential, with high-order electron correlation effects included at a level roughly equivalent to fourth-order super-

molecular many-body perturbation theory, and with the same interaction-optimized orbital basis as used by Mas *et al.* [13]. This method has the advantage over the more commonly used supermolecular methods [14] that it yields directly the intermolecular interaction energy separated into the contributions due to electrostatic, polarization, and dispersion forces, with the inclusion of the short-range effects of charge cloud penetration, as well as the exchange repulsion which is a pure short-range interaction. The knowledge of these separate terms and their geometry dependence was essential to obtain an analytic fit representing the potential surface which matches the accuracy of the computed interaction energies.

The interaction energies were computed for 2560 dimer geometries [15], carefully sampled in regions indicated to be physically relevant by Monte Carlo simulations and calculations of the second virial coefficient. Also the regions of the transition states for different hydrogen bond rearrangement processes were sampled. The pair potential that we present [16] is a site-site model (sites *a* on molecule *A* and sites *b* on molecule *B*), with the functional form

$$V_{AB} = \sum_{a \in A, b \in B} \left[ \left( \sum_{m=0}^3 a_m^{(ab)} R_{ab}^m \right) \exp(-\beta^{(ab)} R_{ab}) + f_1(R_{ab}, \delta_1^{(ab)}) \frac{q_a q_b}{R_{ab}} + \sum_{n=6,8,10} f_n(R_{ab}, \delta_n^{(ab)}) \frac{C_n^{(ab)}}{R_{ab}^n} \right]$$

and 8 sites per molecule (5 symmetry-distinct sites, leading to the notation SAPT-5s). The correct large-distance behavior of the analytic potential was ensured by fixing the three symmetry-distinct point charges  $q_x$  and nine coefficients  $C_n^{(ab)}$ , representing induction and dispersion, to the results of independent *ab initio* calculations of monomer properties and long-range interaction constants. The 65 free parameters,  $a_m^{(ab)}$ ,  $\beta^{(ab)}$ , and  $\delta_n^{(ab)}$ , were obtained from the fit to 2510 *ab initio* data points (the remaining 50 points confirm the accuracy of the fit). The functions  $f_n(R, \delta)$

are Tang-Toennies damping functions [17] which correct the long-range interactions for overlap effects.

The explicit calculation of the three-body interactions was made possible by the recent extension of SAPT. The leading three-body interaction components up to the fourth order were derived [18,19], with the inclusion of exchange effects. The three-body interactions contribute about 15% of the trimer binding energy at the hydrogen bonded equilibrium geometry, and 30% or more to the hydrogen bond rearrangement barriers. The dominant three-body interactions are the second- and third-order polarization effects, but the nonadditive exchange effects are not negligible, especially for the rearrangement barriers. The three-body contributions to the potential needed to compute the torsional levels of the water trimer were directly calculated on a three-dimensional grid with 568 symmetry-distinct points [20]. An additional set of trimer geometries was used to obtain an analytic fit of the three-body interactions that can be applied in MC or MD simulations of liquid water. Details on the SAPT calculations and analytic fits of the pair and three-body potentials will be given in forthcoming papers [21].

The six-dimensional intermolecular potential surface of the water dimer has eight equivalent, permutationally distinct, global minima which correspond to hydrogen bonded geometries. Three different tunneling processes allow the system to interconvert between these minima. Acceptor tunneling, which does not require breaking of the hydrogen bond, is the lowest barrier process; donor-acceptor interchange tunneling and bifurcation tunneling both involve hydrogen bond breaking. For a qualitative view of the corresponding minimum energy pathways, see Fig. 1 of Ref. [22]. Since the potential around the minima is strongly anharmonic and there is tunneling between equivalent minima, the standard (approximate) methods of vibrational analysis are not applicable. In order to compare with spectroscopic data one needs a nearly exact solution of the six-dimensional Schrödinger equation. Only very recently, Leforestier *et al.* were the first to solve this problem, by the use of a pseudospectral method [22]. We have implemented [23] a conventional variational method with the full scattering Hamiltonian [24], which had to be very efficient to handle matrices of dimensions up to 300 000.

Figure 1 shows the VRT levels of the  $\text{H}_2\text{O}$  dimer for  $J, K \leq 2$  calculated from the SAPT-5s *ab initio* pair potential. The smaller splittings resulting from the donor-acceptor interchange and bifurcation tunneling are in remarkably good (within  $0.03 \text{ cm}^{-1}$ ) agreement with experiment [2], for each  $J, K$ . Also the end-over-end rotational constant  $B + C$ , which is a measure for the average intermolecular distance  $R$ , and even the rotational constant  $A$ , which depends sensitively on the average orientations of the molecules in the dimer, are close to the measured values. The frequency of the  $22.3 \text{ cm}^{-1}$  transition observed between the lowest  $K = 1$  and  $K = 2$  levels agrees

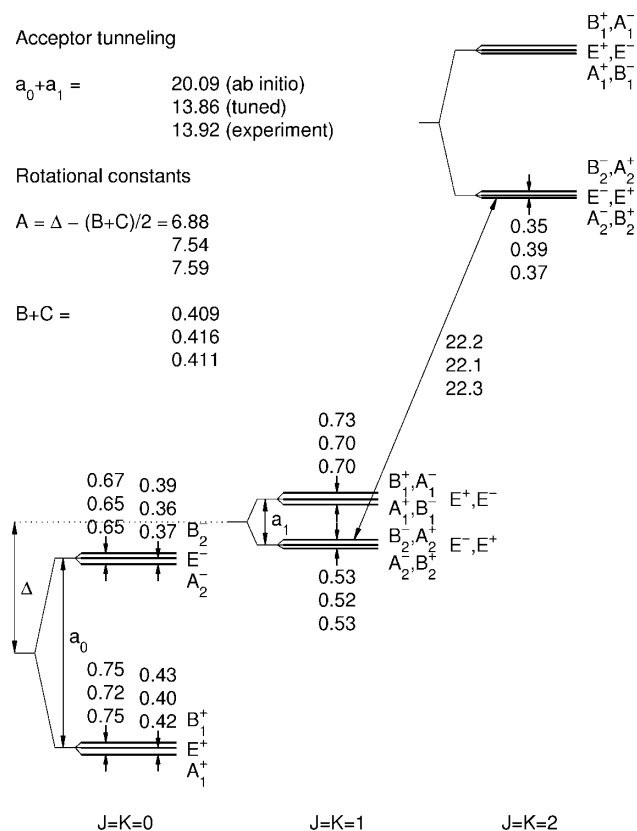


FIG. 1. VRT levels of the  $\text{H}_2\text{O}$  dimer (in  $\text{cm}^{-1}$ ) from converged calculations with the SAPT-5s *ab initio* potential (upper numbers) and the tuned version of this potential (middle numbers), in comparison with experimental data [2] (lower numbers). The labels  $A_{1,2}^{\pm}, B_{1,2}^{\pm}, E^{\pm}$  correspond to the irreducible representations of the permutation-inversion group  $G_{16}$ ;  $J$  and  $K$  are the dimer rotational quantum numbers.

with experiment to  $0.1 \text{ cm}^{-1}$ . The larger acceptor tunneling splittings  $a_K$  have not been directly measured, but the sum  $a_0 + a_1$  is known. This is the only quantity that is not so well reproduced by the *ab initio* calculations: it is overestimated by about 40%. From a comparison with the VRT levels obtained [6,9] from previously available water pair potentials, we may conclude that the SAPT-5s potential represents a significant improvement.

We developed an efficient procedure [23] to further enhance the quality of the SAPT-5s potential. The linear parameters  $a_m^{(ab)}$  were altered in such a way that in a first-order estimate the only quantity which deviates substantially from experiment, i.e., the acceptor tunneling splitting of  $(\text{H}_2\text{O})_2$ , becomes equal to the experimental value and the (already accurate) interchange splittings do not change. A constraint in this parameter variation was that it leaves the potential as close as possible to the *ab initio* potential. Possible small effects of the nonrigidity of the water molecules are implicitly included by this procedure. With this reparametrized SAPT-5s potential (referred to as SAPT-5s tuned) we recomputed the VRT levels of  $(\text{H}_2\text{O})_2$  and obtained excellent agreement with experiment; see

Fig. 1. The tuned potential was then used to compute the energy levels of  $(D_2O)_2$  without any further reparametrization. The 6 times smaller [compared to  $(H_2O)_2$ ] acceptor tunneling splitting agrees with the measurements to within 6%, and the 10 to 20 times smaller interchange tunneling splittings to about 5%. The VRT levels of  $(D_2O)_2$  calculated from the SAPT-5s-tuned potential agree equally well with the experimental data as the results obtained from the VRT(ASP-W) potential [11] which was *fit* to these levels, while the representation of the  $(H_2O)_2$  levels is slightly better with our potential.

The experimental frequencies of the intermolecular vibrations up to  $110\text{ cm}^{-1}$  in  $(D_2O)_2$  (see Fig. 3 in Ref. [11]) were reproduced by the SAPT-5s-tuned potential to within  $3.6\text{ cm}^{-1}$  on average (i.e., to better than 5%). It is remarkable that the agreement is equally good as with the VRT(ASP-W) potential fit to these frequencies, although the tuning of the SAPT-5s potential did not involve any  $(D_2O)_2$  data or any vibrationally excited levels. The second virial coefficients computed with both SAPT-5s potentials [21] agree well with the best experimental data. The well depth  $D_e$  is  $4.86\text{ kcal/mol}$  for SAPT-5s and  $5.03\text{ kcal/mol}$  for SAPT-5s tuned. The most reliable estimate, from the *ab initio* work of Klopper and Lüthi [25], is  $D_e = 5.0 \pm 0.05\text{ kcal/mol}$ . The dimer dissociation energy  $D_0$  with SAPT-5s tuned is  $3.08\text{ kcal/mol} = 1077\text{ cm}^{-1}$  for  $(H_2O)_2$  and  $3.47\text{ kcal/mol} = 1214\text{ cm}^{-1}$  for  $(D_2O)_2$ . The best experimental value [26] of  $D_0$  for  $(H_2O)_2$  is  $1250 \pm 175\text{ cm}^{-1}$ .

For the 12 intermolecular degrees of freedom of the water trimer it is presently not possible to perform calculations as accurate as for the dimer. The equilibrium geometry of the trimer is a cyclic, nonsymmetric structure held together by three hydrogen bonds in which every monomer acts simultaneously as a proton donor and a proton acceptor [4]. From recent experimental [5,7,8] and theoretical [20] work on this trimer it became evident that there is a good adiabatic separation between the relatively fast vibrations of the triangular hydrogen bonded (fairly rigid) framework and the slower torsional motions of the three water monomers about their hydrogen bonds. The latter motions involve flipping between six equivalent minima; see Fig. 1 of Ref. [8]. They do not involve breaking hydrogen bonds and lead to a large splitting of each rovibrational state into six torsional tunneling levels. Given the three-dimensional potential surface in the coordinate space consisting of the three torsional angles, the DVR (discrete variable representation) method of Ref. [20] allowed us to compute the torsional flipping levels of the water trimer very precisely.

Figure 2 shows the torsional levels of the normal and fully deuterated water trimer calculated from the SAPT-5s potential for the pair interactions and additional three-body interactions computed on the three-dimensional DVR grid [27]. The agreement of the lower ( $k = 0, \pm 1, \pm 2, 3$ ) levels with experiment is excellent. For the higher levels,

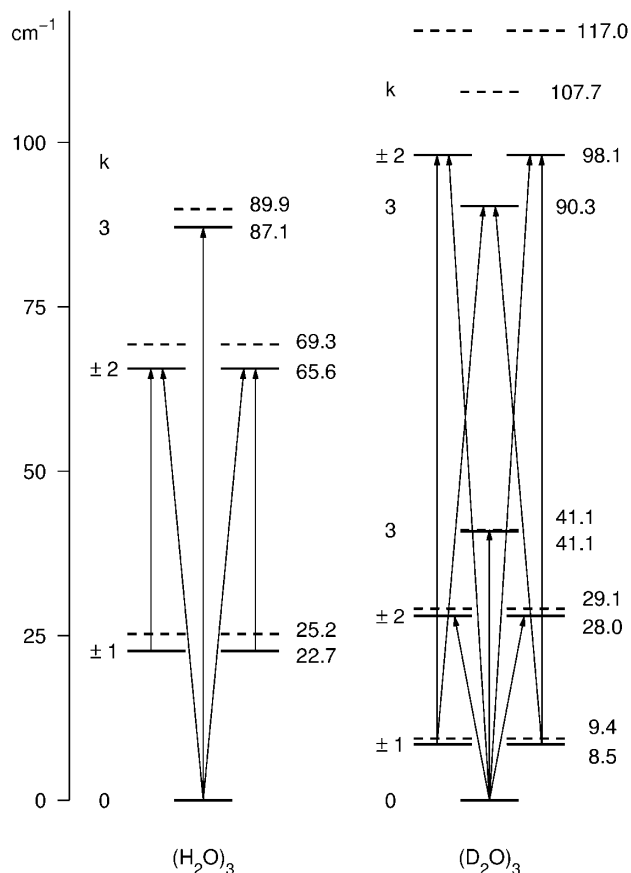


FIG. 2. Torsional levels (in  $\text{cm}^{-1}$ ) of the  $H_2O$  and  $D_2O$  trimers for  $J = 0$ . The labels  $k = 0, \pm 1, \pm 2, 3$  correspond to the irreducible representations of the (cyclic) permutation-inversion group  $G_6$ . The dashed levels are calculated; the solid levels are experimental data [7,8]. Arrows indicate the observed transitions.

measured in  $(D_2O)_3$ , the deviations are larger, but there are several indications [7] that the separation between the torsional motions and other vibrations of the trimer starts breaking down at these higher energies. The torsional levels of both  $(H_2O)_3$  and  $(D_2O)_3$  in Fig. 2 agree considerably better with experiment than those from any of the previously tested global water potentials [10]. Even the replacement of our SAPT-5s pair potential by the “spectroscopic” VRT(ASP-W) potential [11]—which was probably the best pair potential available up to now—gave a substantial quality degradation: the resulting torsional levels became much too dense, as a consequence of the flipping barrier becoming too high by nearly a factor of 3.

In conclusion, this Letter reports a water pair potential derived from *ab initio* calculations which passed the very critical test of quantitatively reproducing detailed dimer spectroscopic data. In addition, it is the first to obtain explicitly the three-body nonadditive interactions in water from *ab initio* calculations to such a high accuracy that, together with the pair potential, they quantitatively reproduce the torsional spectrum of the water trimer. We already started using this pair and three-body potential in MC

simulations of liquid water [21]. Although its functional form is more complicated than that of the model potentials commonly used in such simulations, the computations are not particularly time consuming on modern computers. Simulations with the use of this more complicated and realistic potential may lead to a better understanding of the anomalous properties of water and ice.

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- [27] The separations of  $R = 5.37$  bohrs between the centers of mass of the water molecules and the angles  $\alpha = 21.2^\circ$  describing the nonlinearity of the hydrogen bonds correspond to the trimer equilibrium structure and were kept fixed. The torsional levels computed with the SAPT-5s-tuned potential (not shown in Fig. 2) are about 14% too low, due to a 30% increase of the flipping barrier. From the analytic pair and three-body potential it follows that the flipping barrier in the full twelve-dimensional trimer potential surface is nearly 30% lower than in the three-dimensional surface obtained by freezing the center-of-mass separations  $R$  and the angles  $\alpha$ . The compensation of these two 30% effects will bring the levels from SAPT-5s tuned into equally good agreement with experiment as those from SAPT-5s.