# Existence of a Hydroperoxy and Water (HO 2 ·H 2 O) Radical Complex

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# Existence of a Hydroperoxy and Water ($HO_2 \cdot H_2O$) Radical Complex

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The structure, vibrational spectrum, and binding energy of $HO_2 \cdot H_2O$ are predicted using ab initio molecular methods. Theory predicts that the $HO_2 \cdot H_2O$ complex is bound by 6.9 kcal $mol^{-1}$. The equilibrium structure and rotational constants of the complex have been determined. The OH stretching frequency of the $HO_2$ is red-shifted by 296 $cm^{-1}$ from the isolated molecule. Its infrared intensity is also enhanced by 22 times that of the monomer.

## I. Introduction

Despite the fact that many measurements of weakly bound species have been made in the laboratory, little is known of the role these species play in the chemistry of the atmosphere. Recently, experimental[1] and theoretical studies[2] of the $SO_3 \cdot H_2O$ complex have shown that such species can act to enhance reaction rates. A $ClO \cdot H_2O$ complex has been suggested to enhance the rate of ClO dimer formation.[3] Studies by Frost and Vaida[4] have shown that photodissociation of $O_3 \cdot H_2O$ complexes can lead to the production of more $O(^1D)$, which would lead to the formation of more OH radicals in the troposphere. The role the $HO_x$ family plays (OH and $HO_2$ radicals) is quite important with regard to stratospheric ozone chemistry. Moreover, these species are important in tropospheric oxidation processes. In regions of the atmosphere where the temperature is low or where water-vapor concentration is high, the atmospheric conditions are such that the formation of an association complex, i.e., $HO_2 \cdot H_2O$, is likely. The existence of an $HO_2 \cdot H_2O$ complex has been suggested from previous laboratory studies[5−8] in which the complex has been suggested to enhance the rate of $H_2O_2$ formation by as much as a factor of 3. To date, no study has been reported on the experimental detection of an $HO_2 \cdot H_2O$ complex. In this paper, we use ab initio calculations to determine the stability of the $HO_2 \cdot H_2O$ complex and provide some predictions of its vibrational and rotational spectra that could facilitate the experimental characterization of the complex. We estimate the equilibrium constant for the formation of the complex from the results of the calculations, which is then used to assess if such complexes could be formed in sufficient quantity to play a role in the chemistry of the atmosphere.

## II. Computational Methods

All calculations were performed using GAUSSIAN 94.[9] Geometries for the $HO_2 \cdot H_2O$ complex were optimized with unrestricted second-order Møller−Plesset theory (UMP2).[10,11] They were also done with the Becke's nonlocal three-parameter exchange and correlation functional[12] with the Lee−Yang−Parr correlation functional method (B3LYP).[13] Calculations were performed with a range of medium-to-large basis sets such as 6-31G(d), 6-31++G(d), 6-311++G(d), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(2df,2p), and 6-311++G(3df, 3pd).[14,15] Single-point energy calculations were done using the unrestricted coupled cluster method including single and double excitation and including perturbational estimates of the effects of connected triple excitation [CCSD(T)].[16,17] Vibrational frequencies and zero-point energies for the complexes and their respective monomers were calculated using both MP2 and B3LYP methods. Basis set superposition errors were calculated by applying the full Boys−Bernardi counterpoise correction scheme.[18]

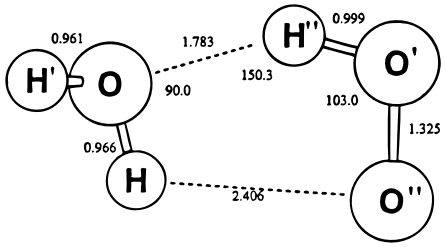


**Figure 1.** Optimized structure for $HO_2 \cdot H_2O$ radical complex. Distances are in angstroms and bond angles are in degrees. The numbers are calculated at the B3LYP/6-311++G(3df,3pd) level of theory. The full geometry can be obtained from the supplemental table.

## III. Results and Discussion

Other researchers[19,20] performed initial ab initio calculations of the $HO_2 \cdot H_2O$ complex using an STO-3G[19,20] and the 4-31G[20] basis set. Their study did not use a fully optimized structure, only a constrained structure. The authors did not perform a frequency calculation on their structure to verify if it was indeed a true minima. We found that the Hamilton and Naleway[19] structure was a saddle point. In that structure, the oxygen of the water $H_2O$ and the hydrogen and middle oxygen of the $HO_2$ are constrained to be collinear. Also, the hydrogen-bond axis is constrained to be in the $\sigma_v$ plane of the water, which fixes the hydrogen atoms of the water to be symmetrical with respect to the hydrogen bond. This does not allow these hydrogen atoms to interact with the terminal oxygen on the $HO_2$ molecule. Rao et al.[20] used a similar structure in their calculation. Figure 1 depicts the most stable conformer we found for the $HO_2 \cdot H_2O$ complex. In the complex, the hydrogen from the $HO_2$ is weakly bound to the oxygen from the water. There is also an attractive interaction between the terminal oxygen in the peroxy radical and one of the hydrogens on the water. This causes the structure to have a floppy five-membered

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**TABLE 1: Geometry of Complexes B3LYP and MP2[a]**

| | bond lengths | | | | | | bond angles | | | | dihedrals | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| basis set | R | O″H | HO | H′O | H″O′ | O′O″ | HOH′ | H′OH″ | OH″O′ | H″O′O″ | dHH′OH″ | dH′OH″O′ | dOH″O′O″ |
| | | | | | | (a) B3LYP | | | | | | | |
| 6-31G(d) | 1.761 | 2.102 | 0.978 | 0.970 | 1.004 | 1.331 | 104.6 | 81.9 | 144.6 | 102.6 | 250.5 | 359.0 | 2.9 |
| 6-31++G(d) | 1.765 | 2.638 | 0.972 | 0.970 | 0.999 | 1.334 | 108.2 | 97.6 | 154.7 | 103.5 | 135.8 | 359.5 | 1.4 |
| 6-311++G(d) | 1.742 | 2.893 | 0.964 | 0.963 | 0.991 | 1.328 | 108.2 | 107.1 | 158.6 | 104.7 | 220.2 | 359.2 | 0.9 |
| 6-311++G(d,p) | 1.774 | 2.627 | 0.965 | 0.962 | 0.992 | 1.328 | 106.5 | 99.1 | 152.8 | 103.9 | 227.1 | 354.9 | 3.8 |
| 6-311++G(2d,2p) | 1.791 | 2.404 | 0.966 | 0.961 | 0.991 | 1.328 | 106.2 | 90.1 | 149.6 | 103.5 | 237.0 | 354.4 | 4.2 |
| 6-311++G(2df,2p) | 1.796 | 2.425 | 0.966 | 0.961 | 0.991 | 1.325 | 106.3 | 90.9 | 149.6 | 103.7 | 235.1 | 354.6 | 3.9 |
| 6-311++G(3df,3pd) | 1.781 | 2.406 | 0.966 | 0.961 | 0.999 | 1.325 | 106.1 | 90.0 | 150.3 | 103.0 | 235.9 | 354.3 | 4.3 |
| | | | | | | (b) MP2 | | | | | | | |
| 6-31G(d) | 1.893 | 2.895 | 0.949 | 0.948 | 0.960 | 1.310 | 106.2 | 102.0 | 157.3 | 104.6 | 232.5 | 356.5 | 11.6 |
| 6-31++G(d) | 1.778 | 2.833 | 0.974 | 0.973 | 0.997 | 1.323 | 105.9 | 101.8 | 159.3 | 103.3 | 232.6 | 358.7 | 2.1 |
| 6-311++G(d) | 1.759 | 3.047 | 0.960 | 0.959 | 0.982 | 1.304 | 108.4 | 111.7 | 161.2 | 105.1 | 210.5 | 357.5 | 1.8 |
| 6-311++G(d,p) | 1.766 | 2.927 | 0.961 | 0.960 | 0.983 | 1.306 | 104.7 | 106.7 | 160.5 | 103.7 | 225.0 | 357.3 | 4.6 |
| 6-311++G(2d,2p) | 1.783 | 2.536 | 0.962 | 0.958 | 0.983 | 1.312 | 105.3 | 93.3 | 153.7 | 103.1 | 235.2 | 354.4 | 4.5 |
| 6-311++G(2df,2p) | 1.789 | 2.535 | 0.962 | 0.958 | 0.990 | 1.301 | 104.9 | 91.4 | 152.9 | 103.5 | 251.1 | 354.9 | 4.5 |

[a] All bond distances are reported in angstroms. All bond angles and dihedrals are reported in degrees.

**TABLE 2: Rotational Constants for the $HO_2 \cdot H_2O$ Complex**

| | rotational constants[a] | | |
|---|---|---|---|
| | *A* | *B* | *C* |
| UMP2/6-311++G(2d,2p) | 33 325 | 5706 | 4921 |
| B3LYP/6-311++G(2d,2p) | 32 186 | 5859 | 5009 |
| UMP2/6-311++G(2df,2p) | 33 528 | 5861 | 5036 |
| B3LYP/6-311++G(2df,2p) | 32 375 | 5824 | 4986 |
| B3LYP/6-311++G(3df,3pd) | 32 510 | 5862 | 5018 |

[a] All rotaional constants are reported in MHz.

ring like structure with an additional hydrogen from the water out of the plane. The bond distances and angles are listed in Table 1. We did explore other structures on the $HO_2 \cdot H_2O$ potential energy surface but found that these structures were not local or global minimas.

We used two different optimization methods in order to explore the potential energy surface to look for minima. The first is the second-order Møller−Plessett perturbation method, and the second is the B3LYP density functional theory method. We used a range of basis sets, from the 6-31G(d) to the 6-311++G(3df,3pd). Both methods yielded similar geometries. Del Bene et al.[21] found that density functional B3LYP/6-31G(d,p) calculations fail to yield reliable intermolecular distances for selected closed-shell hydrogen-bonded complexes. They did, however, find that the addition of diffuse functions improved the agreement but generally found that MP2 results were better. In the present study of $HO_2 \cdots H_2O$, we have performed calculations with both B3LYP and MP2 methods. We find that with the 6-31G(d,p) and the 6-31++G(d) basis sets there are very large differences in the geometry for the intermolecular distances as suggested by Del Bene et al.[21] For example the O″H bond distance is 2.102 Å at the B3LYP/6-31G(d) level, while at the MP2/6-31G(d) level it is 2.895 Å. However, with the large basis sets we find that the results for the MP2 and B3LYP converge. We also performed frequency calculations using these levels of theory and basis sets. The density functional theory method seemed to provide frequencies and intensities closer to those published in the case of the isolated monomers.

The rotational constants for the optimized structure at various levels of theory are reported in Table 2. From the rotational constants, as well as the structure, it is evident that the molecule is an asymmetric rotor. The rotational constants show that spectroscopically $HO_2 \cdots H_2O$ will almost behave like an oblate symmetric rotor because $B_A > B_B \approx B_C$. Since this molecule has a permanent dipole moment, it should be active in the microwave region of the spectrum. This information is useful in characterizing the rotational and the rovibrational spectra of the $HO_2 \cdot H_2O$ complex.

The calculated binding energies for the $HO_2 \cdot H_2O$ complex are given in Table 3. Using the 6-311++G(2d,2p) basis set, we find the predicted $D_e$ to be 9.4 kcal mol$^{-1}$ for UMP2 and 8.9 kcal mol$^{-1}$ for B3LYP methods. Extension of the basis set to the large 6-311++G(3df,3pd) modestly decreases the predicted $D_e$ to 8.8 kcal mol$^{-1}$. This is consistent with the small structural charges between 6-311++G(2d,2p) and 6-311++G(3df,3pd) optimized geometries. The binding energy for $HO_2 \cdot H_2O$ predicts that the complex is more tightly bound than the $HO \cdot H_2O$ complex,[22,23] which has an estimated $D_e$ of 5.6 kcal mol$^{-1}$. It is also higher than the $HO_2 \cdot H_2O$ dimer binding energy studied by Rao et al.[20] At the highest level of theory, CCSD(T)/6-311++G(2df,2p)// B3LYP/6-311++G(2df,2p), the $D_e$ is 9.4 kcal mol$^{-1}$ for $HO_2 \cdot H_2O$. Corrections for vibrational zero-point energy yield a value of $D_0$ of 6.9 kcal mol$^{-1}$. This correction is probably exaggerated because the vibrational zero-point energy correction is calculated in the harmonic approximation, while the actual potential energy surface for the $HO_2 \cdot H_2O$ is anharmonic. The basis set superposition error for this energy calculation is estimated to be 1.0 kcal mol$^{-1}$. With such large binding energies, these calculations suggest that the $HO_2 \cdot H_2O$ complex should be experimentally observable.

Using the experimental binding energy and the thermal energy, we computed the change in enthalpy, $\Delta H$, and the change in entropy, $\Delta S$, at 298 K for reaction 1:

$$HO_2 + H_2O \rightarrow HO_2 \cdot H_2O \qquad (1)$$

The change in enthalpy was calculated using the difference in the electronic and thermal energies of the products and reactants using the following equation

$$\Delta H = (\Delta E_e + \Delta E_{th})_{prod.} - (\Delta E_e + \Delta E_{th})_{react.} - RT \qquad (2)$$

where $\Delta E_e$ is the electronic energy; $\Delta E_{th}$ is the thermal energy, which includes the translational, rotational, and vibrational energies; and the $-RT$ term is included because 1 mol of gas is being lost in this reaction. The enthalpy change we calculated is −7.6 kcal mol$^{-1}$. This is similar to the enthalpy change calculated by Hamilton and Naleway of −7.4 kcal mol$^{-1}$, in which the authors estimated the vibrational energy of the complex by using the data available for the water dimer. The change in entropy at 298 K has been calculated to be −25.5

**TABLE 3: $HO_2 \cdot H_2O$ Complex Binding Energy**

| | $HO_2 \cdot H_2O$ | | $HO_2$ | | $H_2O$ | | binding energy[b] | |
|---|---|---|---|---|---|---|---|---|
| levels of theory | energy[a] | ZPE corrected | energy[a] | ZPE corrected | energy[a] | ZPE corrected | $D_e$ | $D_0$ |
| UMP2/6-311++G(2d,2p) | −227.0048 | −226.9644 | −150.6725 | −150.6579 | −76.3174 | −76.2957 | 9.4 | 6.8 |
| B3LYP/6-311++G(2d,2p) | −227.4401 | −227.4004 | −150.9639 | −150.9497 | −76.4620 | −76.4407 | 8.9 | 6.3 |
| UMP2/6-311++G(2df,2p) | −227.0639 | −227.0235 | −150.7124 | −150.6978 | −76.3362 | −76.3145 | 9.6 | 7.0 |
| B3LYP/6-311++G(2df,2p) | −227.4435 | −227.4039 | −150.9668 | −150.9526 | −76.4626 | −76.4413 | 8.8 | 6.3 |
| B3LYP/6-311++G(3df,3pd) | −227.4469 | −227.4073 | −150.9683 | −150.9542 | −76.4645 | −76.4432 | 8.8 | 6.2 |
| CCSD(T)/6-311++G(2df,2p) | −227.0468 | −227.0072 | −150.7035 | −150.6894 | −76.3282 | −76.3069 | 9.4 | 6.9 |

[a] Single point calculated with the B3LYP/6-311++G(2df,2p) geometry. [b] Binding energies are in kcal $mol^{-1}$.

**TABLE 4: Harmonic Vibrational Frequencies ($cm^{-1}$) and Intensities (km $mol^{-1}$) for the $HO_2 \cdot H_2O$ Complex**

| | | frequency ($cm^{-1}$) [shift ($cm^{-1}$)][a] | | | intensity (km $mol^{-1}$)[b] | | |
|---|---|---|---|---|---|---|---|
| mode no. | mode description | UMP2/ 6-311++G(2d,2p) | B3LYP/ 6-311++G(2d,2p) | B3LYP/ 6-311++G(3df,3pd) | UMP2/ 6-311++G(2d,2p) | B3LYP/ 6-311++G(2d,2p) | B3LYP/ 6-311++G(3df,3pd) |
| 1 | HO(HOH′) asym str. | 3957 (−30) | 3892 (−32) | 3871 (−43) | 111 (1.5) | 103 (1.7) | 103 (1.7) |
| 2 | HO(HOH′) sym str. | 3835 (−32) | 3773 (−49) | 3752 (−62) | 28 (2.8) | 36 (5.1) | 33 (5.5) |
| 3 | H″O′ str. | 3455 (−256) | 3338 (−278) | 3306 (−296) | 584 (11) | 536 (18) | 533 (22) |
| 4 | HOH′ bend | 1664 (+2) | 1640 (+1) | 1625 (+2) | 67 (1.0) | 69 (0.97) | 67 (0.93) |
| 5 | H″O′O″ bend | 1588 (+119) | 1566 (+125) | 1556 (+120) | 64 (2.2) | 84 (2.2) | 83 (2.1) |
| 6 | O′O″ str. | 1281 (+60) | 1193 (+26) | 1183 (+14) | 92 (0.93) | 20 (0.69) | 19 (0.70) |
| 7 | H′OH″ bend | 694 | 686 | 679 | 163 | 161 | 140 |
| 8 | HOH bend | 447 | 479 | 465 | 85 | 108 | 94 |
| 9 | OH″O bend | 296 | 306 | 293 | 154 | 134 | 131 |
| 10 | OH″ str. | 254 | 256 | 255 | 16 | 25 | 24 |
| 11 | HOH′H′ torsion | 174 | 208 | 103 | 64 | 71 | 69 |
| 12 | OH″O′O″ torsion | 79 | 101 | 98 | 34 | 45 | 47 |

[a] Numbers in parentheses are calculated shifts relative to the monomers. [b] Numbers in parentheses are ratios of calculated intensities for the complex relative to the monomers.

cal $mol^{-1}$ $K^{-1}$. This agrees fairly well with Hamilton and Naleway's calculation of −24.5 cal $mol^{-1}$ $K^{-1}$.

In Table 4 the harmonic vibrational frequencies for the $HO_2 \cdot H_2O$ radical complex are shown. By using the B3LYP/6-311++G(3df,3pd) level of theory, we were able to predict the vibrational frequencies of $HO_2$ within a root-mean-square error of 6.1% of the experiment[24−26] and intensities within a factor of 4. This is consistent with previous density functional theory studies on $HO_2$.[27] The frequency shifts are calculated by taking the difference between the vibrational frequencies of the isolated $H_2O$ and $HO_2$ molecules and the radical complex using the same basis set and the same level of theory. At the MP2 and B3LYP levels of theory using 6-311G(2d,2p) and 6-311++G(3df,3pd) basis sets, the shift between the levels of theory are consistently predicted in terms of magnitude and sign. The largest shift results in the H″O′ stretching mode that is red-shifted by 296 $cm^{-1}$. The intensity of this mode is predicted to be 22 times greater than that of the isolated $HO_2$ at the best level of theory. This is because of the increased effect this mode has on the change in the dipole moment of the entire complex. On the $HO_2$ moiety, the H″O′O″ bending mode is blue-shifted by 120 $cm^{-1}$. The calculations predict the H″O′ stretching mode ($\upsilon_3$) in the complex to be the most intense band. There are six intermolecular modes, whose frequencies are well-separated from those of the isolated monomers. These are modes $\upsilon_7$ through $\upsilon_{12}$. The $\upsilon_7$ and $\upsilon_9$ modes, in particular, are predicted to be intense modes. The observation of these vibrational modes in the laboratory could support the existence of the $HO_2 \cdot H_2O$ radical complex.

The equilibrium constant for the following reaction

$$HO_2 + H_2O \rightarrow HO_2 \cdot H_2O \qquad (3)$$

is estimated from partition functions using statistical thermodynamics.[28] The transitional, vibrational, rotational, and electronic partition functions are calculated from the ab initio structural, vibrational, and binding energy data given. The equilibrium constant, which is in units of $cm^3$ $molecule^{-1}$, is found by dividing the total partition function of the product $HO_2 \cdot H_2O$ by the total partition functions of the reactants, $HO_2$ and $H_2O$. The equation for this calculation, as given in reference 28, is

$$K_c(T) = \rho_{HO_2 \cdot H_2O}/\rho_{HO_2}\rho_{H_2O} \qquad (4)$$

where $K_c(T)$ is the temperature-dependent equilibrium constant in terms of concentration and $\rho_{HO_2 \cdot H_2O}$, $\rho_{HO_2}$, and $\rho_{H_2O}$ are the total partition functions of the reactants and product of reaction 1. The equilibrium constant for $HO_2 \cdot H_2O$ is calculated to range from 170 to 320 K and is shown in Figure 2. At the higher temperatures the equilibrium constant is estimated to be on the order of $10^{-18}$, while at lower temperatures it increases by 3 orders of magnitude. Consequently, lower temperatures will

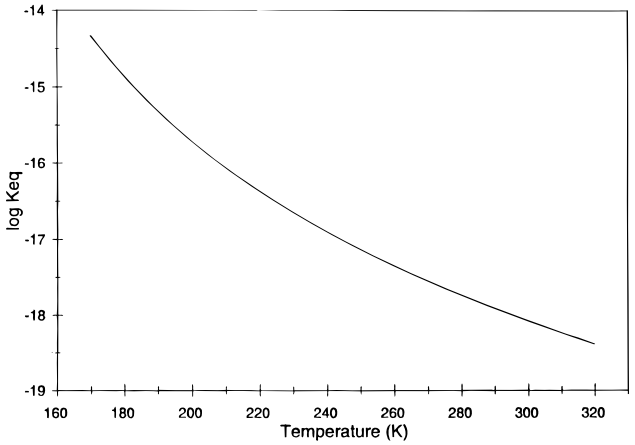


**Figure 2.** $HO_2 \cdot H_2O$ equilibrium constant as a function of temperature. $K_{eq}$ is in units of $cm^3$ $molecule^{-1}$.

favor the complex formation. The largest source of uncertainty lies in the determination of the binding energy of the complex. For the equilibrium constant calculation, we used the binding energy calculated by the CCSD(T)/6-311++G(2df,2p)//B3LYP/6-311++G(2df,2p) level of theory. Using water dimer as a benchmark calculation, the $D_0$ at the same level of theory is found to be within 0.2% of the experimentally determined binding energy.[29] This translates into an error in the equilibrium constant of about 1.2%. The calculated vibrational frequencies reported in Table 4 are harmonic values; consequently, we need to estimate the uncertainty in the equilibrium constant due to the effect of anharmonic corrections for the frequencies. We used a procedure similar to that of Feyereisen et al.[30] First we compared the calculated frequencies of the monomers, $HO_2$ and $H_2O$, to experimental values. An average scale factor of 0.983 for the stretches and 0.977 for the bend were obtained. These scale factors were used for the monomer modes of the dimer. We did not vary the six intermolecular modes of the dimers. We recalculated the equilibrium constant using the scaled vibrational frequencies. An estimate of the error in the equilibrium constant due to the neglect of anharmonicity is $<0.5\%$. Thus, there are no large effects contributing to the equilibrium constant estimation from the anharmonic corrections.

We have asked the question in what regions of the atmosphere are $HO_2{\cdot}H_2O$ complexes most likely to be formed. In regions where the water concentration is low, it seems unlikely that these complexes could be formed in significant number density to have any impact. For example, in the stratosphere at 30 km, the $H_2O$ concentration is $1.6 \times 10^{12}$ molecules cm$^{-3}$, the $HO_2$ density is $1.6 \times 10^7$ molecules cm$^{-3}$, and the mean temperature at this altitude is 232.1 K.[31] This implies that $5.2 \times 10^2$ $HO_2{\cdot}H_2O$ complexes should exist in a column of $1.6 \times 10^7$ $HO_2$ molecules. However, where these species could play a role in the atmosphere is in the marine boundary layer and in the tropical troposphere. In the marine boundary layer,[32] the water density is $2.6 \times 10^{17}$ molecules cm$^{-3}$, the mean temperature is 283.4 K, and the $HO_2$ density is $2.7 \times 10^8$ molecules cm$^{-3}$. Under these conditions we estimate that $1.1 \times 10^8$ $HO_2{\cdot}H_2O$ complexes exist; in other words, 29% of the $HO_2$ is complexed as $HO_2{\cdot}H_2O$. Although the equilibrium constant for complex formation decreases with increasing temperature, the amount of water in the atmosphere may increase dramatically at these higher temperatures. For this reason, larger amounts of the $HO_2{\cdots}H_2O$ complex may be formed in areas where the temperature is higher, such as in the tropics. Let us, as an example, take a warmer air mass with a temperature of 298 and a humidity of 80% ($7.8 \times 10^{17}$ molecules cm$^{-3}$ of $H_2O$). In this region, using the same $HO_2$ concentration as above, 42% of the $HO_2$ could be in the complexed form. Given the various points of uncertainty in the estimation of the equilibrium constant, the present results suggest that $HO_2{\cdot}H_2O$ complexes should exist in significant abundance in the lower region of the atmosphere where conditions of high water density and low temperature should favor its formation. As a result, it would be interesting to know what the implications of such abundances of $HO_2{\cdot}H_2O$ complexes may have on the chemistry of the atmosphere.

**Note Added in Proof.** Subsequent to the submission of this paper, Nelander[33] submitted a paper on the matrix isolation of the $HO_2{\cdot}H_2O$ complex in which vibrational frequencies were reported. The three major fundamental vibrational bands reported are at 3236.2, 1479.3, and 1120.4 cm$^{-1}$. These are in good agreement with our best predictions at 3306, 1556, and 1183 cm$^{-1}$. Our calculations deviate by 2.1%, 5.2%, and 5.6% from the experimental values, respectively. Nelander assigns these modes as $\upsilon_1$, $\upsilon_2$, and $\upsilon_3$, respectively. However, the present work suggest that these modes are attributed to $\upsilon_3$, $\upsilon_5$, and $\upsilon_6$ for the $HO_2{\cdot}H_2O$ complex. Nelander suggested that the binding energy of the $HO_2{\cdot}H_2O$ complex is at least 6 kcal mol$^{-1}$, which is in good agreement with our estimate of 6.9 kcal mol$^{-1}$. The results of Nelander[33] provide confirmation of the present calculations of the existence of the $HO_2{\cdot}H_2O$ radical complex.

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