Potential Energy Surface for the H_2O-H_2 System[†]

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In the present paper, we introduce a representation of the potential energy surface for the $H_2O\cdots H_2$ system based on orthogonal vectors, assuming that the two molecules are rigid. We represent the interaction potential by an expansion in real hyperspherical harmonics depending on the distance between the centers of mass of the two molecules and on four angles, which account for two contributions: an external one depending on the three angle variables which define the mutual orientation of the two molecules and an internal one expressed by the angle which describes the position of the oxygen atom in H_2O with respect to the $H_2O\cdots H_2$ system. The surface was generated in the framework of the supermolecular approach, using the counterpoise-corrected interaction energies at the MP2/aug-cc-pVQZ level. Comparisons with other recent work are presented and features of the representation discussed.

1. Introduction

A detailed study of the water−hydrogen van der Waals clusters is desirable for understanding their properties. For example, the potential energy surface of $H_2O\cdots H_2$ is of great importance for astrophysical processes, such as the formation of molecular hydrogen on icy interstellar dust grains.[1] A complete characterization of such processes ultimately relies on detailed comparisons between experiment and theory.[2] This article presents a new representation which describes the potential energy surface (PES), as a function of the radial distance between the centers of mass of systems $H_2O\cdots H_2$ and their mutual orientation. These systems are described by orthogonal vectors whose lenghts are held fixed. In such a way, vibrational motions are kept frozen and stretching and bending modes are decoupled.

The interaction potential of this five-body problem can be expressed as a function of five variables: the distance between the centers of mass of the molecules, R, and the angles θ_1, θ_2, ϕ, and α (see Figure 1 and section 2). Previous works on simpler systems have exploited hyperspherical harmonics as the proper orthonormal expansion basis set for the manifold spanned by the specific range of angular variables.[3–9]

The energies were calculated by using MP2/aug-cc-pVQZ, in 18 *leading* configurations according to the orientation of the molecules (α, θ_1, θ_2, ϕ) with $0 \le \alpha < 2\pi$ measuring the oxygen position, with $0 \le \theta_1 \le \pi$ and $0 \le \theta_2 \le \pi$ being the polar angles of the orientation of the vectors along the H_2 bonds with respect to R and $0 \le \phi \le \pi$ the torsion angle; see Figure 1. For each leading configuration, the H_2O and H_2 geometries are kept frozen at those of equilibrium. This choice is simpler than taking vibrationally averaged geometries, which should be more accurate (see, for example, Valiron et al.[1] and Hodges et al.[10]). In these rigid approaches, the interaction potential depends only on a coordinate. The R coordinate chosen here, and the mathematical model, hyperspherical harmonics expansion, allows compactness and full account of symmetries. The analytical form of the potential energy surfaces is constructed by fitting the energies to a fifth degree generalized Rydberg function.[11] Accurate results for a system like the $H_2O\cdots H_2$ system have a high computational cost. For example, Valiron et al.,[1] using the CCSD(T) and CCSD(T)-R12 methodologies, computed the reference PES for 75000 points on the 5D grid, consisting of the 3000 random orientations of H_2 relative to H_2O.[1] We show

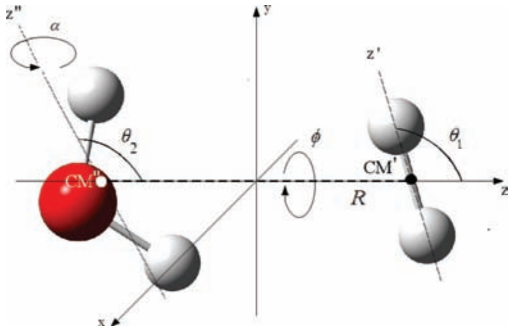

Figure 1. The mutual position of the H_2O and H_2 molecules is expressed by five coordinates in the Cartesian coordinate framework $x\,y\,z$. The axes z' and z'' are also defined, respectively, as the axis parallel to the H−H bond in the H_2 molecule and the axis passing through the center of mass CM″ of the H_2O molecule and parallel to the vector joining the H atoms in H_2O (Jacobi vector). The radial coordinate R is defined as the distance between the center of mass of H_2O, CM″, and the center of mass of H_2, CM′, θ_1 and θ_2 are the angles between the z' and z axes and z'' and z axes, respectively, and they vary between 0 and π, ϕ is the dihedral angle between the plane going through the z'' and z axes and the plane going through the z' and z axes, and its value varies between 0 and π. Finally, α is the angle that describes the rotation of H_2O around the z'' axis and varies between 0 and 2π, α is 0 when the vector joining CM″ and the oxygen atom lays on the plane passing through the z'' and z axes in the configuration where the oxygen atom has the farthest position to CM′, $\alpha = \pi$ when this vector lays on the same plane, but in the closest position to CM′, finally it is $\pi/2$ when the vector is perpendicular to the plane defined by z'' and z.

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that calculating a reduced number of selected geometries (at the MP2 level in this work) permits the construction of an accurate PES useful for studies of the dynamics.

The paper is organized as follows. In section 2, we discuss the representation of the PES. In section 3, the *ab initio* calculation for such configurations are presented, and in section 4, we discuss the results. Conclusions follow in section 5.

2. Representation of the Potential Energy Surface

The parametrization of a five-body system is based on four orthogonal vectors. The natural choice here is a vector along the H−H axis of H_2, denoted as z' (see Figure 1), two vectors referring to the H_2O molecule (one along the H−H distance and another one in the direction of the line connecting the middle of the H−H separation and the O atom). Finally, one vector connects the center of mass CM′ of the H_2 molecule and the center of mass CM″ of H_2. This vector defines the radial coordinate R as the distance between CM′ and CM″. The angle formed by the axis z' passing through CM′ along the H−H bond and the axis z, parallel to R, is called θ_1, while the angle formed by the axis z'' passing through CM′ and parallel to the H−H line in the H_2O molecule and the axis z is named θ_2. The value of both angles varies between 0 and π. ϕ is the angle between the planes defined by the z' and z axes and z'' and z axes, and its value varies between 0 and π. Finally, α is the angle that the water molecular plane forms with respect to R and varies between 0 and 2π.

The PES can be expanded into a series of appropriate angular functions multiplied by radial coefficients (expansion moments), as follows:

$$V(R;\alpha,\theta_1,\theta_2,\phi) = \sum_m \upsilon_m(R)F_m(\alpha,\theta_1,\theta_2,\phi) \qquad (1)$$

where the $\upsilon_m(R)$ coefficients are the expansion moments depending on the R coordinate and $F_m(\alpha, \theta_1, \theta_2, \phi)$ are the angular functions, which can be written in terms of a function $w(\alpha)$ (see below), multiplied by the bipolar spherical harmonic, $Y^{L0}_{L_1L_2}(\theta_1, \theta_2, \phi)$:[12]

$$V(R;\alpha,\theta_1,\theta_2,\phi) = \sum_{L_1,L_2,L} \upsilon_{L_1L_2L}(R)w(\alpha)Y^{L0}_{L_1L_2}(\theta_1,\theta_2,\phi) \qquad (2)$$

with $L_1, L_2 = 0, 1, 2, ..., |L_1 - L_2| \leq L \leq L_1 + L_2$; then, eq 1 can be rewritten as

$$V(R;\alpha,\theta_1,\theta_2,\phi) = \sum_i w_i(\alpha) \sum_{L_1,L_2,L} \begin{pmatrix} L_1 & L_2 & L \\ m & -m & 0 \end{pmatrix} \upsilon_{L_1L_2L}(R) Y^m_{L_1}(\theta_1,0) Y^{-m}_{L_2}(\theta_2,\phi) \qquad (3)$$

where

$$\begin{pmatrix} L_1 & L_2 & L \\ m & -m & 0 \end{pmatrix}$$

is the Wigner $3 - j$ symbol, $-\min(L_1, L_2) \leq m \leq \min(L_1, L_2)$, $Y^m_{L_1}(\theta_1, 0)$ and $Y^{-m}_{L_2}(\theta_2, \phi)$ are the spherical harmonics.

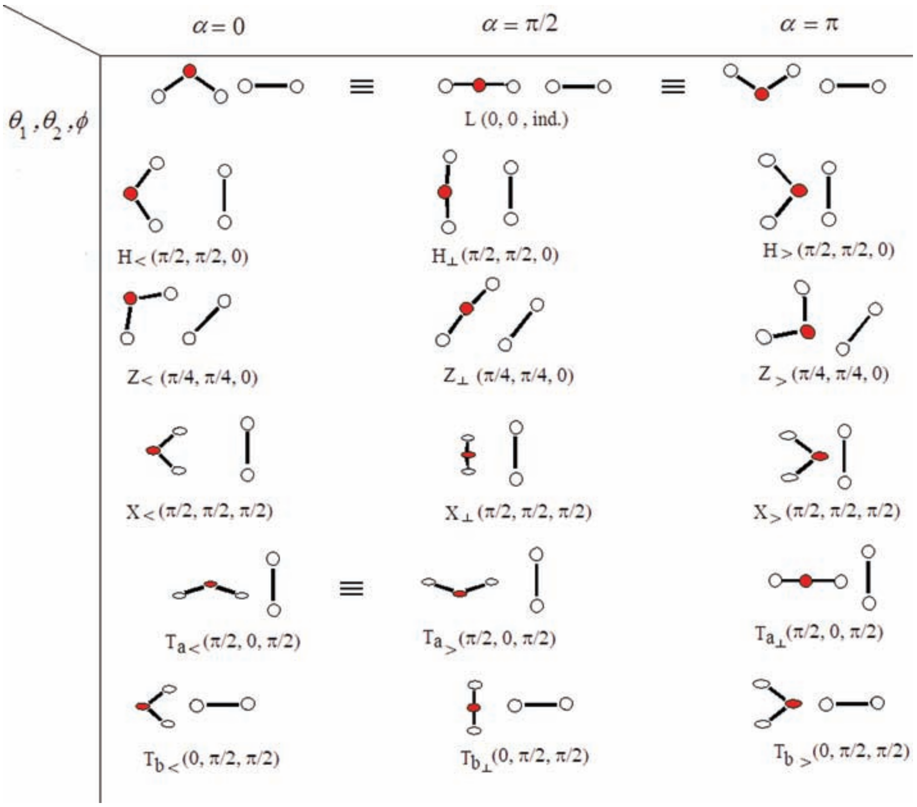

Figure 2. The 18 leading configurations are illustrated. For each configuration, the value of the α angle is reported, indicated by the subscripts <, ⊥, and > for $\alpha = 0$, $\pi/2$, and π, respectively. In parentheses, all three values indicating the angles θ_2, θ_1, and ϕ are reported. As for L, ϕ is undetermined and configurations are equivalent for any value of α, while $T_{a_>}$ and $T_{a_<}$ are equivalent because of symmetry properties, reducing the total to 15 different configurations.

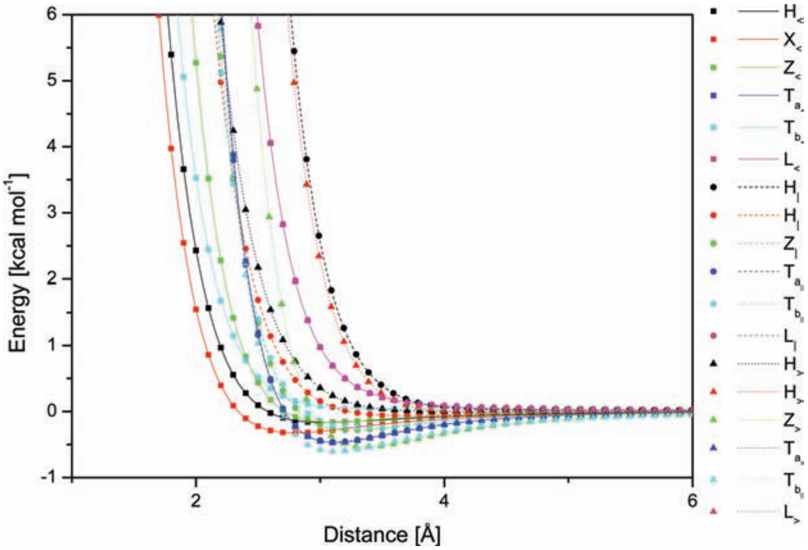

Figure 3. $H_2O\cdots H_2$ interaction energies for the leading configurations of Figure 2 as a function of R, the distance between the centers of mass of the H_2O and H_2 molecules. Symbols indicate *ab initio* points and curves are from Rydberg fits, as described in the text.

Since both molecules involved here, H_2O and H_2, are symmetric with respect to exchange of their hydrogen atoms, only even moments contribute to the sum in eq 3 and it will be shown adequate that the sum can be truncated for $L_1 = L_2 = 2$, as done in previous works for systems involving diatomics, such as $N_2\cdots N_2$, $O_2\cdots O_2$, and $N_2\cdots O_2$.[3–7] Explicitly, after extensive algebraic manipulations, one obtains

$$\begin{aligned}V(R; \alpha, \theta_1, \theta_2, \phi) = {} & \sum_i w_i(\alpha)[\upsilon_{000}(R) + \\ & \frac{\sqrt{5}}{4}\upsilon_{202}(R)(3\cos(2\theta_1) + 1) + \frac{\sqrt{5}}{4}\upsilon_{022}(R)(3\cos(2\theta_2) + \\ & 1) + \frac{\sqrt{5}}{16}\upsilon_{220}(R)[(3\cos(2\theta_1) + 1)(3\cos(2\theta_2) + 1) + \\ & 12\sin(2\theta_1)\sin(2\theta_2)\cos(\phi) + 3(1 - \cos(2\theta_1))\times \\ & (1 - \cos(2\theta_2))\cos(2\phi)] - \frac{5\sqrt{14}}{112}\upsilon_{222}(R)[(3\cos(2\theta_1) + \\ & 1)(3\cos(2\theta_2) + 1) + 6\sin(2\theta_1)\sin(2\theta_2)\cos(\phi) - \\ & 3(1 - \cos(2\theta_1))(1 - \cos(2\theta_2))\cos(2\phi)] + \\ & \frac{3\sqrt{70}}{112}\upsilon_{224}(R)[(3\cos(2\theta_1) + 1)(3\cos(2\theta_2) + 1) - \\ & 8\sin(2\theta_1)\sin(2\theta_2)\cos(\phi) + \frac{1}{2}(1 - \cos(2\theta_1)) \times \\ & (1 - \cos(2\theta_2))\cos(2\phi)]] \qquad (4)\end{aligned}$$

In order to evaluate the expansion moments of the interaction potential $V(R, \theta_1, \theta_2, \phi, \alpha)$, we define 18 leading configurations (see Figure 2), whose choice is due to physical and geometric considerations. The advantage of such a choice is to select a number of configurations which permit interpolation to account fully for the symmetries of the interactions between the molecules forming the system. We can divide the leading configurations into six classes depending on their values of θ_2, θ_1, and ϕ: specifically, L is the configuration with $\theta_2 = \theta_1 = 0$ and ϕ undetermined; for the H configuration $\theta_2 = \theta_1 = \pi/2$ and $\phi = 0$; Z has $\theta_2 = \theta_1 = \pi/4$ and $\phi = 0$; for X, $\theta_2 = \theta_1 = \phi = \pi/2$; T_a has $\theta_2 = 0$ and $\theta_1 = \phi = \pi/2$; finally, T_b has $\theta_1 = 0$ and $\theta_2 = \phi = \pi/2$. For each class, three different configurations exist for α values 0, $\pi/2$, and π that we indicate with subscripts <, ⊥, and >, respectively. Because of the symmetry of the system, $T_{a_>} = T_{a_<}$, while, for L, since ϕ is undetermined, α cannot be defined in these cases. Fixing the α configuration, we have a system with six equations similar to eq 4 that can be algebraically inverted by Cramer's rule:

$$\begin{aligned}\upsilon_{000}(i; R) = {} & \frac{1}{9}(2V_H(i; R) + V_L(i; R) + 2V_{T_a}(i; R) + \\ & 2V_{T_b}(i; R) + 2V_X(i; R))\\ \upsilon_{202}(i; R) = {} & \frac{-2\sqrt{5}}{45}(V_H(i; R) - V_L(i; R) + V_{T_a}(i; R) - \\ & 2V_{T_b} + V_X(i; R))\\ \upsilon_{022}(i; R) = {} & \frac{-2\sqrt{5}}{45}(V_H(i; R) - V_L(i; R) - 2V_{T_a}(i; R) + \\ & V_{T_b} + V_X(i; R))\\ \upsilon_{220}(i; R) = {} & \frac{-2\sqrt{5}}{225}(4V_H(i; R) - V_L(i; R) - 5V_{T_a}(i; R) - \\ & 5V_{T_b} - 5V_X(i; R) + 12V_Z(i; R))\\ \upsilon_{222}(i; R) = {} & \frac{\sqrt{14}}{315}(13V_H(i; R) - V_L(i; R) + 7V_{T_a}(i; R) + \\ & 7V_{T_b} - 14V_X(i; R) - 12V_Z(i; R))\\ \upsilon_{224}(i; R) = {} & \frac{8\sqrt{70}}{525}(V_H(i; R) - V_L(i; R) - 2V_Z(i; R)) \qquad (5)\end{aligned}$$

where i corresponds to the three different values of the α angle, $\alpha = 0, \pi/2, \pi$.

It is now convenient to define the $w(\alpha)$ functions, which establish the weight of each set of leading configuration ($i = 0, \pi/2, \pi$) according to the corresponding α value. Specifically, by expanding it in a cosine series including $\cos(n\alpha)$ terms ($n = 0, 1, 2$), we have, in general,

$$w_i(\alpha) = a_i + b_i\cos(\alpha) + c_i\cos(2\alpha) \qquad (6)$$

for $i = 0, \pi/2, \pi$, specifically:

$$\begin{array}{lll} w_1(0) = 1 & w_1(\pi/2) = 0 & w_1(\pi) = 0 \\ w_2(0) = 0 & w_2(\pi/2) = 1 & w_2(\pi) = 0 \\ w_3(0) = 0 & w_3(\pi/2) = 0 & w_3(\pi) = 1 \end{array} \tag{7}$$

allowing to compute parameters a_i, b_i, and c_i as follows:

$$\begin{aligned} w_1(\alpha) &= \frac{1}{4} + \frac{1}{2}\cos(\alpha) + \frac{1}{4}\cos(2\alpha) \\ w_2(\alpha) &= \frac{1}{2} - \frac{1}{2}\cos(2\alpha) \\ w_3(\alpha) &= \frac{1}{4} - \frac{1}{2}\cos(\alpha) + \frac{1}{4}\cos(2\alpha) \end{aligned} \tag{8}$$

The general expression for the potential is obtained substituting eqs 5 and 8 in eq 4 for each α configuration.

The total isotropic term of potential energy is given by the $\bar{v}_{000}(R)$ function which turns out to be

$$\bar{v}_{000}(R) = \frac{1}{4}v_{000}(\alpha = 0; R) + \frac{1}{2}v_{000}(\alpha = \pi/2; R) + \frac{1}{4}v_{000}(\alpha = \pi; R) \tag{9}$$

This term is important because it can be measured by molecular beam experiments with rotationally hot molecules and can be compared with other systems.[13,14]

3. *Ab Initio* Calculations

The *ab initio* calculations were performed using the Gaussian 03 code.[15] Initially, we optimized the geometries for H_2O and H_2 molecules (Table 1), by using the CCSD(T) method, with the cc-pVXZ and aug-cc-pVXZ basis sets ($X = D, T, Q, 5$). We also used the complete basis set (CBS) extrapolation. Employing asymptotic extrapolation allows calculations of molecular properties with a reasonable degree of accuracy for molecules of relatively high molecular size. In this work, it can be seen that calculations without the diffusion function (basis set without aug function) do not reproduce satisfactorily the polarizability of H_2O and H_2 molecules; therefore, they are not reliable to construct the PES for this system. We therefore have chosen a simple method (MP2) combined with an augmented complete basis set, that appears to give accurate results exemplified in Table 2, which lists well depths and positions for the isotropic component of the potential v_{000}. The representation of the PES is in terms of the mathematical approach (hyperspherical harmonics) outlined in the previous section. With respect to data taken as a reference, for H_2O, the smallest errors are 0.0013 Å for the O−H distance in H_2O and 0.1151° for the HOH angle at aug-cc-pVQZ, while for H_2 the error is 0.0005 Å for the H−H distance. For the frequencies of the vibrational modes, the errors are 42.9, 129.8, and 148.7 cm^{-1} for H_2O and 1.5 cm^{-1} for H_2, both at aug-cc-pVQZ. Our data were compared with experimental polarizabilities and dipole moments: for H_2O, we get an error of 0.1092 au and 0.1128 D, respectively, and 0.0622 au for the H_2 polarizability at aug-cc-pVQZ. According to these results, the geometries to be used will be the ones calculated at CCSD(T)/aug-cc-PVQZ, and the molecules will be kept frozen for further calculations.

The second-order Møller-Plesset (MP2) level and aug-cc-pVQZ basis set were chosen to calculate the PES. In order to eliminate the basis set superposition error, the full counterpoise Boys and Bernardi method[16] was used. According to it, the energies of monomers were calculated using the same full basis set, and the interaction energy is then defined as

$$E_{CP} = E_{AB}(\chi_A + \chi_B) - [E_A(\chi_A + \chi_B) + E_B(\chi_A + \chi_B)] \tag{10}$$

where χ_A and χ_B are the basis sets of each monomer of the complex *AB*. We calculated a set of 101 single potential energy points on the surfaces, which allows us to describe completely the potential energy surface, for each of the 15 configurations (see Figure 2), remembering that we have 18 different schemes, six for $\alpha = 0$, six for $\alpha = \pi/2$, and six for the $\alpha = \pi$ configuration, but $L_> = L_\perp = L_<$ and $T_{a_>} = T_{a_<}$, as described previously (section 2 and Figure 2). All energies were calculated as a function of the distance R between the center of mass CM″ of H_2O and the center of mass CM′ of H_2 at a fixed α, θ_1, θ_2, and ϕ angle (see Figure 1 for further details). The smallest distance R depends on the leading configuration, and can be appreciated by inspection of Figure 3.

The analytical form of the PES, for each of the leading configurations, is constructed by fitting the following fifth degree generalized Rydberg function[11] into the *ab initio* points:

$$V(R) = D_e \sum_{i=1}^{5} (1 + a_i(R - R_{\text{eq}})^i) \exp[-a_i(R - R_{\text{eq}})] + E_{\text{ref}} \tag{11}$$

where D_e, a_i, R_{eq}, and E_{ref} are adjustable parameters. A nonlinear least-squares procedure was used to obtain the values of the adjustable parameters that minimize the differences between analytic energies obtained with the generalized Rydberg function and the MP2/aug-cc-pVQZ data. The largest rms value of these fits is 0.005731 kcal mol^{-1} for the L configuration, and the smallest one is 0.000103 kcal mol^{-1} for the H_1 configuration. (As for the van der Waals systems, also cm^{-1} is a useful unit, here we report the conversion unit 1 kcal mol^{-1} = 349.76 cm^{-1}.)

There are several proposals for "combination formulas" that allow one to predict the strength, ε, and range, R_m, of the van der Waals contribution of systems of the type of the ones studied here. We follow a procedure similar to that outlined in ref 17, which consists of the representation of ε and R_m in terms of the polarizabilities α_1 and α_2 of the interacting partners.[18] Specifically,

$$R_m = 1.767\frac{\alpha_1^{1/3} + \alpha_2^{1/3}}{(\alpha_1\alpha_2)^{0.095}} \tag{12}$$

where R_m is given in Å and α_1 and α_2 in Å^3,

$$\varepsilon = 0.72 C_{\text{LR}} R_m^{-6} \tag{13}$$

$$C_{\text{LR}} = \kappa_\varepsilon \frac{\alpha_1\alpha_2}{\sqrt{\dfrac{\alpha_1}{N_1}} + \sqrt{\dfrac{\alpha_2}{N_2}}} \tag{14}$$

where C_{LR} is an effective long-range London coefficient. κ_ε is a scaling factor and depends on the energy units (for energy in kcal mol^{-1}, $\kappa_\varepsilon = 362.051$). N_1 and N_2 are effective numbers of

TABLE 1: Basis Set Studies for H_2O and H_2 Determined with CCSD(T)

	H_2O							
	geometry		frequencies (cm^{-1})					
basis set	R_{eq} (Å)	A (deg)	ω_1	ω_2	ω_3	μ (D)	α (au)	energy (hartree)
cc-pVDZ	0.9663	101.9150	1690.0	3821.6	3927.6	2.0906	4.8092	−76.2413050
aug-cc-pVDZ	0.9665	103.9353	1637.9	3786.8	3904.7	1.9948	9.2392	−76.2739036
cc-pVTZ	0.9595	103.5371	1669.1	3840.4	3944.7	2.0252	6.9677	−76.3322164
aug-cc-pVTZ	0.9616	104.1851	1645.6	3811.2	3920.3	1.9702	9.4927	−76.3423258
cc-pVQZ	0.9579	104.0872	1659.3	3844.3	3951.0	1.9957	7.8654	−76.3597977
aug-cc-pVQZ	0.9589	104.3626	1649.7	3831.2	3940.8	1.9628	9.5328	−76.3635876
cc-pV5Z	0.9580	104.3277	1653.4	3840.6	3949.6	1.9851	8.5290	−76.3690418
CBS extrapolation[a]	0.9599 ± 0.0026	104.1736 ± 0.2479	1651.4 ± 11.4	3827.5 ± 20.1	3936.8 ± 16.4	1.9841 ± 0.0189	8.7512 ± 1.0037	−76.3471908 ± 0.0247155
reference						1.8546 ± 0.0006[25]	9.642, 9.0658[26]	
	0.9557,[b] 0.961[c]	104.05,[b] 105.1[c]	1640[c]	3820[c]	3919[c]	1.9185,[b] 1.8590[c]		
	0.9589,[d] 0.964[e]	104.16,[d] 102.9[e]	1699[e]	3737[e]	3850[e]	1.9249,[d] 1.85[e]	9.6311,[c] 8.419[e]	

	H_2				
basis set	geometry, R_{eq} (Å)	frequencies, ω (cm^{-1})	μ (D)	α (au)	energy (hartree)
cc-pVDZ	0.7610	4382.2	0.0	2.9614	−1.1636730
aug-cc-pVDZ	0.7617	4345.1	0.0	5.2482	−1.1648995
cc-pVTZ	0.7428	4408.0	0.0	3.9097	−1.1723367
aug-cc-pVTZ	0.7428	4404.6	0.0	5.2184	−1.1726356
cc-pVQZ	0.7419	4404.2	0.0	4.4309	−1.1737965
aug-cc-pVQZ	0.7419	4402.5	0.0	5.1950	−1.1738674
cc-pV5Z	0.7419	4400.8	0.0	4.6938	−1.1742229
aug-cc-pV5Z	0.7419	4400.3	0.0	5.1869	−1.1742521
CBS extrapolation[a]	0.7440 ± 0.0058	4396.9 ± 19.5	0.0	4.8864 ± 0.5124	−1.1727561 ± 0.0025453
reference	0.7414[27]	4401[27]		5.3104[26]	
	0.7430,[f] 0.7432[g]	4402,[f] 4413[g]			

[a] See ref 28, using formula $Y = Y_\infty + Y_0/X^3$. [b] At MP2/TZ(3d2f,3p2d).[29] [c] At X3LYP/aug-cc-pVTZ(-f).[30] [d] At CCSD(T)/TZ2P(f,d)+dif.[31] [e] At CASSCF/aug-cc-pVDZ.[32] [f] At CCSD(T)/aug/cm^3-pVTZ. [g] At B3LYP/aug-cc-pVTZ.[33]

TABLE 2: Comparison of Phenomenological[17,22] Estimates with CCSD(T) Values for Different Basis Sets and Other Data[a]

	without induction correction		with induction correction	
basis set	R_m	ε	R_m	ε
aug-cc-pVDZ	3.5657	0.1289	3.5272	0.1542
aug-cc-pVTZ	3.5731	0.1296	3.5362	0.1538
aug-cc-pVQZ	3.5735	0.1295	3.5370	0.1534
CBS extrapolation[b]	3.5347	0.1237	3.4961	0.1483

	R_m	ε
MP2	3.5704	0.1336
experimental	3.61[2]	0.1115[2]
other calculations	3.52[23]	0.1415[23]
	3.4908[1]	0.1753[1]

[a] Well depth energies, ε (kcal mol^{-1}), and corresponding values for the R coordinate, R_m (Å), for the isotropic component v_{000}. [b] See ref 28, using formula $Y = Y_\infty + Y_0/X^3$.

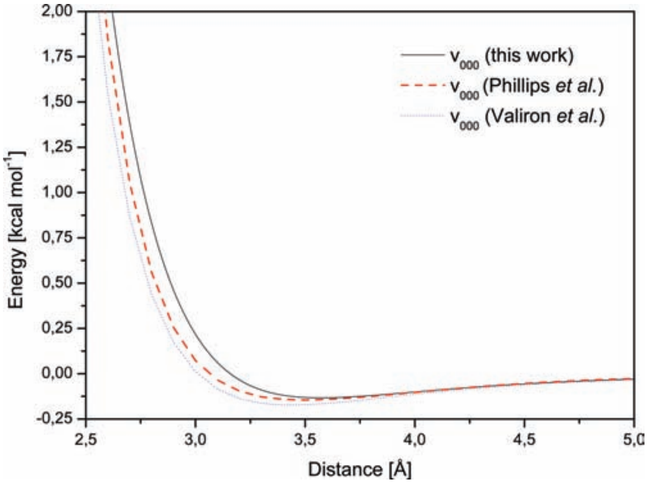

Figure 4. Dependence on distance of the centers of mass of $H_2O\cdots H_2$ molecules of isotropic moments compared with reference data of Valiron et al.[1] and Phillips et al.[23]

electrons which contribute to the polarizability of each partner; numerical coefficients in eqs 12−14 were determined empirically.[18] Equation 14[19] is a generalization of the Slater−Kirkwood equation;[20] it takes into account the various multipole interaction terms and the damping effect (see ref 19 and references therein). The effective number of electron N_1 and N_2 considers not only the external electrons but also the internal ones,[21] whose contribution to polarizability is not negligible.

We also introduce a correction for the induction effects due to the interaction between the permanent dipole moment of H_2O and the induced dipole of H_2.[17,22] These effects are introduced as a correction to the previous formulas adding an attractive *induction* term to the long-range part of the potential. The formula for the induction coefficient C_{IN} is as follows:

$$C_{\mathrm{IN}} = \kappa_i \alpha_2 \mu_1^2 \qquad (15)$$

where μ_1 is the dipole moment of H_2O, α_2 is the polarizability of H_2, and κ_i is a scaling factor depending on units, κ_i = 14.40984 for C_{IN} in kcal/mol Å^6. Accordingly, the corrected equations for R_m and ε are

$$R_m = 1.767 \frac{\alpha_1^{1/3} + \alpha_2^{1/3}}{(\alpha_1 \alpha_2 \rho)^{0.095}} \qquad (16)$$

where $\rho = (C_{\mathrm{LR}} + C_{\mathrm{IN}})/C_{\mathrm{IN}}$, and

$$\varepsilon = 0.72(C_{\mathrm{LR}} + C_{\mathrm{IN}})R_m^{-6} \qquad (17)$$

In this study, we used eqs 16 and 17 to estimate the distance and energy of equilibrium at different levels of calculations, respectively, as presented in Table 2. From these data, we can see that in the values without induction correction using CCSD(T)/aug-cc-pVQZ methodology (3.5735 Å for the distance of equilibrium and 0.1295 kcal mol^{-1} for the energy of equilibrium) the results are close to the experimental data[2] (3.61 Å and 0.1115 kcal mol^{-1}) and more accurate than other methodologies (MP4[23] and CCSD(T)-R12[1]). Therefore, these values without induction correction can guide us to calibrate

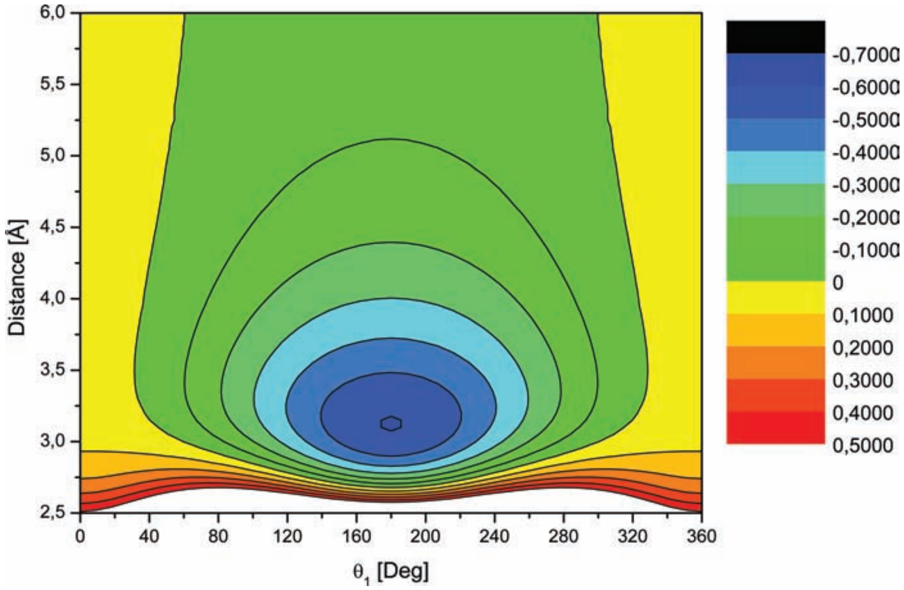

Figure 5. Two-dimensional cut through the $H_2O\cdots H_2$ PES. Contours are given in kcal mol^{-1}. $T_b = (R, \alpha, 0, \pi/2, 0)$ configuration (proton acceptor).

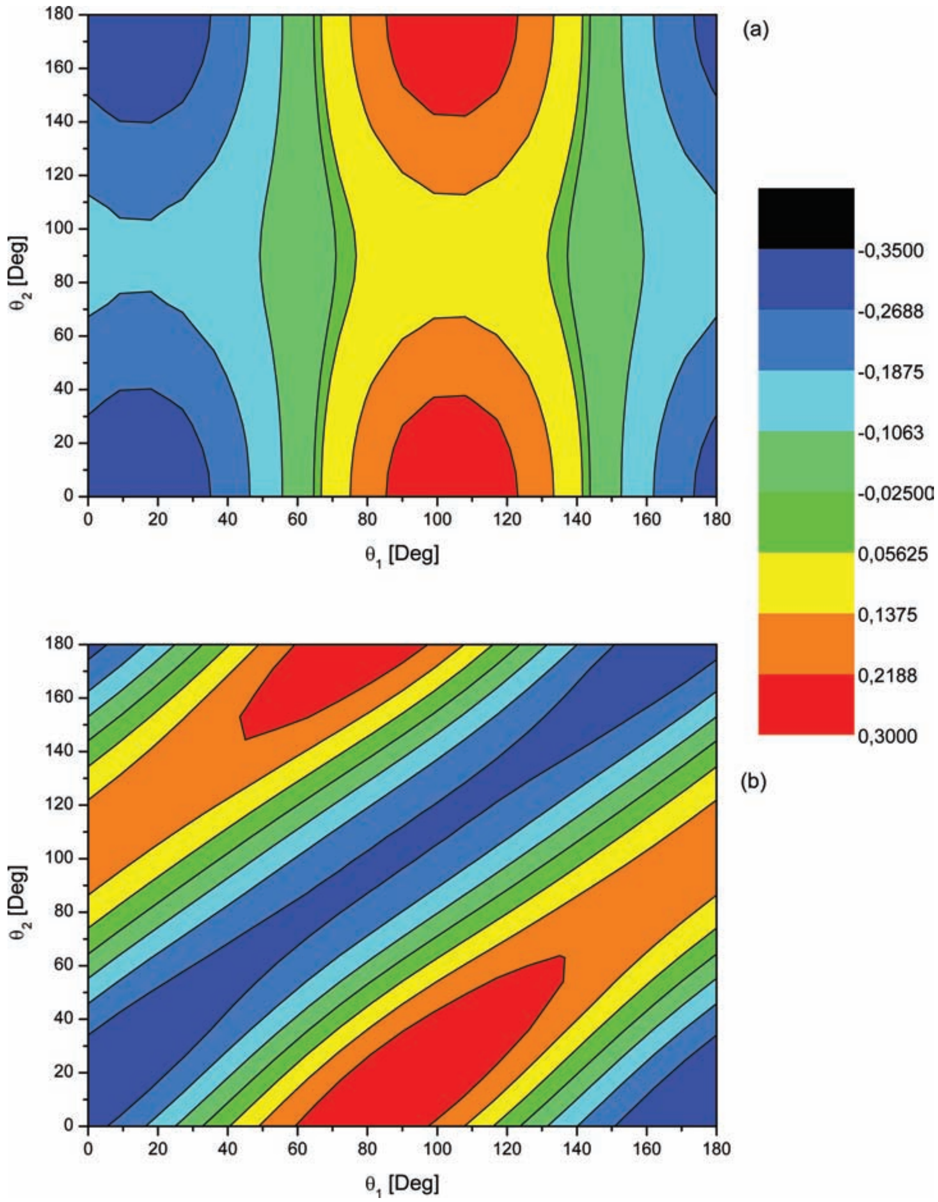

Figure 6. Two-dimensional cut through the $H_2O\cdots H_2$ PES. Contours are given in kcal mol^{-1}. (a) (3.57036, 0, $A_{H_2O} - \theta$, θ_2, $\pi/2$) configuration. (b) (3.57036, A_{H_2O}, $A_{H_2O} - \theta$, θ_2, 0) configuration.

our model to reproduce the distance and energy of equilibrium for the $H_2O\cdots H_2$ system.

4. Results and Discussion

We have considered the 18 leading configurations (of which 15 are different, see Figure 2) for which the $H_2O\cdots H_2$ interaction energy has been calculated at various R (the distance between the centers of mass of the H_2O molecule and of the H_2 molecule) by the *ab initio* methods, as explained in detail in section 3.

Figure 3 shows both the *ab initio* energy points and the corresponding Rydberg curve fitting for the 15 different configurations. Purely repulsive systems are those whose curves do not have a minimum. *Ab initio* calculations show that such systems are those involving $H_\perp$, $X_>$, L, $H_>$, $X_\perp$, and $T_{b_<}$ configurations. The hydrogen bond plays an important role in the stabilization of these systems. According to previous studies[24] regarding the interaction between H_2O and H_2, the H_2O molecule acts as a proton acceptor or proton donor. In the first case, the H−H bond of H_2 is expected to be collinear to the C_2 axis in the direction of the oxygen atom, while, in the second case, one of the two OH bonds is perpendicular to the H−H bond of the H_2 molecule and directed toward the middle point of the H−H distance. $T_{b_>}$ is the configuration with the highest value of minimum in energy (more negative) and corresponds to the proton acceptor case. None of the leading configurations corresponds to the proton acceptor case, although some of them show an attractive character ascribable to hydrogen bond interaction, such as Z and T_a configurations. As for the $Z_>$ configuration, it shows repulsive character like the other configurations with $\alpha = \pi$, but it also presents a minimum, differently from the other configurations with the same value of α. By comparing two $\alpha = 0$ configurations such as $Z_<$ and $T_{b_<}$, the energy of equilibrium of $Z_<$ is lower (more negative) and the intermolecular potential increase is steeper than $T_{b_<}$. The stabilizing effect of the hydrogen bond, with deep minima and steep increasing of interaction potentials at short range, has already been observed in previous works.[8,9] Potential profiles of T_a configurations are very similar, because the position of the oxygen atom has little influence on these geometries.

Figure 4 shows the isotropic part of the potential υ_{000} as a function of R (eq 9) calculated in this work and compared with reference data.[1,23] In Table 2, the distance and energy of equilibrium for υ_{000} are reported. It can be of interest to compare the isotropic term, energy of 0.1336 kcal mol^{-1} at 3.5704 Å, with other systems like $H_2O\cdots He$ where the energy and distance are 0.0633 kcal mol^{-1} at 3.45 Å[13] and 0.066 kcal mol^{-1} at 3.626 Å.[8]

Figure 5 shows the isoenergetic contours for the proton acceptor case $T_{b_{>}}$, as a function of R and α angles. The minimum energy and distance is 0.6014 kcal mol^{-1} and 3.1224 Å to be compared with data of Valiron et al.[1] and of Zhang et al.[24] (0.6723 kcal mol^{-1} at 3.0798 Å and 0.5638 kcal mol^{-1} at 3.1 Å, respectively). The difference in energy is as expected from the relative accuracies of the calculations.

In order to compare our model with the PES presented by Valiron et al.,[1] we show in Figure 6 two isoenergetic contours. In Figure 6a, we kept the distance at the isotropic minimum, $R_m = 3.57036$ Å and $\alpha = 0$, the angle $\theta_1 = A_{H_2O} - \theta$ and $\phi = 0$, where A_{H_2O} is the angle of the HOH bond in H_2O (compared with Figure 8 of ref 1). In Figure 6b, the distance is the same with $\alpha = A_{H_2O}$, $\theta_1 = A_{H_2O} - \theta$, and $\phi = \pi/2$ (compared with Figure 7-f of ref 1). These figures are seen to reproduce adequately the reference data, using a simpler method with a physically motivated and compact representation. We consider that the material provided allows direct comparison of angular dependence with that of previous work (Valiron et al.[1]), although a figure cannot be provided lacking data input for the latter.

5. Conclusion

A representation of the potential energy surface of the rigid $H_2O\cdots H_2$ system based on orthogonal vectors was presented. The interaction potential was represented by an expansion in real hyperspherical harmonics depending on the distance R between the centers of mass of the two molecules and four angular variables θ_1, θ_2, ϕ, and α; three of these account for an external contribution depending on the mutual orientation of the two molecules, and an internal contribution, depending on one angle, α, which describes the position of the oxygen atom in H_2O with respect to the entire system. The system studied in this work is definitely more complex than other systems previously studied by orthogonal vector representation,[8,9,12] where the interatomic potential depends at most on three angle variables. The extension of the dimension of the manifold in this case in not trivial.

The surface was generated in the framework of the supermolecular approach, using the counterpoise-corrected interaction energies at the MP2/aug-cc-pVQZ level. The PES was computed for about one hundred for each of the 18 leading configurations, whose number reduces to 15 because of symmetry properties. Results were compared with experimental and theoretical[1] works with a higher computational cost, involving a very high number of points on the 5D grid and a very large number of random orientations of H_2O and H_2 molecules (for other state-of-the-art *ab initio* calculations of the $H_2O\cdots H_2$ system, see, for example, Hodges et al.[10]). This method allows us to reach a compromise between the accuracy of results and the economicity of the calculations. Especially the expansion used in this method can be employed to calculate the isotropic component of the potential. Hyperspherical harmonics allow us to account for the symmetry properties of the system, providing all of the configurations of the five-dimensional PES for all of the values of R and the angle variables, of use for molecular dynamics simulations.

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Supporting Information Available: Ab initio well depths, ε, and corresponding atom−molecule distance, R_{eq}, for various configurations of the $H_2O\cdots H_2$ system, and parameters for Rydberg fitting of ab initio curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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