**Anchoring the potential energy surface of an important
atmospheric van der Waals dimer, the $\text{H}_2\text{O} \cdots \text{O}_2$ complex**

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Abstract

The focus of this paper is the weakly-bound $\text{H}_2\text{O} \cdots \text{O}_2$ van der Waals dimer. The global minimum has an electronic dissociation energy of $0.70 \text{ kcal mol}^{-1}$ at the spin unrestricted CCSD(T) level of theory (UCCSD(T)) in conjunction with a correlation consistent quadruple-zeta basis set augmented with diffuse functions on all heavy atoms, denoted haQZ (i.e., cc-pVQZ for H and aug-cc-pVQZ for O). Eleven other stationary points are also characterized at the UCCSD(T)/haQZ level of theory, all of which lie within $0.5 \text{ kcal mol}^{-1}$ of the global minimum and have at least one imaginary frequency ($\nu_i \geq 1$). The spin unrestricted MP2 method (UMP2) yields very similar structures and energies for the twelve stationary points. However, the UMP2 vibrational frequencies provide a qualitatively different description of the potential energy surface (more than a single minimum), of the frequency shifts upon complexation and of the resulting infrared intensities of the complex. The UCCSD(T)/haQZ computations indicate only one of the twelve $\text{H}_2\text{O} \cdots \text{O}_2$ structures is a minimum and that it exhibits appreciable infrared intensity for one of the lowest energy intermolecular vibrational modes, unlike the related $\text{H}_2\text{O} \cdots \text{N}_2$ system.

1. Introduction

Earth’s atmosphere is comprised of 78% N₂, 21% O₂, and less than 1% of other gases, under completely dry conditions [1]. The amount of water vapor in the atmosphere is variable at any given time, but typical values range from 1-4% depending on temperature and altitude. Given the high abundances of N₂, O₂ and H₂O, along with water’s propensity to form non-covalent complexes, the chemistry of van der Waals complexes plays an important role in the troposphere. (H₂O)₂ is a strong absorber of near infrared (IR) radiation, particularly in the OH stretching region [2, 3]. H₂O⋯O₂ and H₂O⋯N₂ have also been evaluated as enhanced absorbers of IR radiation [4–7]. Upon complexation, new intermolecular vibrational modes are formed between the fragments that could have appreciable IR activity. In addition, the monomer vibrations can be perturbed in the complex, leading to enhanced IR activity. An increase in the IR intensity of one or more vibrational modes of the fragments and/or a large IR intensity for any newly-formed intermolecular modes of the complex could point to enhanced greenhouse effects from these van der Waals complexes [4], but it is important to note that other changes, such as to the width of the vibrational transitions, can also affect radiative transfer. Large frequency shifts or IR intensity changes after dimerization could also be helpful for directly detecting a particular complex in the atmosphere or laboratory [5].

A number of prior studies of the H₂O⋯O₂ complex have utilized Møller-Plesset perturbation theory to characterize stationary points on the potential energy surface [4, 8–13]. The most extensive *ab initio* investigation of the potential energy surface examined twelve different structures of H₂O⋯O₂ at the MP2/aug-cc-pVTZ level of theory [8]. In some cases, quadratic configuration interaction or coupled-cluster single point energy computations (e.g. QCISD and CCSD) were also performed to recover more dynamical electron correlation which slightly reduced the dissociation energy of global minimum [5, 6, 14–22]. Several studies also considered the multireference nature of O₂, which has a $^3\Sigma_g^-$ ground state. However, the results from multi-reference computations were consistent with those from single-reference MP2 calculations [8, 11, 20].

The global minimum identified by these studies (structure I, shown in Fig. 1) is a C_s structure with a $^3A''$ electronic state and an electronic dissociation energy well below 1 kcal mol^{−1}. Most correlated wavefunction based methods with basis sets of at least triple-zeta quality yield dissociation energies for the global minimum of just over 0.7 kcal mol^{−1} [5, 8]. There is, however, significant variation in some intermolecular geometrical parameters of the optimized structures. The OH⋯O and OO⋯H angles (denoted α and β , respectively, in Fig. 1) exhibit variations of more than 20 degrees because the potential energy surface of H₂O⋯O₂ is very shallow [6, 11, 20]. Eleven other stationary points with C_s or C_{2v} symmetry (structures II–XII, Fig. 1) have also been identified that are within 0.5 kcal mol^{−1} of the global minimum.

In this work, coupled-cluster theory (specifically the CCSD(T) method) is used to characterize these twelve stationary points on the potential energy surface of the H₂O⋯O₂ complex (Fig. 1), six C_{2v} structures and six C_s structures

(including the global minimum). Dissociation energies, geometrical parameters and harmonic vibrational frequencies of both the fragments and complex are compared to those from second-order Møller-Plesset perturbation theory. Frequency shifts and IR intensity changes are used to monitor changes in the spectroscopic fingerprints of each monomer species upon complexation. The IR intensities of the low-energy intermolecular vibrational frequencies ($< 150 \text{ cm}^{-1}$) are also examined to discern the potential of the $\text{H}_2\text{O} \cdots \text{O}_2$ complex to play a role as an enhanced absorber in the atmosphere. Our group performed a similar analysis of six key stationary points on the potential energy surface of $\text{H}_2\text{O} \cdots \text{N}_2$ [7]. As such, this paper also provides a direct comparison of these two important complexes, $\text{H}_2\text{O} \cdots \text{O}_2$ and $\text{H}_2\text{O} \cdots \text{N}_2$.

2. Computational Methods

Full geometry optimizations and harmonic vibrational frequency computations were performed for each dimer structure and the isolated fragments with second order Møller-Plesset perturbation theory[23] and coupled-cluster method with single, double, and perturbative triple substitutions[24] using a spin unrestricted Hartree-Fock (UHF) reference wavefunction for all open-shell species (O_2 and $\text{H}_2\text{O} \cdots \text{O}_2$) and a spin restricted Hartree-Fock (RHF) reference for the closed-shell systems (H_2O). These computations were performed with the analytic gradients and Hessians available in **CFOUR**[25], and the corresponding results are labeled as UMP2 and UCCSD(T). All energies, optimized structures and harmonic vibrational frequencies were computed with the correlation consistent family of basis sets in which diffuse functions were added to the “heavy” (non-hydrogen) atoms (i.e. cc-pVXZ for H and aug-cc-pVXZ for O where X = T, Q, and 5). These basis sets are denoted haXZ throughout the remainder of this manuscript. In addition, a series of single point MP2 and CCSD(T) energies were computed that employed a spin restricted Hartree-Fock (ROHF) reference for the open shell systems, (i.e. ROMP2 and ROCCSD(T)). Explicitly correlated F12 single point energies were also computed with the ha5Z basis set and associated default density fitting basis sets in the **Molpro2010**[26] program to estimate the complete basis set (CBS) limit. Partially spin-restricted explicitly correlated coupled-cluster computations (denoted ROCCSD(T)-F12) employ an ROHF reference, and a cluster operator that neglects some spin coupling in order to reduce spin contamination [27, 28]. Unrestricted explicitly correlated coupled-cluster computations (denoted UCCSD(T)-F12) also used an ROHF reference, but the method is more susceptible to spin contamination because the unmodified cluster and spin-squared operators do not commute [27, 28]. The **Gaussian09**[29] software package was used for all UMP2 and ROMP2 calculations. All UCCSD(T) and ROCCSD(T) calculations were done using **CFOUR**, whereas **Molpro2010** was used for the explicitly correlated computations. Pure angular momentum functions (5*d*, 7*f*, 9*g*) were used rather than Cartesian functions (6*d*, 10*f*, 15*g*). All Cartesian forces associated with the optimized structures have been converged to less than $1 \times 10^{-4} E_h/a_0$.

Figure 1: Twelve structures and point group symmetries of the $\text{H}_2\text{O} \cdots \text{O}_2$ system along with select intermolecular parameters (R_{eq} , α , β) described in the text.

3. Results and Discussion

3.1. O_2 and H_2O Fragments

Table 1 lists the intramolecular bond lengths and bond angle along with harmonic vibrational frequencies and IR intensities of O_2 and H_2O . The differences between the optimized haTZ and haQZ bond lengths and bond angle are minimal, less than $0.006 \text{ \AA}$ and 0.2° , and deviations between corresponding harmonic vibrational frequencies do not exceed 25 cm^{-1} . Higher-order correlation effects have a more substantial impact on the fragments, particularly for O_2 . Relative to the UCCSD(T) results, UMP2 overestimates the OO bond length by $0.01 \text{ \AA}$ and underestimates the frequency by 120 cm^{-1} with both haTZ and haQZ basis sets. The deviations between MP2 and CCSD(T) for the H_2O fragment are smaller, with maximum unsigned deviations of $0.001 \text{ \AA}$ for the OH bond length, 0.1° for the HOH angle, and 30 cm^{-1} for any frequency. At the CCSD(T)/haQZ level, the largest IR intensity of 73 km mol^{-1} corresponds to

the HOH bend at 1651 cm^{-1} . For the twelve $\text{H}_2\text{O}\cdots\text{O}_2$ structures discussed in the following sections, the OO and OH bond lengths change by no more than $0.004\text{ \AA}$ and the HOH bond angle by less than 0.2° .

Table 1: Equilibrium geometrical parameters (R in $\text{\AA}$, θ in degrees) of O_2 and H_2O along with harmonic vibrational frequencies (ω in cm^{-1}) and non-zero IR intensities (in parentheses in km mol^{-1})

	R(OO)	ω	R(OH)	$\theta(\text{HOH})$	ω_1	ω_2	ω_3
UMP2/haTZ	1.224	1454.7	0.961	104.1	3824.5 (7.6)	1630.1 (73.8)	3951.9 (75.8)
UMP2/haQZ	1.219	1479.7	0.959	104.3	3840.5 (6.8)	1632.8 (73.5)	3966.4 (78.5)
UCCSD(T)/haTZ	1.213	1574.4	0.962	104.2	3813.6 (4.6)	1647.9 (72.4)	3924.3 (54.9)
UCCSD(T)/haQZ	1.208	1595.7	0.959	104.4	3831.8 (4.2)	1650.5 (72.5)	3941.4 (57.8)
Experiment ^a	1.208	1580.2	0.957	104.5	3832.2 (3.2)	1648.5 (64)	3942.5 (46)
QCISD ^b Ref. [5]	—	1620.7	—	—	3879.8 (7.1)	1686.5 (65.6)	3982.0 (56.1)

^a O_2 data from [30]. H_2O R, θ and ω values from [31]. IR intensities from experimental oscillator strengths tabulated to 2 significant figures in [32].

^b QCISD/6-311++G(2d, 2p) results from supporting information in [5].

The coupled-cluster equilibrium bond lengths and bond angles obtained with the haQZ basis set are in near perfect agreement with the experimental values for both O_2 [30] and H_2O [31] provided in the last row of Table 1. For water, the experimental and coupled-cluster haQZ harmonic vibrational frequencies do not differ by more than 2.0 cm^{-1} . In contrast the UMP2 results deviate from the experimental values by roughly $10\text{--}20\text{ cm}^{-1}$ for H_2O . The high-spin open-shell O_2 system is a bit more challenging, but the experimental harmonic vibrational frequency still falls between the UCCSD(T)/haTZ and UCCSD(T)/haQZ results whereas the UMP2 method underestimates the frequency by 100 cm^{-1} or more with both basis sets. Interestingly, the QCISD/6-311++G(2d, 2p) harmonic frequencies reported in the supporting information of an earlier study [5] are consistently about 40 cm^{-1} too large for both H_2O and O_2 . The coupled-cluster IR intensities are qualitatively consistent with the experimental oscillator strengths. The coupled-cluster intensities computed with the haQZ basis set are within 12 km mol^{-1} of the experimental values (on average too large by 7 km mol^{-1} for the 3 vibrational modes of water). In contrast, the MP2 intensities are appreciably larger for the asymmetric stretch (ω_3), suggesting the intensity for that mode is nearly identical to that of the bend (ω_2) which is qualitatively different than experiment.

3.2. Nature and Structures of the Dimer

The structures in Figure 1 are shown in the order of increasing electronic energy at the UMP2/haQZ level of theory, with I as the global minimum and XII as the highest energy stationary point. Six C_{2v} structures (II, III, VII, X-XII) have been considered, one of which is a local minimum (structure VII) on the UMP2 surface. The other six stationary points have C_s symmetry (I, IV-VI, VIII, IX), including the global minimum (structure I). Although structure I is consistently identified as the global minimum here and elsewhere [6, 8, 11],

some variation in the exact orientation of the O₂ fragment relative to H₂O is observed for this stationary point. As such, the following discussion primarily focuses on the geometrical parameters of structure I. The UCCSD(T)/haQZ optimized global minimum has intermolecular angles of $\alpha=110^\circ$ and $\beta=106^\circ$ and an intermolecular separation of $R_{eq}=2.64$ Å (Fig. 1). Using either UMP2 or UCCSD(T) with a haTZ or haQZ basis, α and β change by less than $\pm 10^\circ$ for structure I. Similar parameters were reported at the QCISD/6-311++G(2*d*,2*p*) level of theory ($\alpha=126^\circ$, $\beta=109^\circ$, $R_{eq}=2.57$ Å) [5] and from MP2/aug-cc-pVTZ optimizations ($\alpha=102^\circ$, $\beta=112^\circ$, $R_{eq}=2.57$ Å) [8, 11].

Table 2: Number of imaginary frequencies n_i

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
UMP2/haTZ	0	1	1	0	1	2	0	1	2	2	1	1
UMP2/haQZ	0	1	1	1	1	2	0	1	2	2	1	2
UCCSD(T)/haTZ	0	1	1	1	1	2	1	1	2	2	1	2
UCCSD(T)/haQZ	0	1	1	1	1	2	1	1	2	2	1	2

Table 2 lists the number of imaginary frequencies associated with structures I – XII of the H₂O...O₂ complex. One of the most significant features of the data is that the number of minima changes with computational protocol. At the UMP2/haTZ level of theory, three of the stationary points (structures I, IV, and VII) examined in this study are minima. With the larger haQZ basis set, however, structure IV becomes a transition state with an a'' imaginary frequency of $37i$ cm⁻¹, whereas structure XII changes from a transition state to a second order saddle point ($n_i = 2$). Structure VII is also a transition state with both the haTZ and haQZ basis sets at the UCCSD(T) level, having a single imaginary frequency with b_2 symmetry. The global minimum is structure I, regardless of method or basis set. As can be seen in Table 2, structures II, III, IV, V, VII, VIII and XI are transition states and structures VI, IX, X and XII are second-order saddle points on the UCCSD(T)/haTZ and UCCSD(T)/haQZ surfaces.

Structure VI provides a more extreme example of this sensitivity. Reference 4 reported a minimum H₂O...O₂ structure from MP2 computations with the 6-311++G(2*df*,2*pd*) basis set that had geometrical parameters ($\alpha = 178^\circ$, $\beta = 179^\circ$, $R_{eq} = 2.43$ Å) very similar to those for structure VI at the UMP2/haTZ ($\alpha = 180^\circ$, $\beta = 169^\circ$, $R_{eq} = 2.47$ Å). However, structure VI is a second-order saddle point ($n_i = 2$) at all levels of theory employed in this study while it is a minimum at the MP2/6-311++G(2*df*,2*pd*) level of theory regardless of whether the core electrons are correlated or not. Although structure I was not considered in Reference 4, it remains a lower-energy minimum on the MP2/6-311++G(2*df*,2*pd*) potential energy surface.

Table 3 lists key UMP2/haXZ and UCCSD(T)/haXZ (X=T,Q) intermolecular separations, R_{eq} , for each optimized structure. Cartesian coordinates, harmonic vibrational frequencies, and IR intensities for every optimized structure are available in the Supplementary Material. The intermolecular separation of

Table 3: Intermolecular separations (R_{eq} in Å)

	I ^a	II ^b	III ^b	IV ^b	V ^a	VI ^a	VII ^a	VIII ^a	IX ^a	X ^a	XI ^a	XII ^a
UMP2/haTZ	2.81	3.12	3.16	3.13	2.46	2.47	2.86	2.90	2.60	2.92	3.82	3.15
UMP2/haQZ	2.75	3.14	3.20	3.16	2.47	2.48	2.87	2.91	2.62	2.92	3.83	3.18
UCCSD(T)/haTZ	2.66	3.13	3.18	3.15	2.42	2.48	2.85	2.88	2.56	2.87	3.81	3.13
UCCSD(T)/haQZ	2.64	3.17	3.22	3.18	2.43	2.49	2.87	2.89	2.54	2.88	3.83	3.15

^a R(H···O)^b R(O···MP) where MP denotes the midpoint of the OO bond

structures II-IV is measured from the midpoint of the O₂ bond to the oxygen of H₂O while R_{eq} for structures I and V-XII is the shortest intermolecular O···H distance (Fig. 1). For structures II-XII, these intermolecular parameters are quite similar regardless of method or basis set used for the optimization, never differing by more than 0.05 Å. The global minimum (structure I) has slightly larger deviations (> 0.1 Å), indicating a large basis and substantial amounts of electron correlation are needed to adequately describe the non-covalent interaction. However, R_{eq} changes by less than 0.02 Å between UCCSD(T)/haTZ and UCCSD(T)/haQZ for structure I.

3.3. Harmonic Vibrational Frequencies and IR Intensities

As shown in Table 2, structure I is the only minimum at the UCCSD(T) level of theory, and the nature of each stationary point remains consistent with both haTZ and haQZ basis sets. For this reason, after a brief discussion of experimental results, the remainder of this section will focus on the harmonic vibrational frequencies of the global minimum (structure I).

Experimentally, the ground state of the H₂O···O₂ complex determined via microwave spectroscopy has C_{2v} symmetry like that seen in structure II [14]. Computationally, however, structure II is a transition state with an imaginary frequency of b₂ symmetry at 40i cm⁻¹ at the UCCSD(T)/haQZ level of theory. A previous study investigated rotations of the O₂ and H₂O fragments in structure I and found the conrotatory motion to be degenerate while the disrotatory motion experiences a slight splitting [8]. That study noted that the transitions between these low-lying states due to the small barrier of the disrotatory intermolecular vibration would be interpreted by microwave spectroscopy as a structure with C_{2v} symmetry [8].

The UMP2 and UCCSD(T) harmonic vibrational frequencies and IR intensities are listed in Table 4. Although there is reasonable agreement between the two methods (average absolute deviations of 14 cm⁻¹ and 13 cm⁻¹ for the haTZ and haQZ basis sets, respectively), it is worth noting that the relative order of the a' and a'' intermolecular modes (ω_5 through ω_9) differs. Although an earlier study of mono-hydrated atmospheric species primarily focused on the vibrations of water, QCISD/6-311++G(2d, 2p) harmonic vibrational frequencies and IR intensities were reported in the supporting information [5]. Unfortunately, direct comparison to that data is not straightforward because the symmetry

Table 4: Harmonic vibrational frequencies (ω in cm^{-1}) and IR intensities (in parentheses in km mol^{-1}) of Structure I

Mode		UMP2 haTZ		UMP2 haQZ		UCCSD(T) haTZ		UCCSD(T) haQZ	
ω_1	a'	3947.5	(73.4)	3962.4	(76.4)	3921.8	(54.4)	3939.3	(58.6)
ω_2	a'	3819.8	(6.3)	3836.2	(5.7)	3810.6	(3.2)	3829.1	(2.9)
ω_3	a'	1642.4	(70.7)	1639.9	(78.2)	1645.2	(95.0)	1647.7	(93.6)
ω_4	a'	1574.3	(19.0)	1577.4	(11.9)	1582.9	(0.3)	1601.3	(0.4)
ω_5	a'	127.8	(42.5)	108.4	(49.6)	85.7	(71.5)	83.5	(73.7)
ω_6	a'	72.7	(16.2)	74.4	(17.6)	80.5	(9.5)	78.7	(4.9)
ω_7	a'	48.6	(28.7)	45.8	(22.6)	47.3	(13.9)	41.3	(17.2)
ω_8	a''	117.4	(0.7)	111.3	(3.4)	103.7	(4.4)	103.2	(< 0.1)
ω_9	a''	86.4	(225.5)	79.7	(217.5)	71.7	(214.8)	67.5	(215.5)

of the vibrational modes was not specified. We repeated the QCISD computations to obtain this information. While these computations exactly matched the frequencies and intensities for the fragments (Table 1), they yielded completely different values for the complex even though the electronic energies match to $0.3 \mu E_h$. Both sets of QCISD/6-311++G(2*d*, 2*p*) results are provided in the Supplementary Material accompanying this paper where differences approaching 20 cm^{-1} and 40 km mol^{-1} can be seen. When compared to the UCCSD(T)/haQZ frequencies, the performance of the UMP2 and QCISD methods are comparable in terms of their average and maximum absolute deviations.

Frequency shifts and IR intensities can often provide the means to spectroscopically identify non-covalent complexes. For the global minimum at the UMP2/haQZ level of theory, there is a substantial shift ($+98 \text{ cm}^{-1}$) and slight increase in the IR intensity (from 0 to 12 km mol^{-1}) for the OO stretch in the dimer at 1577 cm^{-1} , which can be seen in Table 4. The OO stretch is strongly coupled to the HOH bend on the UMP2 surface. However, the frequency shift decreases to only $+6 \text{ cm}^{-1}$ and the mode remains IR inactive on the UCCSD(T)/haQZ surface (1601.3 cm^{-1} and $<1 \text{ km mol}^{-1}$). At the UCCSD(T)/haQZ level of theory, the mode associated with HOH bend shifts by close to -3 cm^{-1} and has an increase in IR intensity of $+21 \text{ km mol}^{-1}$. The changes are even smaller for the symmetric and asymmetric OH stretches of H_2O , not exceeding $\pm 3 \text{ cm}^{-1}$ and $\pm 1 \text{ km mol}^{-1}$. As such, the HOH bend is the only intramonomer mode with any appreciable increase in IR intensity (from 73 to 94 km mol^{-1} , almost 29%).

By inspecting the far IR (less than 150 cm^{-1}) intermolecular modes of the $\text{H}_2\text{O} \cdots \text{O}_2$ system, another potential mechanism leading to green house effects can be evaluated. Structure I has five modes in this region (Table 4). However, only two modes have substantial IR intensities at the UCCSD(T)/haQZ level of theory. One a' mode is moderately IR active and has an intensity of 74 km mol^{-1} at 84 cm^{-1} . The largest IR intensity corresponds to the lowest energy mode of a'' symmetry at 68 cm^{-1} and with an intensity of 216 km mol^{-1} , more than double the IR intensity of any other inter- or intramolecular mode

of the $\text{H}_2\text{O} \cdots \text{O}_2$ global minimum. By way of comparison, analogous frequency computations on $(\text{H}_2\text{O})_2$ indicate that the lowest-energy intermolecular mode has appreciably higher energy (126.1 cm^{-1}) and less than half the IR intensity (*ca.* 90.7 km mol^{-1}) [33].

3.4. Energetics

Relative electronic energies of structures I-XII with respect to the global minimum (structure I) are listed in Table 5. In addition to UMP2/haXZ and UCCSD(T)/haXZ energies, ROMP2 and ROCCSD(T) single point computations were performed based on the corresponding UMP2/haXZ or UCCSD(T)/haXZ optimized geometry. Explicitly correlated UCCSD(T)-F12 and ROCCSD(T)-F12 energies at UCCSD(T)/haQZ optimized geometries were included to probe convergence to the CBS limit. It is readily apparent from Table 5 that the potential energy surface is extremely flat with all relative electronic energies within $0.5 \text{ kcal mol}^{-1}$ of the global minimum for structures II-XII. Energetically, increasing the basis set from haTZ to haQZ has little effect, less than $0.05 \text{ kcal mol}^{-1}$ for UMP2 or UCCSD(T). As expected from the diradical nature of O_2 and $\text{H}_2\text{O} \cdots \text{O}_2$, the energetics are more sensitive to electron correlation than basis set effects with maximum deviations of $0.08 \text{ kcal mol}^{-1}$ when comparing UMP2 to UCCSD(T).

The spin formalism has a noticeable affect on the MP2 results. ROMP2 underestimates the relative electronic energies by more than $0.1 \text{ kcal mol}^{-1}$ in some cases. In contrast, the spin restricted and unrestricted coupled-cluster results are virtually indistinguishable. ROCCSD(T)/haXZ and UCCSD(T)/haXZ have deviations less than $0.01 \text{ kcal mol}^{-1}$. UCCSD(T)-F12/ha5Z and ROCCSD(T)-F12/ha5Z differ by no more than $0.02 \text{ kcal mol}^{-1}$. The T_1 and D_1 diagnostics [34] from these explicitly correlated coupled-cluster computations with the ha5Z basis set never exceed 0.01 and 0.02, respectively.

Table 5: Relative Electronic Energies in kcal mol^{-1}

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	D_e^a
UMP2/haTZ	0.00	0.06	0.13	0.15	0.25	0.27	0.27	0.29	0.32	0.31	0.33	0.45	0.72
UMP2/haQZ	0.00	0.07	0.16	0.17	0.23	0.26	0.28	0.30	0.30	0.31	0.38	0.47	0.70
ROMP2/haTZ ^b	0.00	0.01	0.05	0.05	0.23	0.21	0.12	0.19	0.29	0.25	0.13	0.25	0.56
ROMP2/haQZ ^b	0.00	0.01	0.07	0.06	0.18	0.18	0.12	0.19	0.24	0.24	0.17	0.27	0.53
UCCSD(T)/haTZ	0.00	0.10	0.16	0.18	0.17	0.28	0.28	0.28	0.25	0.28	0.33	0.44	0.74
UCCSD(T)/haQZ	0.00	0.11	0.18	0.19	0.18	0.27	0.26	0.27	0.24	0.28	0.37	0.44	0.70
ROCCSD(T)/haTZ ^b	0.00	0.10	0.16	0.18	0.17	0.28	0.28	0.28	0.25	0.28	0.33	0.44	0.74
ROCCSD(T)/haQZ ^b	0.00	0.11	0.17	0.19	0.18	0.27	0.26	0.27	0.24	0.28	0.37	0.44	0.69
UCCSD(T)-F12a/ha5Z ^c	0.00	0.11	0.18	0.19	0.18	0.27	0.25	0.26	0.23	0.28	0.38	0.43	0.66
UCCSD(T)-F12b/ha5Z ^c	0.00	0.11	0.18	0.19	0.18	0.27	0.25	0.26	0.23	0.28	0.39	0.43	0.66
ROCCSD(T)-F12a/ha5Z ^c	0.00	0.09	0.17	0.18	0.18	0.26	0.23	0.24	0.22	0.26	0.37	0.42	0.64
ROCCSD(T)-F12b/ha5Z ^c	0.00	0.09	0.17	0.18	0.18	0.26	0.23	0.24	0.22	0.26	0.37	0.42	0.64

^a $D_e = E(\text{O}_2) + E(\text{H}_2\text{O}) - E(\text{I})$

^b Single point energies with UMP2/haXZ or UCCSD(T)/haXZ optimized structures

^c Single point energies with UCCSD(T)/haQZ optimized structures

The deviations between UCCSD(T)/haQZ and UCCSD(T)-F12/ha5Z relative electronic energies are less than $0.02 \text{ kcal mol}^{-1}$, indicating that this property is well converged to the CBS limit. The electronic dissociation energies (D_e , the energy of the fully optimized isolated monomers relative to structure I) obtained with the explicitly correlated methods, tend to be about $0.04 \text{ kcal mol}^{-1}$ smaller than the corresponding UCCSD(T)/haQZ and ROCCSD(T)/haQZ results. D_e is $0.70 \text{ kcal mol}^{-1}$ on both UMP2/haQZ and UCCSD(T)/haQZ surfaces, which decreases to $\approx 0.65 \text{ kcal mol}^{-1}$ according to the explicitly correlated coupled-cluster computations. Previous estimates from MP2/aug-cc-pVTZ and QCISD/6-311++G(2*d*,2*p*) computations are nearly identical, predicting slightly larger energies of 0.76 and $0.72 \text{ kcal mol}^{-1}$, respectively [5, 8, 11]. Correcting the UCCSD(T)/haQZ electronic dissociation energy with the harmonic zero-point vibrational energy, yields a D_0 value of $0.17 \text{ kcal mol}^{-1}$. Interestingly, the dimer is slightly unbound on the UMP2/haQZ surface ($D_0 = -0.04 \text{ kcal mol}^{-1}$), but both values would certainly change if anharmonic effects were evaluated.

Figure 2: Global minima of the $\text{H}_2\text{O} \cdots \text{O}_2$ (left) and $\text{H}_2\text{O} \cdots \text{N}_2$ (right) dimers along with select intermolecular geometrical parameters (R_{eq} , α , β) described in the text.

3.5. Comparison to $\text{H}_2\text{O} \cdots \text{N}_2$

The results obtained in this study for the $\text{H}_2\text{O} \cdots \text{O}_2$ global minimum brings up several interesting points of divergence with the related $\text{H}_2\text{O} \cdots \text{N}_2$ van der Waals system (Fig. 2). The following section compares and contrasts geometrical parameters, harmonic vibrational frequencies, IR intensities, and energetics of the $\text{H}_2\text{O} \cdots \text{O}_2$ global minimum to those of the $\text{H}_2\text{O} \cdots \text{N}_2$ global minimum.

Geometrically, the global minimum of the $\text{H}_2\text{O} \cdots \text{N}_2$ complex has the greatest similarity to structure VI of the $\text{H}_2\text{O} \cdots \text{O}_2$ system, a second-order saddle point on the UCCSD(T)/haQZ surface. The CCSD(T)/haQZ intermolecular arrangement of the $\text{H}_2\text{O} \cdots \text{N}_2$ minimum is more linear, with both α and β (Fig. 2) near 170° compared to roughly 110° in the $\text{H}_2\text{O} \cdots \text{O}_2$ global minimum. R_{eq} of the $\text{H}_2\text{O} \cdots \text{N}_2$ global minimum is $2.35 \text{ \AA}$, nearly $0.3 \text{ \AA}$ shorter than the corresponding intermolecular separation in structure I of the $\text{H}_2\text{O} \cdots \text{O}_2$ system [7].

Although the potential energy surface of $\text{H}_2\text{O} \cdots \text{N}_2$ is also quite flat, no discrepancies in the number of imaginary frequencies were observed for any structure when using the same basis sets and comparable electronic structure methods. As with $\text{H}_2\text{O} \cdots \text{O}_2$, frequency shifts upon complexation are small according to coupled-cluster computations, although the associated IR intensity changes are generally larger for $\text{H}_2\text{O} \cdots \text{N}_2$ (e.g., roughly $+60 \text{ km mol}^{-1}$ and

+20 km mol⁻¹ for the asymmetric and symmetric OH stretches, respectively) [7]. The global minimum of H₂O...N₂ has only a single intermolecular mode in the far IR with moderate IR intensity on the CCSD(T)/haQZ surface: an a' mode at 165 cm⁻¹ with an intensity of 81 km mol⁻¹, which is smaller than that of the intramolecular OH asymmetric stretch (117 km mol⁻¹) [7]. In contrast, the H₂O...O₂ complex, has an a'' intermolecular mode at 68 cm⁻¹ with an IR intensity of 216 km mol⁻¹ which is more than two times larger than that of any other mode.

The global minimum of the H₂O...N₂ system has a dissociation energy of 1.22 kcal mol⁻¹ at the CCSD(T) CBS limit estimated from CCSD(T)-F12/ha5Z computations. Comparatively, structure I of H₂O...O₂ has a CCSD(T) CBS D_e of 0.65 kcal mol⁻¹ estimated from ROCCSD(T)-F12/ha5Z and UCCSD(T)-F12/ha5Z explicitly correlated coupled-cluster computations.

4. Conclusions

To summarize the results of this research, structure I is the only minimum on the UCCSD(T)/haQZ surface out of the twelve H₂O...O₂ stationary points examined. The global minimum has an electronic dissociation energy of approximately 0.65 kcal mol⁻¹ near the CCSD(T) CBS limit. According to coupled-cluster theory, there were no significant frequency shifts, IR intensity changes, or geometrical changes of the fragments upon complexation. Although the UMP2 energetics are similar to those from coupled-cluster computations, the method incorrectly identifies two structures as minima. In addition, the UMP2 results suggest the OO harmonic frequency shift upon complexation is substantially larger (ca. +100 cm⁻¹) than the UCCSD(T) value (ca. +5 cm⁻¹). Both methods indicate there are two intermolecular modes (one a' and one a'') with appreciable IR intensity in the far IR region. The IR intensity of the lowest a'' mode exceeds 200 km mol⁻¹, which is more than double the largest IR intensity of any other mode. Even though the related H₂O...N₂ complex is more strongly bound, it does not possess any intermolecular vibrational modes with IR intensities as large as those seen here for the H₂O...O₂ system.

5. Acknowledgements

This work was supported in part by the National Science Foundation (EPS-0903787, CHE-1338056). The Mississippi Center for Supercomputing Research (MCSR) also provided a generous allocation of time on their resources. Katelyn Mae Dreux would also like to thank Thomas Ellington for helpful discussions concerning and additional data for the H₂O...N₂ system. The authors also thank Coleman Howard for providing the IR intensities associated with the CCSD(T)/haQZ harmonic vibrational frequencies reported in Reference [33]

Appendix A. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/x>.

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Graphical Abstract

The global minimum on the H₂O...O₂ potential energy surface has been identified with an electronic dissociation energy of 0.65 kcal mol⁻¹ at the UCCSD(T) complete basis set limit.