J. Phys. Chem. A **2009,** *113,* 12285–12294

Vibration–Rotation–Tunneling Levels of the Water Dimer from an ab Initio Potential Surface with Flexible Monomers

Claude Leforestier

Institut Charles Gerhardt Montpellier, UMR 5253-UM2-CNRS-ENSCM-UM1, CTMM, Bâtiment 15, CC 1501, Université Montpellier 2, 34095 Montpellier, Cedex 05, France

Rob van Harrevelt and Ad van der Avoird*

Theoretical Chemistry, Institute for Molecules and Materials, Radboud University Nijmegen, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

Received: March 5, 2009; Revised Manuscript Received: April 27, 2009

The 12-dimensional ab initio potential for the water dimer with flexible monomers from Huang et al. (*J. Chem. Phys.* **2008**, *128*, 034312) was used in accurate calculations of the vibration–rotation–tunneling (VRT) levels of $(H_2O)_2$ and $(D_2O)_2$ involving the intermolecular rovibrational and tunneling states as well as the intramolecular vibrations. For the intermolecular VRT levels we used a 6 + 6d model in which the fast intramolecular vibrations are adiabatically separated from the much slower intermolecular vibrations, tunneling motions, and overall rotations. We also tested two six-dimensional (6d) rigid monomer models in which the monomers were frozen either at their equilibrium geometry or at their ground state vibrationally averaged geometry. All the results from the 6 + 6d model agree well with the large amount of detailed experimental data available from high-resolution spectroscopy. For most of the parameters characterizing the spectra the results of the two 6d rigid monomer models do not significantly differ from the 6 + 6d results. An exception is the relatively large acceptor tunneling splitting, which was the only quantity for which the 6d model with the monomers frozen at their equilibrium geometry was not in good agreement with the experimental data. The 6d model with monomers at their vibrationally averaged geometry performs considerably better, and the full 6 + 6d results agree with the measurements also for this quantity. For the excited intramolecular vibrations we tested two 6 + 6d models. In the first model the excitation was assumed to be either on the donor in the hydrogen bond or on the acceptor, and to hop from one monomer to the other upon donor–acceptor interchange. In the second model the monomer excitation remains localized on a given monomer for all dimer geometries. Almost the same frequencies of the intramolecular vibrations were found for the two models. The calculations show considerable variations in the frequencies of the intramolecular modes for transitions involving different tunneling levels and different values of the rotational quantum number K. For $K = 0 \rightarrow 0$ transitions these variations largely cancel, however. A comparison with experimental data is difficult, except for the acceptor asymmetric stretch mode observed in high-resolution spectra, because it is not clear how much the different transitions contribute to the (unresolved) peaks in most of the experimental spectra. The large red shift of the donor bound OH stretch mode is correctly predicted, but the value calculated for this red shift is too small by more than 20%. Also in the smaller shifts of the other modes we find relatively large errors. It is useful, however, that our detailed calculations including all ground and excited state tunneling levels provide an explanation for the splitting of the acceptor asymmetric stretch band observed in He nanodroplet spectra, as well as for the fact that the other bands in these spectra show much smaller or no splittings.

I. Introduction

In order to understand the intriguing properties of water and ice by means of simulations, one has to know precisely the complete water force field. It has become obvious that many-body interactions between the water molecules play an important role in determining the structure and dynamics of the hydrogen bonded network in water, but it is also of utmost importance to accurately know the water pair potential.[1,2] Two high-quality water pair potentials, CC-pol-8s and HBB, were recently obtained from ab initio electronic structure calculations at the CCSD(T) [coupled cluster with singles, doubles, and perturbatively included triples] level for many geometries of the water dimer. In calculations of the water dimer high-resolution spectrum[3] it was established that the CC-pol-8s potential is the most accurate six-dimensional (6d) potential for rigid water monomers. It is based on the same ab initio data as its predecessor, CC-pol,[4] but the analytical form used to represent these data is somewhat more complex and fits the data much more accurately. Also the HBB potential[5,6] is based on a large number of ab initio data and an accurate analytical fit to these data. Six-dimensional calculations of the water dimer spectrum similar to those made for the CC-pol-8s potential confirm that the HBB potential is accurate, too.[6] It slightly underestimates the binding energy of the water dimer, however.

Several attempts have been made to extract also the effects of monomer flexibility in water from ab initio calculations by constructing a full-dimensional (12d) potential surface for the

10.1021/jp9020257 CCC: $40.75

water dimer.[5,7,8] The SAPT-5sf potential was tested in 12d calculations of the water dimer vibration−rotation−tunneling (VRT) levels[8] similar to those described in the present paper. It still showed some of the small defects of its rigid monomer predecessor, SAPT-5s, which was the first ab initio potential that gave fairly good agreement with the measured high-resolution data for the water dimer,[9−11] but needed some empirical tuning to get full agreement. The 12d HBB potential gave such good agreement with the experimental water dimer spectrum in 6d calculations[6] that it is interesting to investigate with this potential what are the effects of monomer flexibility on the calculated water dimer spectrum. This investigation is the topic of the present paper. Let us mention here that the 12d HBB potential surface was obtained[5,6] from ab initio calculations at the CCSD(T) level for about 30 000 geometries of the water dimer, followed by an accurate fit of the computed data points in terms of symmetry-adapted polynomials in the exponentially scaled interatomic distances.

Full 12d quantum calculations of the bound levels of the water dimer by a method that is able to account for the large-amplitude strongly anharmonic intermolecular vibrations and tunneling processes are still not possible. A method has been devised,[12] however, to treat the 12 nuclear motion degrees of freedom in the water dimer in a 6 + 6d adiabatic model. It is based on the adiabatic separation between the six fast intramolecular vibrations and the six much slower intermolecular vibrations and tunneling motions, which is well justified at least when the molecules are in their vibrational ground state. For vibrationally excited monomers some complications arise that will be discussed in detail below. Here we apply this method to the 12d potential HBB and compare the results with 6d calculations based on rigid monomer models to investigate the effect of monomer flexibility on the intermolecular vibration−rotation−tunneling (VRT) levels. In addition, we use the 6 + 6d adiabatic method to compute the frequency shifts of the monomer vibrations. The method is outlined in section II; the results are discussed and compared with experimental data in section III. Section IV presents the conclusions.

II. Calculation of the Vibration−Rotation−Tunneling Levels

In the global potential energy surface of the water dimer, one finds 48 equally deep minima that correspond to 48 equivalent equilibrium structures. Starting from one minimum, the dimer has access to seven other of these minima without breaking any of the strong OH bonds within the monomers. Hence, the barriers between these eight minima are relatively low, on the order of a few hundreds of cm^{-1}, and quantum mechanical tunneling between the equivalent minima gives rise to observable splittings in the water dimer high-resolution spectrum. In terms of the molecular symmetry group[13] the equivalent equilibrium structures are related by the interchange of identical nuclei. The interchange operations between the eight minima connected by tunneling are called “feasible”. Combined with inversion, they generate the permutation−inversion (PI) symmetry group G_{16} of the water dimer. The VRT levels of this dimer are commonly labeled with the irreducible representations (irreps) $A_1^\pm$, $B_1^\pm$, $A2\ \pm$, $B_2^\pm$, and $E^\pm$ of G_{16}. It was demonstrated in several earlier papers[1,2,6,11,14−18] that the VRT levels of the water dimer measured by high-resolution microwave and terahertz molecular beam spectroscopies[19−27] provide an extremely critical test of the water pair potential. In such a test one has to ensure, however, that the VRT levels are very accurately computed, so that all deviations between the calculated levels and the experimental data are due only to the remaining errors in the potential surface. In most of the previous papers this was achieved by the use of a fully coupled treatment in all six intermolecular degrees of freedom, with the monomers frozen either at their isolated molecule equilibrium geometry or at the average geometry of their vibrational ground state.

Leforestier et al.[12] have presented a method to lift the constraint of monomer rigidity and to consider all 12 internal degrees of freedom of the water dimer, both inter- and intramolecular. Here, we apply this method to the 12d HBB potential.[6] As mentioned in the Introduction, the 6 + 6d method of Leforestier et al. is based on the adiabatic separation between the six fast intramolecular vibrations and the six much slower intermolecular vibrations and tunneling motions of the water dimer. The method is described in detail in ref 12; here we give a brief summary.

The Hamiltonian for the nuclear motion of the water dimer is written exactly in terms of 12 Jacobi coordinates. These coordinates are obtained by defining two monomer frames with their origins in the centers of mass of the monomers. The vector $\mathbf{R}$ points from the origin of the coordinate frame on monomer A to the origin of the frame on B, and the Euler angles $\mathbf{\Omega}_A$, $\mathbf{\Omega}_B$ determine the orientations of the monomer frames with respect to a dimer frame with its z-axis along $\mathbf{R}$. Only five of these Euler angles are needed to determine the relative orientations of the monomer frames; together with the distance R, the length of the vector $\mathbf{R}$, they form the six intermolecular coordinates. The six intramolecular coordinates $\mathbf{q}_A$, $\mathbf{q}_B$ define the geometries of the monomers. The first step in the 6 + 6d method is to obtain 6d adiabatic intermolecular potentials by computation of the intramolecular vibrational energy levels for each point on a 6d grid in the intermolecular coordinates R, $\mathbf{\Omega}_A$, $\mathbf{\Omega}_B$. In the second step the intermolecular VRT states are calculated with the intermolecular terms of the kinetic energy operator in the Hamiltonian and the adiabatic potential $V_i(R,\mathbf{\Omega}_A,\mathbf{\Omega}_B)$ computed for the intramolecular ground or excited state i that one wishes to consider.

The calculation of the adiabatic intermolecular potentials in the first step proceeds as follows. For each intermolecular grid point the geometries of monomers A and B, i.e., the coordinates $\mathbf{q}_A$ and $\mathbf{q}_B$, are first optimized. Then, monomer B is kept at its optimum geometry and the vibrational eigenvalues of monomer A, in the field of monomer B, are obtained from fully anharmonic three-dimensional (3d) DVR (discrete variable representation) calculations in the coordinates $\mathbf{q}_A$. Analogously, the vibrational eigenvalues of monomer B, in the field of monomer A with $\mathbf{q}_A$ optimized, are obtained from 3d DVR calculations in $\mathbf{q}_B$. In ref 12 it was checked by perturbation theory that the simultaneous deformation of A and B from their optimum geometries has only a negligible effect on the results. The adiabatic intermolecular potentials $V_i(R,\mathbf{\Omega}_A,\mathbf{\Omega}_B)$ are constructed by adding one of the vibrational eigenvalues of monomer A to one of the eigenvalues of monomer B, for each point on the 6d dimer grid. If both monomers are in their vibrational ground state, the dimer VRT states are calculated on the lowest adiabatic intermolecular potential surface with $i = 0$. In calculations of the frequency shifts of the monomer vibrations, one uses the 6d intermolecular potentials with $i > 0$ obtained by adding, for each 6d dimer grid point, one of the excited vibrational eigenvalues of one monomer to the ground state eigenvalue of the other monomer.

In the second step of the 6 + 6d method, the calculation of the 6d intermolecular VRT states on one of the adiabatic potentials $V_i(R,\mathbf{\Omega}_A,\mathbf{\Omega}_B)$, we used a pseudospectral method that employs both an analytical basis and a numerical grid basis. In the Lanczos algorithm applied to iteratively determine the lower eigenvalues of the Hamiltonian operator, Krylov spaces are constructed which are spanned by so-called Lanczos vectors. These vectors are obtained by repeatedly operating with the Hamiltonian on an initial (arbitrary) seed vector. The kinetic energy operator is rather easily evaluated in the analytical basis, while the potential is diagonal in the grid basis: its elements are simply the values of the potential at the grid points. The Lanczos method is applied in the analytical basis, adapted to the irreps of the PI group G_{16}. In the potential energy calculation, one transforms to the grid basis, multiplies with the potential on the grid, and then transforms back to the symmetry-adapted analytical basis. This makes this method very economical both in the use of storage and in computer time. The overall rotation of the dimer with total angular momentum J is included as well. The angular basis functions are coupled products of Wigner D-functions for the internal and overall rotations, and the angular grid points are the appropriate quadrature points.[28] A potential-optimized DVR method is used for the coordinate R. Note that we also included the off-diagonal Coriolis coupling between angular basis functions of different K, the projection of the angular momentum J on the dimer axis $\mathbf{R}$. Still, this quantum number K remains sufficiently well conserved to use it as a label of the VRT levels, in addition to J. In some previous work on the water dimer[2,6] off-diagonal Coriolis coupling was omitted, but it was shown in ref 3 that it has a nonnegligible effect on the end-over-end rotational constants $B + C$.

In principle, the intramolecular vibrations can be excited in combination with the intermolecular vibrations. Here, we are interested in the frequency shifts of the intramolecular vibrations, and for $i > 0$ we only consider the intermolecular vibrational ground state. Both the ground and vibrationally excited states are split by tunneling into levels of different PI symmetries, however. One should realize that the number of grid points required to obtain well-converged intermolecular VRT states is very large, on the order of 10^7 when the PI symmetry is exploited. Therefore, the calculation of the monomer vibrational eigenvalues in the first step had to be performed many times.

A basic problem arises with the 6 + 6d adiabatic separation between the inter- and intramolecular coordinates if one of the monomers is vibrationally excited. If the excitation is localized on a given monomer the PI symmetry is broken, because the two monomers are no longer equivalent. As a result, the 6d adiabatic potentials for the excited states that are obtained from the vibrational eigenvalues of the monomers are not symmetric with respect to the interchange of the two monomers. In reality, the excitation can hop from one monomer to the other, and in fact it does so, in combination with the donor−acceptor interchange tunneling that interchanges the role of the two monomers in the hydrogen bond. From the high-resolution spectral data available[29] it can be concluded, however, that the interchange tunneling splitting is reduced by an order of magnitude in the vibrationally excited state with respect to the ground state. In other words, donor−acceptor interchange is hindered in the excited state because it has to be accompanied by a simultaneous hop of the vibrational excitation from one monomer to the other. A fully correct theoretical description of this process requires the use of two equivalent potential surfaces. Each of these potentials is not symmetric with respect to interchange. These two potentials can be obtained from monomer calculations with the assumption that the excitation stays localized on one monomer or on the other one, irrespective of the dimer geometry. Equivalently, the second potential can simply be obtained from the first one by an interchange of the monomer coordinates. The corresponding treatment of the excited intermolecular VRT states, with the use of the full PI symmetry, requires the simultaneous inclusion of both these potentials. In other words, one has to use a nonadiabatic model involving two potential surfaces, corresponding to vibrational states on each of the two monomers.

TABLE 1: Monomer Data Computed from the HBB Potential and Used in 6d Calculations

	r_{OH} (Å)	HOH angle (deg)
H_2O		
equilibrium geometry	0.9615	104.20
vibration averaged	0.9794	104.09
D_2O		
equilibrium geometry	0.9615	104.20
vibration averaged	0.9745	104.09

In our calculations we used a single-potential approach and applied two different approximations to a full nonadiabatic treatment. In the first approximation we defined a single effective symmetry-adapted potential by using the appropriate excited state eigenvalue of the donor or the acceptor, irrespective of which monomer plays this role. This requires a criterion to distinguish the donor from the acceptor, even for dimer geometries that are not obviously hydrogen bonded. Such a criterion, involving the smallest intermolecular O−H distance, is given in ref 12. This model seems realistic as it appears from the experimental data (discussed below) that the monomer vibrational modes in the water dimer can indeed be assigned to the donor or to the acceptor. Our second model assumes that the excitation stays localized on a given monomer for all dimer geometries. The intermolecular potential is not symmetric with respect to interchange of the monomers; hence, we used only the subgroup G_8 obtained from the full PI group G_{16} by omitting the interchange operation P_{AB}. Instead of using only the lowest eigenvalue for each G_{16} irrep, we then considered the lowest two eigenvalues for each G_8 irrep. In practice, it was no problem to assign these to a vibration of the donor or the acceptor. The comparison of the monomer frequency shifts obtained from these two extreme models gave us an indication of their quality, with respect to the full nonadiabatic two-state treatment. One should realize, of course, that these models cannot be used to compute the excited state interchange tunneling splitting. The first model strongly overestimates this splitting; the second model makes the two monomers inequivalent and, thereby, quenches (or at least underestimates) interchange tunneling.

In addition to the 6 + 6d calculations on the full 12d potential HBB, we performed 6d calculations of the intermolecular VRT levels. The corresponding potentials were obtained from the full 12d potential by fixing the monomer geometries, either at their calculated free monomer equilibrium values or at the values corresponding to a vibrationally averaged free monomer geometry. Both the monomer equilibrium coordinates and the vibrationally averaged values were obtained from the 12d potential of ref 6 by moving the other monomer to a very large distance. In the calculation of the vibrationally averaged monomer coordinates, we computed the free monomer vibrational ground state by the same 3d DVR method as used in the full 6 + 6d calculations (described in the last paragraph of this section). The resulting monomer coordinates are listed in Table 1.

The quantities that we use to characterize the spectra are the same as used by the experimentalists and are defined in refs 24−27. For $K = 0$ the origins o_1 and o_2 are the average energies of the $J = 0$ levels of A_1^+ and B_1^+ symmetry and of A_2^- and B_2^- symmetry, respectively. The end-over-end rotational constant $B + C$ for $K = 0$ was obtained as the difference between levels with $J = 1$ and $J = 0$. For $K \neq 0$ the levels occur in nearly degenerate pairs, $A_1^\pm$, $B_1^\mp$ and $A_2^\mp$, $B_2^\pm$. The origins o_1 and o_2 were obtained from averaging the $A_1^\pm$ and $B_1^\mp$ levels and the $A_2^\mp$ and $B_2^\pm$ levels, respectively. Then, according to the convention used by experimentalists, the origins were calculated from the levels with the lowest value of J ($=K$) by subtraction of $(B + C)K/2$. The much larger rotational constant A for rotation about the prolate axis (nearly coinciding with the vector $\mathbf{R}$) was obtained as the difference between the $K = 1$ and $K = 0$ averages $(o_1 + o_2)/2$.

The largest tunneling splitting, denoted by $a(K)$, is the so-called acceptor splitting, which is strongly K dependent. It is caused by an interchange of the two hydrogen atoms of the hydrogen bond acceptor monomer. The splitting $a(K)$ can be extracted from the (calculated or measured) spectra as the energy difference between the origins o_2 and o_1. The interchange splittings, denoted by i_1 and i_2, correspond to the interchange of the donor and acceptor molecules. These tunneling splittings can be extracted from the spectra as well: i_1 is the difference between the $B_1^\pm$ and $A_1^\pm$ levels and i_2 is the difference between the $B_2^\mp$ and $A_2^\mp$ levels. The very small shifts of the $E^\pm$ levels with respect to the average energies of the $A_1^\pm$ and $B_1^\pm$ levels and the $A_2^\pm$ and $B_2^\pm$ levels by bifurcation tunneling are not considered here; they were discussed in ref 3.

At the end of this section we list some technical details. The intramolecular Jacobi coordinates $\mathbf{q}_A$ and $\mathbf{q}_B$ were r_{HH}, the H−H distance; r_{OM}, the distance from the O nucleus to the midpoint M between the two H atoms; and θ, the angle between the vectors $\mathbf{r}_{HH}$ and $\mathbf{r}_{OM}$. The DVR grids used in the calculations of the monomer vibrational states consisted of seven equidistant points in both r_{HH} and r_{OM}, and 29 Legendre quadrature points in θ. In the 6d calculations of the intermolecular VRT states on the adiabatic potentials, we used an analytic basis of Wigner D-functions on the monomers A and B with maximum values of j_A and j_B equal to 11 for $(H_2O)_2$ and 12 for $(D_2O)_2$. The corresponding DVR grids consisted of 14 and 15 Legendre quadrature points in the two polar angles for $(H_2O)_2$ and $(D_2O)_2$, respectively, with 24 and 30 equidistant points in the three azimuthal angles. The primitive radial basis contained 30 sine functions, and the corresponding DVR grid had 33 points in the range $4 \leq R \leq 10\ a_0$. The potential-optimized contraction scheme according to Harris et al.[30] was used with nine values of R.

III. Discussion of the Results

Before discussing the results for the dimer, let us briefly consider the H_2O and D_2O monomer properties given in Table 1. These properties, used in our 6d rigid monomer calculations, were obtained from the HBB potential by choosing a sufficiently large value of the intermolecular distance. The equilibrium value of 0.9615 Å for the OH bond length is somewhat larger than the best available value of 0.9589 Å.[31] Accordingly, the vibrationally averaged values of r_{OH} and r_{OD} are slightly too large also and, as one will see below, the OH stretch frequency is too small by about 18 cm^{-1}. The HOH angle of 104.20° is very close to the best calculated value of 104.16°,[31] and the HOH bend frequency (see below) agrees well with experimental data. Since these features were derived from the 12d potential HBB used for the calculation of the dimer VRT states with flexible monomers, and we wish to compare with 6d rigid monomer results on the same potential surface, we have not tried to correct for these small differences. We could have extracted only the intermolecular part of the HBB potential and replaced its intramolecular contribution by a very accurately known water monomer potential,[32,33] but the intramolecular contribution is not explicitly given and we wanted to use the HBB potential as it was calculated and fitted.[5,6]

III.A. Intermolecular VRT States. The dimer VRT levels of $(H_2O)_2$ and $(D_2O)_2$ computed in 12d (actually 6 + 6d) calculations from the HBB potential are given in Tables 2 and 3, respectively. These tables also contain the corresponding results from 6d rigid monomer calculations with the monomers fixed at their equilibrium geometry or at their ground state vibrationally averaged geometry. The latter was chosen because it has been demonstrated[34] that the choice of vibrationally averaged geometries in rigid monomer calculations gives results that, in general, are closer to the results from full flexible monomer calculations than the results obtained when the monomers are frozen at their equilibrium geometries. In ref 34 this was numerically illustrated on a non-hydrogen-bonded complex, Ar−HF. One will see below that it also holds for a strongly hydrogen-bonded complex. Moreover, the accurate CC-pol[1,4] and CC-pol-8s[3] rigid monomer potentials for water dimer are based on the vibrationally averaged monomer geometry and we would like to estimate the additional effects that will be obtained when these potentials are extended with monomer flexibility.

First we consider the dissociation energy D_0. The value of D_0 from 12d calculations is larger than the value from 6d calculations with the monomers at their equilibrium geometry by 24.0 cm^{-1} for $(H_2O)_2$ and by 23.4 cm^{-1} for $(D_2O)_2$. This difference is caused by the lowering of the monomer zero point vibrational energies in the dimer. In section III.B we show that for some of the monomer modes there is an upward shift of the fundamental frequencies, but that indeed the downward shifts, especially for the donor bound OH stretch mode, are more dominant. The values of D_0 for $(H_2O)_2$ and $(D_2O)_2$ from the 12d (actually 6 + 6d) calculations, 1022 and 1161 cm^{-1}, may be compared with the values of 1040 and 1169 cm^{-1} from 12d diffusional quantum Monte Carlo calculations.[6] In the 6d calculations with monomers frozen at their vibrationally averaged geometry, the intermolecular potential used is given relative to the energy of the monomers at this geometry, which is higher than the monomer equilibrium energy by 126.6 cm^{-1} per monomer. The well depth D_e in this intermolecular potential is 1709 cm^{-1} for $(H_2O)_2$ and 1694 cm^{-1} for $(D_2O)_2$, while it is 1657 cm^{-1} for the potential with the monomers at their equilibrium geometry and 1666 cm^{-1} when the monomers are relaxed. These differences in the D_e values explain the corresponding differences in the D_0 values. The experimental values of D_0 for $(H_2O)_2$ and $(D_2O)_2$ have large uncertainties. We should mention that the value of D_e for the HBB potential, 19.9 kJ/mol, is smaller than the best calculated value[31] of 20.99 kJ/mol by 91 cm^{-1}. We expect, therefore, that our values of D_0 are too low also.

The dimer VRT levels are characterized by the same quantities that have been extracted from the experimental high-resolution spectra: the dimer rotational constants A and $B + C$, the band origins o_1 and o_2 of the intermolecular vibrations of different PI symmetries for $K = 0$ and $K = 1$, and the level splittings $a(K)$, i_1, and i_2 caused by acceptor tunneling and donor−acceptor interchange tunneling. The A' and A'' labels of the intermolecular vibrations denote their even or odd symmetry under reflection in the symmetry plane of the equilibrium structure with point group C_s.

TABLE 2: Properties of $(H_2O)_2$ (in cm^{-1}) Calculated with the HBB Potential in 12d Calculations, Compared with Results from 6d Rigid Monomer Calculations and Experimental Data From Refs 20, 21, and 25−27[a]

			6d (equilib)	6d (vib av)	12d	experiment
dissociation energy						
D_0			997.7	1029.6	1021.7	
rotational constants						
A			7.46	7.54	7.73	7.44/7.59
$B + C$			0.4016	0.4070	0.3998	0.4112
acceptor tunneling splittings (ground state)						
$a(K=0)$			13.31	12.22	10.83	
$a(K=1)$			3.20	2.93	2.37	
sum			16.52	15.15	13.20	13.92
interchange tunneling splittings (ground state)						
	$K = 0$	i_1	0.745	0.785	0.717	0.752
		i_2	0.641	0.681	0.647	0.651
	$K = 1$	i_1	0.691	0.740	0.677	0.705
		i_2	0.519	0.555	0.522	0.541
vibrational band origins						
ground state (A')	$K = 0$	o_1	0	0	0	0
		o_2	13.31	12.22	10.83	11.18[b]
	$K = 1$	o_1	15.72	15.12	14.33	14.39
		o_2	12.52	12.20	11.95	11.66
donor torsion (A'')	$K = 0$	o_1	115.64	115.07	116.03	
		o_2	60.64	62.22	66.15	64.52
	$K = 1$	o_1	85.74	86.40	89.52	87.75
		o_2	92.47	92.23	93.49	
acceptor wag (A')	$K = 0$	o_1	106.82	105.81	103.52	107.93
		o_2	106.08	106.03	103.26	108.89
	$K = 1$	o_1	106.77	107.29	106.19	109.98
		o_2	121.07	121.12	119.79	123.56
acceptor twist (A'')	$K = 0$	o_1	130.23	128.86	128.29	
		o_2	116.19	117.38	118.60	120.19
	$K = 1$	o_1	141.10	141.19	140.19	
		o_2	135.04	135.37	134.39	
donor torsion overtone (A')	$K = 0$	o_1	126.75	127.98	130.46	
		o_2	146.86	147.91	145.83	153.62
	$K = 1$	o_1	148.94	150.70	149.51	
		o_2	146.32	148.34	147.49	
stretch (A')	$K = 0$	o_1	139.44	142.17	141.78	
		o_2	183.91	183.97	182.30	

[a] In the rigid monomer model we used the equilibrium geometry of the free monomers or the ground state vibrationally averaged geometry; see Table 1. All symbols are defined in the text. [b] Since the experimental values of o_2 were given relative to the ground state value of o_2, we added the estimated ground state acceptor splitting $a(K=0) = 11.18$) cm^{-1} [11] to all experimental values.

Note that the 6d results for fixed monomers in their equilibrium geometry differ slightly from those obtained for the same HBB potential in ref 6 because we now used the method of Leforestier et al., whereas in ref 6 they were computed by the method of Groenenboom et al.[11] Although in both methods the basis set, grid size, etc., were converged, some small differences remain that result mostly from the truncation of the spherical expansion of the potential in the method of Groenenboom et al.; cf. ref 3. Note also that we now included off-diagonal Coriolis coupling, while it was omitted in ref 6. As established in ref 3, the inclusion of off-diagonal Coriolis coupling decreases the $B + C$ values by about 0.01 cm^{-1} for $(H_2O)_2$ and by almost 0.02 cm^{-1} for $(D_2O)_2$.

When comparing the 6d and 12d results in Tables 2 and 3, we notice that most quantities do not change much. In other words, most of the properties considered in the comparison with experimental spectroscopic data are not very sensitive to the rigid monomer approximation. The only really significant change occurs for the acceptor tunneling splitting $a(K)$, which decreases by 25% for $(H_2O)_2$ and by 38% for $(D_2O)_2$ when the monomers become flexible. This finding is very satisfactory as it was concluded in ref 6 that all properties calculated from the HBB potential in 6d calculations agreed well with the experimental data, except for the acceptor tunneling splitting which was 19% too high for $(H_2O)_2$ and 31% too high for $(D_2O)_2$. The acceptor tunneling splitting obtained from the calculations with flexible monomers agrees well with experiment; the remaining errors are only 5% for both isotopologues. The already good agreement of the other properties stays intact. Another significant change seems to occur for the ground state origins o_1 and o_2 for $K = 0$ and $K = 1$, but these are in fact mostly determined by the ground state acceptor splittings $a(K)$.

When looking in more detail, we see changes of a few percent, at most, in the other quantities as well, but they are less systematic. A relatively large change of about 9% occurs, for example, in the lower origin o_2 of the donor torsion mode. One should realize, however, that this quantity is partly determined by the acceptor splitting for this mode, which is much larger than for the ground state. Also for this property the agreement with experiment improves when the monomers are made flexible. For other quantities, where the changes are still smaller and less systematic, the agreement with the experimental data is not always improved. The remaining discrepancies are quite small, however.

It is interesting to consider the 6d model with the monomers frozen at their vibrationally averaged geometry, especially for the quantity for which the difference between the 6d and 12d results is significant: the acceptor splitting. As expected from

TABLE 3: Properties of $(D_2O)_2$ (in cm^{-1}) Calculated with the HBB Potential in 12d Calculations, Compared with the Results from 6d Rigid Monomer Calculations and Experimental Data from Refs 19, 22−24, 26, and 27[a]

			6d (equilib)	6d (vib av)	12d	experiment
dissociation energy						
D_0			1137.6	1163.9	1161.0	
rotational constants						
A			4.19	4.17	4.16	4.17
$B + C$			0.3533	0.3540	0.3547	0.3622
acceptor tunneling splittings (ground state)						
$a(K=0)$			2.37	2.06	1.74	1.77
$a(K=1)$			0.76	0.65	0.52	0.62
sum			3.13	2.71	2.26	2.39
interchange tunneling splittings (ground state)						
	$K = 0$	i_1	0.0399	0.0419	0.0386	0.0391
		i_2	0.0367	0.0387	0.0364	0.0361
	$K = 1$	i_1	0.0364	0.0386	0.0358	0.0359
		i_2	0.0331	0.0351	0.0329	0.0331
vibrational band origins						
ground state (A')	$K = 0$	o_1	0	0	0	0
		o_2	2.37	2.06	1.74	1.77[b]
	$K = 1$	o_1	5.75	5.53	5.29	5.36
		o_2	5.00	4.88	4.77	4.74
donor torsion (A'')	$K = 0$	o_1	75.15	75.30	76.67	75.38
		o_2	55.63	57.55	60.50	59.59
	$K = 1$	o_1	64.98	66.53	69.20	68.27
		o_2	69.21	70.37	72.21	71.81
acceptor wag (A')	$K = 0$	o_1	78.82	79.67	78.82	82.64
		o_2	80.30	81.44	80.15	84.40
	$K = 1$	o_1	81.76	82.91	82.13	85.57
		o_2	86.14	86.93	85.73	89.56
acceptor twist (A'')	$K = 0$	o_1	90.00	90.29	90.28	92.91
		o_2	87.17	87.94	88.39	90.37
	$K = 1$	o_1	95.86	96.42	96.15	
		o_2	93.41	93.97	94.12	
donor torsion overtone (A')	$K = 0$	o_1	98.59	101.02	103.74	104.24
		o_2	129.58	130.20	130.02	
	$K = 1$	o_1	122.52	122.85	124.27	
		o_2	114.23	115.15	117.39	
donor torsion + acceptor wag (A'')	$K = 0$	o_1	129.18	131.36	132.60	
		o_2	135.96	136.28	136.91	
stretch (A')	$K = 0$	o_1	130.99	133.23	133.50	
		o_2	141.94	142.83	142.73	

[a] In the rigid monomer model we used the equilibrium geometry of the free monomers or the ground state vibrationally averaged geometry; see Table 1. All symbols are defined in the text. [b] Since the experimental values of o_2 were given relative to the ground state value of o_2, we added the experimental estimate[23] for the ground state acceptor splitting $a(K=0) = 53$ GHz $= 1.7679$ cm^{-1} to all experimental values.

the analysis in ref 34, use of the vibrationally averaged geometry for the monomers indeed gives results that are closer to the full 12d results than the 6d results for monomers at their equilibrium geometry. The deviations of the acceptor splitting from the 12d model by 25% and 38% [for $(H_2O)_2$ and $(D_2O)_2$, respectively] for the equilibrium geometry 6d model are reduced to 15% and 20% for the 6d model with monomers at the vibrationally averaged geometry. This finding is useful also in view of the results obtained from the CC-pol-8s potential,[3] in which the monomers were kept at their vibrationally averaged geometry. The agreement with the experimental spectroscopic data for $(H_2O)_2$ and $(D_2O)_2$ in 6d calculations with this potential[3] was even better than for the HBB potential.[6] Again, the only quantity that deviated significantly from the measurements was the acceptor tunneling splitting. However, the overestimate of this quantity with respect to the experimental data was only 10% for $(H_2O)_2$ and 12% for $(D_2O)_2$, considerably smaller than for the 6d model with monomers at their equilibrium geometry. From the present results one can conclude that this smaller overestimate will probably be corrected for when the monomers are made flexible.

The 6d rigid monomer results in ref 6 showed a remarkably good agreement of the end-over-end rotational constant $B + C$ with the experimental data. Here, we find that the effect of monomer flexibility on $B + C$ is very small, but we confirm the conclusion in ref 3 that the full inclusion of Coriolis coupling leads to a significant change in the value of $B + C$. It should be kept in mind, however, that this change has only become significant because of the high level of agreement with experiment that we have now reached. Therefore, we conclude that the excellent agreement with the experimental values of $B + C$ in ref 6 was partly fortuitous. If Coriolis coupling is fully taken into account, the $B + C$ values become slightly too small. This is in line with the dimer binding energy D_e being somewhat underestimated by the HBB potential and the equilibrium distance R_e being slightly too large.

III.B. Frequency Shifts of the Monomer Vibrations. The vibrational frequencies of free H_2O calculated with the HBB potential are 1595.39, 3638.49, and 3738.20 cm^{-1} for the HOH bend, the symmetric OH stretch, and the asymmetric OH stretch, respectively. The experimental values are 1594.59, 3656.65, and 3755.79 cm^{-1}.[35] Thus we see that the bend frequency agrees quite well with experiment, but that the OH stretch frequencies are too low by about 18 cm^{-1}. Water monomer potentials are available[32,33] that produce these fundamental frequencies in much better agreement with experiment, but we are interested in the

TABLE 4: Frequency Shifts of the Monomer Vibrations in $(H_2O)_2$ with Respect to the Calculated Free Monomer Frequencies, Obtained from the G_{16} and G_8 Models Explained in the Text[a]

	transition $J = 0 \rightarrow 1$		frequency shift (cm^{-1})	
	symmetry	$K \rightarrow K'$	G_{16} model	G_8 model
donor bend	$A_1^+ \rightarrow A_1^-$	$0 \rightarrow 0$	10.51	10.09
donor bound OH stretch	$A_1^+ \rightarrow A_1^-$	$0 \rightarrow 0$	−41.16	−41.42
donor free OH stretch	$A_1^+ \rightarrow A_1^-$	$0 \rightarrow 0$	−0.70	−1.01
acceptor bend	$A_1^+ \rightarrow A_1^-$	$0 \rightarrow 0$	3.47	3.08
acceptor sym stretch	$A_1^+ \rightarrow A_1^-$	$0 \rightarrow 0$	0.69	0.26
acceptor asym stretch	$A_2^- \rightarrow A_1^+$	$0 \rightarrow 1$	9.47	9.86

[a] The shifts of the donor bound OH and free OH stretch modes are given relative to the symmetric and asymmetric stretch frequencies of free H_2O, respectively.

frequency shifts in the water dimer and we expect these to be fairly accurate, since the discrepancy of the monomer OH stretch frequencies is only 0.5%.

In section II we explained that the adiabatic 6 + 6d approximation does not apply directly, as in the ground state, if one of the monomers is vibrationally excited. We proposed two approximate 6 + 6d adiabatic models that will probably give a good approximation to the “two-state” nonadiabatic model that seems appropriate for the vibrationally excited states. In the first model it is assumed that the vibrational excitation hops from one monomer to the other, simultaneously with the donor−acceptor interchange that occurs by quantum mechanical tunneling. In other words, it is always the donor or the acceptor that is excited, irrespective of which monomer fulfills this role. The adiabatic dimer 6d potential then has the full G_{16} symmetry, and we call this the G_{16} model. In the second model, on the contrary, the excitation is assumed to stay on a given monomer, A or B, independently of whether this monomer is the donor or the acceptor. The adiabatic approximation then yields a 6d dimer potential that is slightly asymmetric with respect to the interchange P_{AB} of the two monomers. Hence, the PI symmetry of the dimer Hamiltonian is reduced from G_{16} to G_8 and we call this the G_8 model. In reality the monomer vibrational excitation hops from one monomer to the other upon donor−acceptor interchange, but the interchange is much slower in the excited state than it is in the vibrational ground state.[29] Therefore it may be expected that a comparison of the results of the G_{16} and G_8 models for the vibrational frequency shifts will give us a good indication of the accuracy of the shifts calculated by either model.

The frequency shift of each monomer vibration was obtained by subtracting the energy of the dimer ground state level computed on the lowest adiabatic 6d potential (with both monomers in their ground state) from the dimer ground state level computed on the excited adiabatic potential obtained for the corresponding monomer vibration. In the G_8 model one can choose which monomer is excited, A or B; the results should be the same. We tried both and found that the calculated frequency shifts are indeed the same. Since a given monomer excited state gives rise to two dimer excitations in the G_8 model, one on the donor and one on the acceptor, we had to consider the lowest two eigenvalues from each calculation. By comparison with the shifts obtained from the G_{16} model, it is immediately clear how to assign these two eigenvalues. A comparison of the results from the G_{16} and G_8 models is given in Table 4. These results were computed with a somewhat smaller dimer basis than used in the final calculations: internal rotor basis functions with a maximum j_A, j_B of 10 instead of 11 and a maximum k_A, k_B of 8 instead of 11. It is clear from Table 4 that the shifts from the two models are very similar. Each irrep of G_8 is induced to two irreps of G_{16} through the interchange operation P_{AB}. For example, the G_8 irrep A_1^+ yields the G_{16} irreps A_1^+ and B_1^+, A_2^- yields A_2^- and B_2^-, etc. The small differences between the shifts calculated by the two models are about half the size of the ground state interchange tunneling splitting between the B_1^+ and A_1^+ levels in G_{16}; cf. Table 2. All further calculations were made with the G_{16} model in the full basis.

In order to explain the symmetry of the intramolecular vibrations and the appropriate selection rules, we start with the observation that the water dimer in its equilibrium geometry has point group symmetry C_s. The donor monomer lies in the plane of reflection symmetry, and its symmetric and asymmetric OH stretch modes become localized. The localized modes are the donor bound OH and free OH stretch modes in the dimer; these are both of A' symmetry. The two hydrogen atoms of the acceptor monomer are not in the symmetry plane, but are interchanged by the reflection symmetry operator. The acceptor symmetric and asymmetric OH stretch modes can still be distinguished by their respective A' and A'' symmetries in the dimer. The HOH bend modes of both monomers have A' symmetry in the dimer. In more global terms, considering the eight equivalent equilibrium geometries connected by the operations of the PI group G_{16}, the intramolecular vibrations are all of A_1^+ symmetry, except for the acceptor asymmetric OH stretch, which is of A_2^+ symmetry. Actually, if the acceptor asymmetric stretch mode were adapted to the full G_{16} symmetry, one would obtain A_2^+ and B_2^+ symmetry components, but we already explained above that the adiabatic separation of the monomer vibrational coordinates and the intermolecular coordinates does not apply to the excited intramolecular vibrations. Hence, it is reasonable to apply the selection rules of the subgroup G_8, as it was done in the interpretation of the high-resolution spectra in ref 29. In G_8 symmetry the G_{16} irreps A_2^+ and B_2^+ become equivalent. If one (or more) of the intermolecular (tunneling or vibrational) modes is excited, their symmetries should be combined with those of the intramolecular modes, as well as with those of the overall rotation functions of the dimer. The transition dipole moment operator has A_1^- symmetry, which tells us that transitions are allowed between irreps of the same type, except for the “±” labels that must be reversed. This is a strict selection rule. In addition, there are approximate selection rules based on the separability between the intra- and intermolecular vibrations. Furthermore, there may be approximate selection rules if the vibrations have small amplitudes and can be well separated from the overall rotations. This does not apply to the intermolecular vibrations,[36] but it holds for the intramolecular modes which obey the selection rules of the point group C_s. All fundamental intramolecular modes are allowed in the water dimer, as they are in the free monomers.

Table 5 lists the calculated frequency shifts of the monomer modes in the dimer with no intermolecular vibrations excited. The different symmetries indicated refer to the tunneling levels of the dimer vibrational ground state. It should be kept in mind that for $(H_2O)_2$ the $A_1^\pm$, $B_1^\pm$, $A_2^\pm$, and $B_2^\pm$ levels have nuclear spin statistical weights 1, 0, 3, and 6, respectively. In addition, there are transitions between the levels of $E^\pm$ symmetry with weight 3 which are not shown; their shifts are intermediate between those involving the $A_1^\pm$, $A_2^\pm$ and $B_1^\pm$, $B_2^\pm$ levels. The small differences between the shifts of the transitions involving the ground state A_1^+ and B_1^+ levels and the A_2^- and B_2^- levels are due to the interchange tunneling splittings between these levels. The

TABLE 5: Calculated Frequency Shifts of the Monomer Vibrations in $(H_2O)_2$ for $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 0$ Dimer Transitions[a]

		frequency shift (cm^{-1})		
intramolecular mode	symmetry	$K = 0 \rightarrow 0$	$K = 0 \rightarrow 1$	$K = 1 \rightarrow 0$
donor bend	$A_1^+ \rightarrow A_1^-$	10.526	24.494	−6.008
	$B_1^+ \rightarrow B_1^-$	8.917	22.932	−4.439
	$A_2^- \rightarrow A_2^+$	10.130	11.215	6.998
	$B_2^- \rightarrow B_2^+$	8.686	9.914	8.317
donor bound OH stretch	$A_1^+ \rightarrow A_1^-$	−41.201	−27.864	−57.351
	$B_1^+ \rightarrow B_1^-$	−42.425	−29.064	−56.167
	$A_2^- \rightarrow A_2^+$	−42.583	−40.880	−45.388
	$B_2^- \rightarrow B_2^+$	−43.699	−41.903	−44.397
donor free OH stretch	$A_1^+ \rightarrow A_1^-$	−0.999	12.745	−17.228
	$B_1^+ \rightarrow B_1^-$	−2.306	11.475	−15.961
	$A_2^- \rightarrow A_2^+$	−1.965	−0.362	−4.855
	$B_2^- \rightarrow B_2^+$	−3.170	−1.455	−3.774
acceptor bend	$A_1^+ \rightarrow A_1^-$	3.464	17.597	−12.892
	$B_1^+ \rightarrow B_1^-$	2.033	16.211	−11.500
	$A_2^- \rightarrow A_2^+$	3.424	4.268	0.447
	$B_2^- \rightarrow B_2^+$	2.134	3.097	1.612
acceptor sym stretch	$A_1^+ \rightarrow A_1^-$	0.686	14.424	−15.788
	$B_1^+ \rightarrow B_1^-$	−0.864	12.916	−14.278
	$A_2^- \rightarrow A_2^+$	−0.006	1.297	−3.090
	$B_2^- \rightarrow B_2^+$	−1.403	0.042	−1.818
acceptor asym stretch	$A_1^+ \rightarrow A_2^-$		18.533	−5.604
	$B_1^+ \rightarrow B_2^-$		18.403	−5.333
	$A_2^- \rightarrow A_1^+$		9.712	1.802
	$B_2^- \rightarrow B_1^+$		9.827	1.863

[a] The symmetries indicated pertain to the intermolecular tunneling levels that produce allowed transitions in combination with the intramolecular mode. For the $K = 1 \rightarrow 0$ transitions the symmetries of the initial and final states are reversed.

energy gap between the A_1^+, B_1^+ levels and the A_2^-, B_2^- levels, caused by acceptor tunneling, is much larger. This gap is not visible in the frequency shifts of the $K = 0 \rightarrow 0$ transitions because these transitions are from the lower to the lower or from the upper to the upper acceptor tunneling levels. Such transitions are not allowed for the acceptor asymmetric stretch mode, due to the A_2^+ symmetry of this mode. The acceptor tunneling splitting is considerably smaller for $K = 1$ than for $K = 0$ and the order of the tunneling levels is reversed; hence, the $K = 0 \rightarrow 1$ and $K = 1 \rightarrow 0$ transitions have rather different frequency shifts for transitions involving the A_1^+, B_1^+ levels and the A_2^-, B_2^- levels.

The accuracy of the experimental data available for the intramolecular modes in the water dimer is quite different for the different modes. For most of the modes it is not possible to give a detailed comparison of the different allowed transitions calculated and listed in Table 5 with the measured spectra. The most direct comparison can be made with the acceptor asymmetric stretch spectrum that was measured in high resolution by Huang and Miller.[29] We will therefore discuss this mode first and then consider the acceptor symmetric stretch mode, next the donor bound and free OH stretch modes, and, finally, the two HOH bend modes.

The high-resolution spectrum of the acceptor asymmetric stretch mode in ref 29 contains three different bands corresponding to the $K = 1 \rightarrow 0$, $K = 0 \rightarrow 1$, and $K = 1 \rightarrow 2$ transitions, and many rotational lines were assigned and fitted. The frequencies obtained for the $K = 1 \rightarrow 0$ and $K = 0 \rightarrow 1$ transitions of $A_2^- \rightarrow A_2^+$ symmetry are 3738.4 and 3752.6 cm^{-1}, respectively, which corresponds to shifts of −17.4 and −3.2 cm^{-1} with respect to the H_2O monomer asymmetric stretch frequency. Our calculated values for these shifts are −5.5 and 9.8 cm^{-1}. The same mode was observed by Kuyanov and Vilesov[37] for the water dimer in He nanodroplets in a molecular beam setup. These authors reported two peaks with frequency shifts of −3.4 and 4.4 cm^{-1}. These are probably not the $K = 1 \rightarrow 0$ and $K = 0 \rightarrow 1$ transitions observed by Huang and Miller, since the energy gap between them is smaller by nearly a factor of 2 and it is believed that the $K = 1$ levels are not populated at the temperature of 0.4 K of the He droplets. Our calculations show that they are probably due to the A_2^-, B_2^- and A_1^+, B_1^+ tunneling components of the $K = 0 \rightarrow 1$ transition. We obtain shifts of 9.8 and 18.5 cm^{-1} for these components. All these data lead to the conclusion that the energy gaps between the various bands observed for this mode are correctly reproduced by our calculations but that our frequencies are too high by 12−14 cm^{-1}.

Huang and Miller[29] also reported a partially resolved band for the acceptor symmetric stretch mode, but this band was later[38,39] assigned to the donor bound OH stretch. Furthermore, they reported bands near 3530 and 3730 cm^{-1}, but size-selective measurements described in refs 38 and 39 have shown that these bands actually belong to the water trimer spectrum.

The frequency of the acceptor symmetric stretch mode was determined in matrix spectra.[40,41] Extrapolation of the spectra from different matrices yields a frequency between 3655 and 3660 cm^{-1}, i.e., a shift between −2 and 3 cm^{-1}. In the He droplet spectra[37] this band was observed at 3654.4 cm^{-1}, which amounts to a shift of −2.2 cm^{-1}. We computed a shift of about −1 cm^{-1} for the $K = 0 \rightarrow 0$ transitions.

The donor bound and free OH stretch modes were observed in lower resolution by Huisken et al.[38,39] A narrow peak at 3601 cm^{-1}, shifted by −56 cm^{-1} with respect to the monomer symmetric stretch mode, was assigned to the bound OH stretch. Apart from the reassignment, this agrees well with the (incomplete) high-resolution data for this band in ref 29. Absorption intensity at 3735 cm^{-1}, obtained by subtraction of two spectra, was ascribed to the donor free OH stretch; this amounts to a shift of −21 cm^{-1} with respect to the monomer asymmetric stretch mode. It is not at all clear which transitions tabulated in Table 5 contribute to these bands. The He droplet spectra of the water dimer[37] give a shift of −59.0 cm^{-1} for the donor bound OH stretch mode and two, not completely separated peaks with shifts of −25.3 and −26.3 cm^{-1} for the donor free OH stretch. If we assume that the intensity is dominated by the $K = 0 \rightarrow 0$ transitions, we find shifts of −43 and −2 cm^{-1} for the donor bound and free OH modes, respectively, but there is a large spread in the frequencies if $K = 0 \rightarrow 1$ and $K = 1 \rightarrow 0$ transitions are also involved. It seems that our calculations yield frequencies that are considerably too high, however, just as for the acceptor asymmetric stretch mode. Note that we calculated frequency shifts, not absolute frequencies, so that it does not play a role that the HBB potential yields too-low OH stretch frequencies of the free monomers.

Interesting additional remarks can be made regarding the He nanodroplet spectra,[37] which show bands for all four OH stretch modes. Only for the acceptor asymmetric stretch mode a large splitting (7.8 cm^{-1}) was measured, while for the other modes only a small splitting (1.0 cm^{-1} for the donor free OH stretch) or no splitting was observed. A similar splitting of the acceptor asymmetric stretch band was measured and explained by interchange tunneling[23] for $(D_2O)_2$. It should be kept in mind that the acceptor asymmetric stretch mode is the only one for which $K = 0 \rightarrow 0$ transitions are forbidden. As explained above, we believe that the peaks in the He droplet spectra assigned to the acceptor asymmetric stretch mode belong to a $K = 0 \rightarrow 1$

band; our calculations predict an acceptor tunneling splitting of the correct size for this band. As also explained above, we predict much smaller tunneling splittings for $K = 0 \rightarrow 0$ transitions. This implies that the absorption intensity of all bands in the He droplet spectra except for the acceptor asymmetric stretch band is probably dominated by $K = 0 \rightarrow 0$ transitions.

The donor and acceptor bend modes were observed by Paul et al. in cavity ring-down spectra.[42] A peak at 1600.6 cm^{-1}, i.e, a blue shift of 6 cm^{-1}, was assigned to the acceptor bend, probably involving a parallel $\Delta K = 0$ transition. Our calculations produce a shift of about 3 cm^{-1} for the $K = 0 \rightarrow 0$ transitions in the acceptor bend mode. From three peaks at 1613.8, 1614.7, and 1628.6 cm^{-1} in the spectrum[42] it was estimated that the donor bend frequency is 1615−1620 cm^{-1}, a blue shift of more than 20 cm^{-1} with respect to the monomer bend. According to ref 42 these bands are dominated by perpendicular $\Delta K = \pm 1$ transitions. Our shifts calculated for $K = 0 \rightarrow 0$ transitions in the donor bend mode are about 10 cm^{-1}; for the $K = 0 \rightarrow 1$ and $K = 1 \rightarrow 0$ transitions they vary from −6 to 25 cm^{-1}. It is not clear which components dominate the intensities of these bands.

IV. Summary and Conclusions

The 12d HBB potential for a water dimer with flexible monomers obtained from ab initio calculations[5,6] was used in accurate calculations of the dimer VRT levels involving the intermolecular rovibrational and tunneling states as well as the intramolecular vibrations. The intermolecular VRT levels were computed at three different levels of accuracy. At the highest level we used a 6 + 6d model in which adiabatic intermolecular potentials were obtained from calculations of the monomer vibrational eigenvalues at each dimer geometric grid point, in total for about 10^7 dimer geometries. The results from this model were compared with 6d calculations in which the monomer geometries were frozen either at the equilibrium geometry of the free monomers or at their ground state vibrationally averaged geometry. It was found that the results from the 6 + 6d model agree well with the large amount of detailed experimental data available from high-resolution spectroscopy. For most of the quantities extracted from the spectra, the results of the two 6d rigid monomer models are also in good agreement with experiment and do not significantly differ from the 6 + 6d results. An exception is the relatively large level splitting due to acceptor tunneling. The 6d model with monomers frozen at their equilibrium geometry overestimates this splitting by 19% for $(H_2O)_2$ and by 31% for $(D_2O)_2$. The 6d model with monomers at their vibrationally averaged geometry performs considerably better, and the full 6 + 6d results agree well with the measured tunneling splitting.

For the excited intramolecular vibrations we tested two 6 + 6d models: one in which the excitation was assumed to hop from one monomer to the other one, depending on which monomer is the donor or the acceptor in the hydrogen bond, and one in which the monomer excitation was assumed to remain localized on a given monomer irrespective of the dimer geometry. These models cannot be used to compute the excited state donor−acceptor interchange tunneling splitting, which is considerably smaller than the corresponding splitting in the ground state. The first model yields fully symmetric adiabatic intermolecular potentials for the excited states, but produces too-large interchange splittings, nearly equal to the splitting in the ground state. The second model yields adiabatic intermolecular potentials in which the monomers are not equivalent and underestimates the excited state interchange tunneling splitting. Our tests show, however, that the frequencies of the intramolecular vibrations are almost the same for the two models. In most calculations of the frequency shifts of the intramolecular modes with respect to the free monomer vibrations we used the first model.

It is not easy to fully evaluate the quality of the calculated frequency shifts by comparison with the experimental data. High-resolution, rotationally and tunneling level resolved and assigned, spectra are available only for the acceptor asymmetric stretch mode. The calculations show that there are considerable variations in the frequency of each intramolecular mode for transitions involving different tunneling levels and different values of the rotational quantum number K. Except for the acceptor asymmetric stretch bands measured in high resolution, it is not clear how much the different transitions contribute to the (unresolved) peaks in the experimental spectra. Given the very good agreement of the results for the intermolecular modes with a large amount of experimental data, we find the results for the intramolecular modes somewhat disappointing. The large red shift of the donor bound OH stretch mode is correctly predicted, but the value calculated for this red shift is too small by more than 20%. Also in the smaller shifts of the other modes we find relatively large errors. Similar errors were found in studies of the intramolecular modes in the water dimer with a "flexibilized" SAPT-5s potential[8] and with an empirical flexible potential fitted to experimental spectroscopic data.[12,43] On the other hand, it is satisfactory that our detailed calculations including all ground and excited state tunneling levels provide an explanation for the substantial frequency splitting between the two acceptor asymmetric stretch peaks observed in He nanodroplet spectra,[37] as well as for the fact that the other bands in these spectra show much smaller or no splittings.

Acknowledgment. We thank Xinchuan Huang, Bastiaan J. Braams, and Joel M. Bowman for providing us with the code of the HBB potential. We are grateful to Andrey Vilesov for valuable discussions and for making available his unpublished results. C.L. thanks the CNRS for a CNRS/USA grant, and R.v.H. thanks the Nederlandse Organisatie voor Wetenschappelijk Onderzoek NWO, gebied Chemische Wetenschappen, for a VENI grant.

References and Notes

(1) Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; van der Avoird, A. *Science* **2007**, *315*, 1249–1252.
(2) Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; van der Avoird, A. *J. Chem. Phys.* **2008**, *128*, 094314.
(3) Cencek, W.; Szalewicz, K.; Leforestier, C.; van Harrevelt, R.; van der Avoird, A. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4716.
(4) Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; van der Avoird, A. *J. Chem. Phys.* **2008**, *128*, 094313.
(5) Huang, X.; Braams, B. J.; Bowman, J. M. *J. Phys. Chem. A* **2006**, *110*, 445–451.
(6) Huang, X.; Braams, B. J.; Bowman, J. M.; Kelly, R. E. A.; Tennyson, J.; Groenenboom, G. C.; van der Avoird, A. *J. Chem. Phys.* **2008**, *128*, 034312.
(7) Fanourgakis, G. S.; Xantheas, S. S. *J. Phys. Chem. A* **2006**, *110*, 4100–4106.
(8) Szalewicz, K.; Murdachaew, G.; Bukowski, R.; Akin-Ojo, O.; Leforestier, C. In *Lecture Series on Computer and Computational Science: ICCMSE 2006*; Maroulis, G., Simos, T., Eds.; Brill Academic Publishers: Leiden, 2006; Vol. 6, p 482.
(9) Groenenboom, G. C.; Mas, E. M.; Bukowski, R.; Szalewicz, K.; Wormer, P. E. S.; van der Avoird, A. *Phys. Rev. Lett.* **2000**, *84*, 4072–4075.
(10) Mas, E. M.; Bukowski, R.; Szalewicz, K.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A. *J. Chem. Phys.* **2000**, *113*, 6687–6701.
(11) Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A.; Mas, E. M.; Bukowski, R.; Szalewicz, K. *J. Chem. Phys.* **2000**, *113*, 6702–6715.

(12) Leforestier, C.; Gatti, F.; Fellers, R.; Saykally, R. *J. Chem. Phys.* **2002**, *117*, 8710–8722.

(13) Bunker, P. R.; Jensen, P. *Molecular Symmetry and Spectroscopy*, 2nd ed.; NRC Research Press: Ottawa, 1998.

(14) Leforestier, C.; Braly, L. B.; Liu, K.; Elrod, M. J.; Saykally, R. J. *J. Chem. Phys.* **1997**, *106*, 8527.

(15) Fellers, R. S.; Leforestier, C.; Braly, L. B.; Brown, M. G.; Saykally, R. J. *Science* **1999**, *284*, 945.

(16) Fellers, R. S.; Braly, L. B.; Saykally, R. J.; Leforestier, C. *J. Chem. Phys.* **1999**, *110*, 6306.

(17) Chen, H.; Liu, S.; Light, J. C. *J. Chem. Phys.* **1999**, *110*, 168.

(18) Goldman, N.; Fellers, R.; Brown, M.; Braly, L.; Keoshian, C.; Leforestier, C.; Saykally, R. *J. Chem. Phys.* **2002**, *116*, 10148–10163.

(19) Zwart, E.; ter Meulen, J. J.; Meerts, W. L. *Chem. Phys. Lett.* **1990**, *173*, 115.

(20) Zwart, E.; ter Meulen, J. J.; Meerts, W. L.; Coudert, L. H. *J. Mol. Spectrosc.* **1991**, *147*, 27.

(21) Fraser, G. T. *Int. Rev. Phys. Chem.* **1991**, *10*, 189.

(22) Karyakin, E. N.; Fraser, G. T.; Suenram, R. D. *Mol. Phys.* **1993**, *78*, 1179.

(23) Paul, J. B.; Provencal, R. A.; Saykally, R. J. *J. Phys. Chem. A* **1998**, *102*, 3279.

(24) Braly, L. B.; Cruzan, J. D.; Liu, K.; Fellers, R. S.; Saykally, R. J. *J. Chem. Phys.* **2000**, *112*, 10293.

(25) Braly, L. B.; Liu, K.; Brown, M. G.; Keutsch, F. N.; Fellers, R. S.; Saykally, R. J. *J. Chem. Phys.* **2000**, *112*, 10314.

(26) Keutsch, F. N.; Goldman, N.; Harker, H. A.; Leforestier, C.; Saykally, R. J. *Mol. Phys.* **2003**, *101*, 3477–3492.

(27) Keutsch, F. N.; Braly, L. B.; Brown, M. G.; Harker, H. A.; Petersen, P. B.; Leforestier, C.; Saykally, R. J. *J. Chem. Phys.* **2003**, *119*, 8927–8937.

(28) Leforestier, C. *J. Chem. Phys.* **1994**, *101*, 7357.

(29) Huang, Z. S.; Miller, R. E. *J. Chem. Phys.* **1989**, *91*, 6613.

(30) Harris, D. O.; Engerholm, G. G.; Gwinn, W. D. *J. Chem. Phys.* **1965**, *43*, 1515.

(31) Tschumper, G. S.; Leininger, M. L.; Hoffman, B. C.; Valeev, E. F.; Schaefer, H. F.; Quack, M. *J. Chem. Phys.* **2002**, *116*, 690.

(32) Partridge, H.; Schwenke, D. W. *J. Chem. Phys.* **1997**, *106*, 4618.

(33) Kain, J. S.; Polyansky, O. L.; Tennyson, J. *Chem. Phys. Lett.* **2000**, *317*, 365–371.

(34) Jeziorska, M.; Jankowski, P.; Szalewicz, K.; Jeziorski, B. *J. Chem. Phys.* **2000**, *113*, 2957.

(35) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Bureau of Standards: Gaithersburg, 1972; Vol. I.

(36) Smit, M. J.; Groenenboom, G. C.; Wormer, P. E. S.; van der Avoird, A.; Bukowski, R.; Szalewicz, K. *J. Phys. Chem. A* **2001**, *105*, 6212.

(37) Kuyanov-Prozument, K.; Vilesov, A. F. Unpublished results, 2009.

(38) Huisken, F.; Kaloudis, M.; Kulcke, A. *J. Chem. Phys.* **1996**, *104*, 17.

(39) Buck, U.; Huisken, F. *Chem. Rev.* **2000**, *100*, 3863.

(40) Nelander, B. *J. Chem. Phys.* **1988**, *88*, 5254.

(41) Ceponkus, J.; Uvdal, P.; Nelander, B. *J. Phys. Chem. A* **2008**, *112*, 3921–3926.

(42) Paul, J. B.; Provencal, R. A.; Chapo, C.; Roth, K.; Casaes, R.; Saykally, R. J. *J. Phys. Chem. A* **1999**, *103*, 2972.

(43) Scribano, Y.; Goldman, N.; Saykally, R. J.; Leforestier, C. *J. Phys. Chem. A* **2006**, *110*, 5411.

JP9020257