van der Waals Complexes of Water with Oxygen and Nitrogen: Infrared Spectra and Atmospheric Implications

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Weakly bonded complexes of water with oxygen and nitrogen are studied using ab initio methods; their thermodynamic functions and infrared spectra are calculated. Infrared spectra for these complexes exhibit several interaction-induced low-frequency modes, while their estimated atmospheric fractions appear to be larger than for many recognized "greenhouse" species. This implies that atmospheric H_2O-O_2 and H_2O-N_2 complexes may absorb more of the earth's surface radiation than individual molecules and thus contribute to a "greenhouse" effect.

1. Introduction

Atmospheric water vapor plays an important role in the radiative balance of the earth. Water molecules can absorb both the short-wavelength solar radiation arriving in the atmosphere and the outgoing infrared (IR) surface radiation.[1] Current observations and climate models suggest that atmospheric absorption due to water vapor across the far-IR (wavenumbers smaller than 500 cm^{-1}) may have a particularly significant "greenhouse" effect upon the earth's climate system.[2,3] Pure rotational bands of water that lie in the far-IR are now explicitly accounted for in climate (radiative transfer) models.[3] We will argue here that an additional "greenhouse" trapping of the long-wavelength IR radiation may result from an interaction of water vapor with major atmospheric gases, such as oxygen and nitrogen.

It is now well-documented that the water molecule can form weak (van der Waals) complexes with O_2 and N_2.[4−6] Although individual O_2 and N_2 molecules are transparent in the far-IR region, their interactions with water molecules may induce low-frequency intermolecular modes that can absorb IR radiation. The H_2O-N_2 complex has been recently studied by Mokomela et al.[4] using high-level ab initio calculations. They have examined its electronic structure and IR spectrum and have found several low-lying interaction-induced vibrational modes. Theoretical electronic structure studies have been carried out for the H_2O-O_2 complex.[5,6] However, no IR data have been reported, presumably due to difficulties in converging the ground-state configuration to a global minimum.[5]

It is the main purpose of this ab initio study to investigate the ground-state configurations for the H_2O-O_2 cluster and to determine its infrared absorption properties. We also report the IR spectrum for the H_2O-N_2 complex determined at the same level of theory. Finally, we estimate the equilibrium concentrations of the van der Waals H_2O-N_2 and H_2O-O_2 complexes under ambient atmospheric conditions.

2. Computational Details

Ab initio electronic structure calculations for the H_2O-O_2 and H_2O-N_2 systems were performed using the Gaussian-92 program.[7] The chosen basis set, 6-311++G(2d,2p), contains both polarization and diffuse functions; earlier studies employing smaller basis sets had difficulties in locating the global minimum-energy configuration.[5,6] It is worth noting that this rather large basis set was found to describe reasonably accurately the water dimer, including its geometry and infrared spectrum.[14] The second-order Møller−Plesset perturbation theory (MP2-(full) method) was employed to account for the effects of electron correlation.[8] Several complementary electronic structure calculations were performed using the MP4(full) and density-functional (B3LYP) methods.[9] The basis set superposition error (BSSE) was estimated using the counterpoise correction technique of Boys and Bernardi.[10]

3. Results and Discussion

Five possible ground-state configurations for the H_2O-O_2 complex have been examined. Their geometries optimized at the MP2(full)/6-311++G(2d,2p) level are shown in Figure 1. Their total and binding energies and the counterpoise estimates of the BSSE are listed in Table 1. These results essentially confirm previous investigations in that various dimer conformations differ only slightly in their stability and that the energy surface for the H_2O-O_2 complex exhibits a few flat shallow depressions.[5,6] Configurations **I−IV** have been studied by Palmer, Byers Brown, and Hillier[6] and by Seminario, Concha, Murray, and Politzer[5] using respectively 6-311++G(2d,p) and 6-311+G(d,p) basis sets. The latter authors have carried out an analysis of the vibrational frequencies and have found imaginary values, indicating that these H_2O-O_2 configurations do not correspond to a global minimum. In addition to configurations **I−IV** we have considered the linear "hydrogen-bonded" dimer **V**, and it is this H_2O-O_2 arrangement that appears to have the lowest energy. We point out that a similar structure has been identified by Mokomela et al.[4] as the most stable H_2O-N_2 configuration.

We have performed single-point energy calculations at the MP4(full)/6-311++G(2d,2p) and the density functional, B3LYP/6-311++G(2d,2p), levels for two H_2O-O_2 configurations, **I**

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TABLE 1: Total and the Binding Energies, E_{tot} and E_b, Respectively, and the Basis Set Superpositon Errors, BSSE[a]

	MP2[b]			MP4[c]			B3LYP[d]		
structure	E_{tot}	E_b	BSSE	E_{tot}	E_b	BSSE	E_{tot}	E_b	BSSE
H_2O	−76.317 357			−76.330 658			−76.461 966		
O_2	−150.103 868			−150.125 956			−150.373 941		
H_2O-O_2 **(I)**	−226.422 267	−0.001 042	0.000 447	−226.457 645	−0.001 032	0.000 380	−226.836 110	−0.000 203	0.000 111
H_2O-O_2 **(II)**	−226.422 177	−0.000 952	0.000 334						
H_2O-O_2 **(III)**	−226.421 899	−0.000 674	0.000 462						
H_2O-O_2 **(IV)**	−226.422 147	−0.000 922	0.000 300						
H_2O-O_2 **(V)**	−226.422 316	−0.001 094	0.000 293	−226.457 774	−0.001 160	0.000 294	−226.836 168	−0.000 261	0.000 113
N_2	−109.363 508								
H_2O-N_2 **(V)**	−185.683338	−0.002473	0.000735						

[a] E_b is defined as $E_b = E_{tot}(\text{complex}) - \sum E_{tot}(\text{reactant})$. All energies are in hartrees. [b] MP2(full)/6-311++G(2d,2p)//MP2(full)/6-311++G(2d,2p).¶ [c]MP4(full)/6-311++G(2d,2p)//MP2(full)/6-311++G(2d,2p). [d] B3LYP/6-311++G(2d,2p)//MP2(full)/6-311++G(2d,2p).

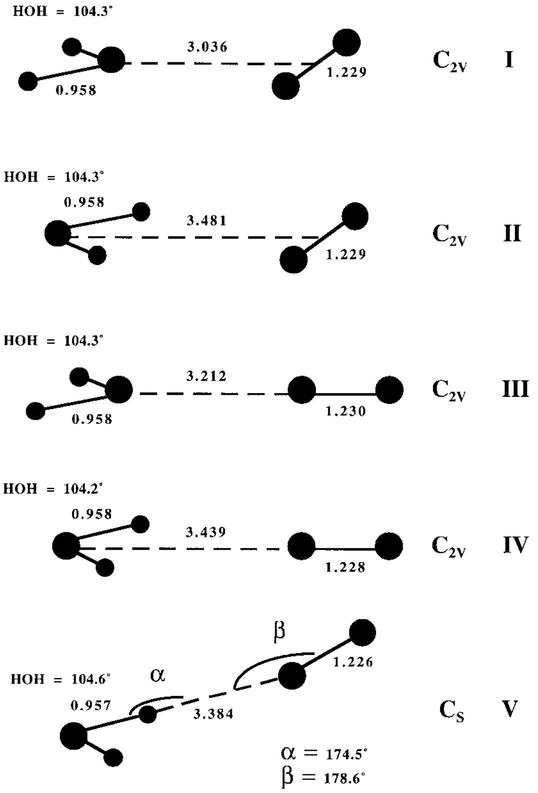

Figure 1. MP2(full)/6-311++G(2d,2p) optimized geometries for various H_2O-O_2 configurations and their point groups. Distances are in angstroms and angles are in degrees. For the isolated water molecule $\angle OHO = 104.4°$ and $R_{OH} = 0.957$ Å; for the oxygen molecule $R_{OO} = 1.230$ Å.

and **V**. These results are included in Table 1. MP4 binding energies conform well with their MP2 values, while B3LYP values are significantly smaller (by about 80%). These observations are consistent with those of Jeong and Han,[11] who noted difficulties in properly describing van der Waals complexes of ethene and ethyne with chlorine using density functional methods (such as B3LYP and BLYP).

The infrared vibrational frequencies (wavenumbers) and intensities for the lowest energy (with no negative eigenvalues) H_2O-O_2 configuration **V** are listed in Table 2. We have also calculated the IR spectrum for the H_2O-N_2 complex with the same geometry, **V**, at the same level of theory, MP2(full)/6-311++G(2d,2p)//MP2(full)/6-311++G(2d,2p). These results can be found in Table 2. Both complexes exhibit a number of intense interaction-induced vibrational modes lying in the far-IR region of the spectrum (at 95 and 133 cm^{-1} for H_2O-O_2 and at 181 and 269 cm^{-1} for H_2O-N_2). It would be interesting to examine in future studies the anharmonicity effects on these intermolecular vibrations.

TABLE 2: Infrared Spectra for H_2O-O_2 (V), H_2O-N_2 (V), and H_2O[a]

H_2O-O_2		H_2O-N_2		H_2O	
freq (cm$^{-1)}$	int (km/mol)	freq (cm^{-1})	int (km/mol)	freq (cm^{-1})	int (km/mol)
39.5	2.8	70.1	14.2		
43.5	3.7	81.1	0.01		
57.8	0.4	91.2	1.7		
95.7	86.8	181.1	82.6		
133.2	123.6	269.1	91.6		
1482.2	0.3	1668.0	51.7		
1664.4	60.7	2182.6	0.34	1660.7	66.0
3872.4	17.1	3867.7	34.3	3869.8	10.2
3981.25	104.1	3985.0	149.9	3990.1	74.5

[a] Vibrational frequencies for individual O_2 and N_2 molecules are 1435.8 and 2179.4 cm^{-1}, respectively. Their IR intensities are zero.

TABLE 3: Dimerization Enthalpies, ΔH, Entropies, ΔS, and Gibbs Free Energies, $\Delta G = \Delta H - T\Delta S$, at 298.16 K and 1 atm, for H_2O-O_2 (V) and H_2O-N_2 (V)

function	H_2O-O_2	H_2O-N_2
ΔH (kJ/mol)	1.33	−2.17
ΔS (J/(mol deg))	−0.046	−0.068
ΔG (kJ/mol)	15.12	18.23

The thermochemical data, the dimerization enthalpies, ΔH, and entropies, ΔS, at 298.16 K and 1 atm, for the H_2O-O_2 and H_2O-N_2 complexes are given in Table 3. These data enabled us to estimate their equilibrium atmospheric concentrations under ambient conditions ($T = 298.16$ K and total $P = 1$ atm), using the standard expression

$$\Delta G = \Delta H - T\Delta S = -RT \ln\left(\frac{P[H_2O-O_2]}{P[H_2O]\,P[O_2]}\right) \qquad (1)$$

where P denotes the partial pressures of the species. In the atmosphere oxygen and nitrogen remain at fairly constant concentrations (or partial pressures), at approximately 21 and 78 vol %, respectively. The water vapor fraction varies significantly depending upon climate and weather conditions; we have assumed 1% as an approximate estimate.[12] Substituting these into eq 1 gives the equilibrium concentrations of about 0.000 48% (4.8 ppm, parts per million) and 0.000 50% (5 ppm) for H_2O-O_2 and H_2O-N_2, respectively. It is necessary to emphasize that the estimated atmospheric concentrations for H_2O-O_2 and H_2O-N_2 are larger than those for CH_4 (1.7 ppm), N_2O (0.31 ppm), CO (0.03−02 ppm), and CFCs and their replacements (0.01−0.6 ppb), the species that are believed to be crucially important in “greenhouse” forcing of the climate.[13]

In principle, the water dimer which exhibits several interaction-induced low-frequency IR modes may also contribute to a "greenhouse" effect. We have estimated the equilibrium concentration of the water dimer under ambient atmospheric conditions using ab initio, MP2(full)/6-311++G(2d,2p), thermochemical data obtained by Kim et al.[14] It follows from these estimates that the water dimer with its ambient concentration of about 0.43 ppm is far less abundant in the atmosphere than H_2O-O_2 or H_2O-N_2, by approximately an order of magnitude.

In this work we have analyzed the stability and the infrared spectra of the H_2O-O_2 and H_2O-N_2 complexes using high-level ab initio calculations. These van der Waals complexes exhibit a number of low-frequency intermolecular vibrational modes which can absorb long-wavelength IR radiation, and they are more abundant in the atmosphere than many other "greenhouse" species. Atmospheric complexes of water with oxygen and nitrogen appear to be an important yet unaccounted factor in our understanding of a "greenhouse" effect. Further efforts are clearly needed to incorporate our theoretical results into climate models; this work is currently underway.

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