Identification of H₂O·HO in Argon Matrices

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Abstract: The infrared spectrum of OH in Ar matrices at temperatures of 11.5 ± 0.5 K has been investigated as a function of water concentration for H_2O:Ar ratios ranging from 1:70 to 1:1000. These data and evidence gathered from earlier experimental and theoretical work lead to an assignment of bands at 3452 and 3428 cm^{-1} to the $H_2O \cdot HO$ complex. This is the first time that a definitive assignment has been made to an isolated $H_2O \cdot HO$ complex. This observation may have important implications for fields as diverse as molecular biology, astrochemistry, atmospheric chemistry, and electrochemistry.

Introduction

Over the years free radical OH has been the subject of intensive research in both the physical and biological sciences. It is surprising that although OH is an extremely important oxidant in biological systems,[1] the possible existence of hydroxyl−water complexes ($H_2O \cdot HO$) has received so little attention when the biological solvent is water. We are aware of only one article that deals with this complex in a biological context. In 1976, Hobza and Zahradník[2] performed semi-empirical quantum-mechanical calculations in which $H_2O \cdot HO$ was predicted to be a stronger oxidant than OH. This aspect of their work does not appear to have been followed up with higher level calculations.

Our own interest in $H_2O \cdot HO$ stems from the fact that although OH is a well-known radiolysis[3] and photolysis[3,4] product in H_2O ice, and is stably trapped at temperatures less than 100 K via hydrogen bonding to molecules of the ice lattice,[5] its optical spectroscopy in this environment is rather poorly characterized.[4] Perturbations of the electronic and vibrational structure of OH in ice remain untreated. As a consequence, the identification of OH and $H_2O \cdot HO$ in cold, icy extraterrestrial environments, such as comets and planetary surfaces, may have been confused.

In the past decade several theoretical studies of the ground state of the $H_2O \cdot HO$ complex have been made. OH may hydrogen bond to H_2O through either its oxygen or its hydrogen atom. Kim et al.[6] used ab initio methods to treat the former case, finding two minima belonging to the C_s point group with $^2A''$ and $^2A'$ symmetry (structures **1** and **2**; Figure 1). Later, density functional calculations by Wang et al.[7] showed that structure **2** is a turning point and not a true minimum. Hence, Table 1 does not include computed data for structure **2**. The
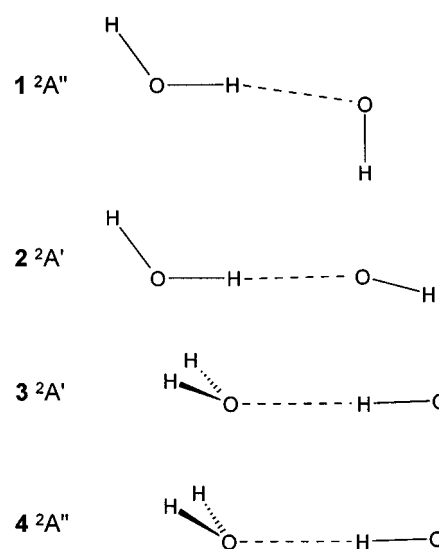

Figure 1. Calculated structures for minima in the $H_2O \cdot HO$ complex.[8] Structure 3 is the global minimum for the $H_2O \cdot HO$ system.

vibrational frequency shifts from those of free H_2O and OH are relatively small because the complex is rather weakly bound.

More recent calculations employing ab initio[8] and density functional[7] methods have found that the global minimum of the $H_2O \cdot HO$ system has the H atom of OH bonded to the O atom of H_2O. The structures of the global minimum ($^2A'$ symmetry) and the next-lowest minimum are shown in Figure 1 as structures **3** and **4**, respectively. The binding energy of the $^2A'$ structure (Table 1) is slightly larger than that of the water dimer,[8] suggesting that $H_2O \cdot HO$ should be stable and readily observable at low temperatures. The $^2A''$ structure (**4**; Figure 1) is only slightly less stable than the $^2A'$ structure, differing from $^2A'$ only by the orientation of the partially occupied π orbital on OH. Because structures **3** and **4** are more strongly bound than structure **1**, there are quite large red-shifts of the OH stretching frequency and the transition intensity is strongly enhanced (Table 1), particularly in the density functional results.

In addition to the above, brief references to neutral $H_2O \cdot HO$ species have appeared in theoretical calculations of processes

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Table 1. Dissociation Energies, Vibrational Energies,[a] and Intensities[b] (in parentheses) for $H_2O \cdot HO$ Structures

	1[c]		**3**		**4**	
	RHF[d] (ref 6)	B3LYP[e] (ref 7)	RCISD[d] (ref 8)	B3LYP[e] (ref 7)	RCISD[f] (ref 8)	B3LYP[e] (ref 7)
D_e/kJ mol^{-1}	14.6[g]	15.1	23.7[h]	24.6	22.4[h]	23.2
H$_2$O stretches:						
a″ asymmetric	4230 (154)	3898 (106)	4075 (104)	3915 (92)	4114 (76)	3912 (88)
a′ symmetric	4119 (87)	3749 (139)	3975 (25)	3815 (16)	3996 (20)	3814 (16)
OH stretch (a′)	4057 (53)	3703 (35)	3790 (273)	3558 (346)	3813 (214)	3556 (331)
H$_2$O bend (a′)	1773 (84)	1648 (54)	1709 (77)	1639 (74)	1703 (87)	1643 (74)
OH···OH$_2$			618 (146)	650 (142)	560 (212)	549 (163)
torsion (a″):						
H···OH bend			429 (173)	435 (201)	525 (239)	547 (163)
O···H stretch			184 (16)	197 (97)	190 (58)	213 (213)
H$_2$O rock			165 (7)	186 (2)	197 (1)	203 (1)
H$_2$O wag			132 (190)	175 (84)	160 (186)	177 (15)
isolated species:						
H$_2$O stretches:						
a″ asymmetric	4245	3927 (62)	4082 (77)	3927 (62)	4123 (43)	3927 (62)
a′ symmetric	4142	3825 (8)	3980 (13)	3825 (8)	3999 (9)	3825 (8)
OH stretch (a′)	4066	3715 (15)	3889 (23)	3715 (15)	3894 (8)	3715 (15)
H$_2$O bend (a′)	1762	1639 (71)	1708 (78)	1639 (71)	1698 (86)	1639 (71)

[a] Vibrational energies in cm^{-1}. [b] Intensities (in km mol^{-1}) are in parentheses after the vibrational frequency. [c] Intermolecular vibrational modes of structure **1** differ from those of structures **3** and **4**, so only the water and hydroxyl stretches are included here. [d] Triple-ζ basis set with two sets of polarization functions (TZ2P). [e] Triple-ζ basis set with multiple sets of diffuse and polarization functions (6-311++G(2d,2p)). [f] Double-ζ plus polarization (DZP) basis set. [g] Estimated actual D_e from a number of calculations in ref 6. [h] Computed using the RCISD(Q) method, including Davidson correction.

occurring at the O$_2$ electrode in an alkaline H$_2$−O$_2$ fuel cell[9] and in theoretical and experimental studies of the gas-phase proton-transfer reaction H$_2$O + OH → HO + H$_2$O.[10,11] A portion of a very recent review[12] on radical−water complexes in Earth's atmosphere has been devoted to this reaction and in particular to a discussion of the hydroxyl−water complex.

The aim of the present study was to utilize the above theoretical results[6−8] to experimentally identify and assign absorption bands of H$_2$O·HO in the infrared (IR) spectrum of OH embedded in argon matrices (OH/Ar). Because a substantial body of quality experimental work on OH/Ar has been reported already,[13−15] we primarily reinterpret the earlier results, and supplement them with a simple study in which the initial water concentration is varied. The bands assigned here to H$_2$O·HO exhibit isotopic,[14,15] thermal,[14,15] and concentration-dependent behavior consistent with our assignment. Our work supports the very recent suggestion of Khriachtchev et al.[16] that a band appearing occasionally at 3424 cm^{-1} in their H$_2$O$_2$ photolysis experiments is due to H$_2$O·HO.

Experimental Section

Triply distilled water[17] was degassed several times by the freeze− pump−thaw method before mixing its vapor with high-purity argon in H$_2$O:Ar ratios of 1:70 to 1:1000 using standard manometric techniques. The reservoir and deposition line were constructed primarily from stainless steel.

Matrices containing OH/Ar were made by using the method that Lund et al.[18] used to prepare NH/Ar. We describe this method only briefly here, noting that it was used to prepare OH/Ar previously.[19,20] The flow of the H$_2$O:Ar mixture (∼5−8 mmol h^{-1}) was regulated by a needle valve and introduced into the matrix-isolation system through a Pyrex glass tube where it was subjected to a radio frequency discharge produced by a Tesla coil. The discharged mixture was then deposited on a sapphire sample window held at 11.5 ± 0.5 K by a closed-cycle helium refrigerator (CTI-Cryogenics 8300 compressor and 350CP displacer). The sample temperature was measured with an accuracy of ±0.5 K by using a Lakeshore DT-470 silicon diode sensor.

IR spectra of the matrices were obtained by using a Mattson Sirius 100 FTIR spectrometer. The spectral resolution was 0.5 cm^{-1}.

Results and Discussion

Figure 2 shows a region of the IR spectrum of the discharge products of H$_2$O:Ar mixtures as a function of the predischarge water concentration. The spectra obtained are independent of deposition rate over the range of flows employed here. Significant quantities of intact H$_2$O molecules survive the weak radio frequency discharge for all H$_2$O concentrations, but the fraction decomposed is highest for low H$_2$O concentrations. It should be noted that while this behavior does not complicate our later discussion, it does hinder modeling of the data using the easily calculated probability that a given OH molecule will lie near a water molecule. Bands at ca. 3574, 3516, and 3413 cm^{-1} have been assigned previously to the H$_2$O dimer and trimer[21,22] and HO$_2$,[23,24] respectively (Table 2).

Acquista et al.[13] originally assigned bands at 3452 and 3428 cm^{-1} to OH, because they exhibited isotopic shifts characteristic of gas-phase OH. They concluded that the two bands arose from site effects in the matrix. Later work by Suzer and Andrews[14] appeared to confirm the conclusions of Acquista et al.[13]

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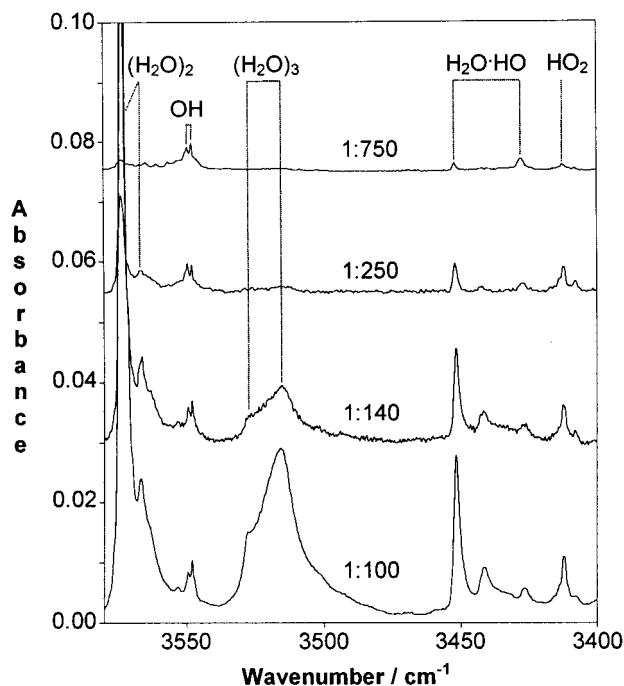(24) Smith, D. W.; Andrews, L. *J. Chem. Phys.* **1974**, *60*, 81−85.

Figure 2. Dependence on H_2O concentration of the absorption bands in the OH/Ar spectral region at a temperature of 11.5 ± 0.5 K. The spectra are scaled to the same integrated OH/Ar absorption. Assignments are given on the figure and in Table 2.

Table 2. Observed Energies and Assignments of Bands in Figure 2

energy^a/cm^{-1}	assignment	references
3573.6 ± 0.3	H₂O dimer	21, 22
3566.5 ± 0.3	H₂O multimer	22
3549.6 ± 0.3	OH	28
3548.1 ± 0.3	OH	15
3528 ± 1	H₂O trimer	22
3516 ± 1	H₂O trimer	22
3452.2 ± 0.5	H₂O•HO ^{b}	this work
3428 ± 0.5	H₂O•HO ^{b}	this work
3412.7 ± 0.5	HO₂	23, 24

^{a} Some bands red-shift slightly as the water concentration increases (notably the H₂O•HO band at ~3428 cm^{-1}); we use the value from runs with low water concentration. ^{b} Formerly assigned to OH by Acquista et al.[13] and Suzer and Andrews.[14]

However, Cheng et al.[15] have since shown that these bands do not correspond to isolated OH radicals. In their experiments, Cheng et al.[15] formed OH by reaction of H atoms with NO₂, O₃, or O instead of using water as a precursor. They attributed a band at 3548.2 cm^{-1} to OH/Ar, because it exhibited isotope effects essentially identical to gas-phase OH *and* appeared at the lowest reactant concentrations whereas the 3452- and 3428-cm^{-1} bands were weak or absent. Hence the OH absorption is red-shifted by only ~21 cm^{-1} from the gas phase[25] and *not* by 117 and 141 cm^{-1} as concluded from the earlier assignment.[13] Cheng et al.[15] suggested that the lines observed by Acquista et al.[13] and Suzer and Andrews[14] were possibly due to OH bonded to a single Ar atom (see ref 26) or to a water molecule, but did not attempt a more definite assignment. In fact the red-shift from isolated OH/Ar to the 3452- and 3428-cm^{-1} bands corresponds very well with theoretical predictions for structures **3** and **4** (Figure 1; Table 1) when isolated OH is complexed by

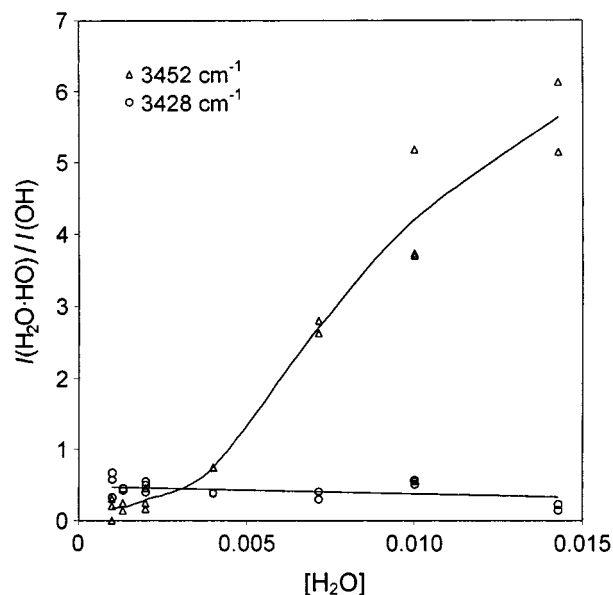(25) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*, *Volume 4: Constants of Diatomic Molecules*; van Nostrand Reinhold: New York, 1979.
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Figure 3. Integrated intensities of the H₂O•HO bands at 3452 cm^{-1} scaled by the integrated intensity of the isolated OH band as a function of the water concentration. Each point on the graph represents the result obtained for a single experiment. Two or three independent experiments were performed for each water concentration.

H₂O. The measured values of 96 and 120 cm^{-1} lie in the middle of the range spanned by the two computational methods (~75−160 cm^{-1}). This fact first inspired our assignment of these bands to H₂O•HO, which we show now to be consistent with a large body of evidence from the following seven matrix-isolation experiments.

First, we present a simple test of our assignment to H₂O•HO. One would expect to observe *increased* intensity in the 3452- and 3428-cm^{-1} bands as the water concentration increases if we scale the data by the OH intensity. Such behavior is indeed evident in Figure 2, in which the spectra are scaled to the same integral area under the OH/Ar bands. (Scaling is approximate due to uncertainties caused by overlapping bands.) Figure 3 shows the relationship more clearly: the integrated intensities of the 3452- and 3428-cm^{-1} bands are divided by the integrated OH/Ar intensity at the initial water concentration. We note that the integral of the isolated OH band for the 1:70 sample also contains a significant contribution from a water multimer band that we observed in our control H₂O/Ar spectra, which reduces the ratio plotted in Figure 3. The behavior in Figures 2 and 3 is consistent with an assignment of the 3452-cm^{-1} band to H₂O•HO. The 3428-cm^{-1} band has intensity roughly independent of concentration over the range of concentrations used. However, we assign it to H₂O•HO occupying a much less favorable site at higher H₂O concentrations because of its isotopic dependence[13-15] and other behavior described below. The high intensity of the 3452- and 3428-cm^{-1} bands with respect to OH is due to the intensity enhancement that occurs on complexation (Table 1). Hence, even when only a small percentage of OH radicals are complexed to H₂O (e.g. 1.2% for 1:500 H₂O:Ar), the high intensity means that the bands are readily observed.

Second, formation of H₂O•HO in the Ar matrix requires that there be H₂O molecules present to complex the OH radical. The observation of Cheng et al.[15] that the bands assigned to OH/Ar by Acquista et al.[13] were either very weak or absent in experiments with the smallest mole fractions of H atoms reacted with NO₂ is in agreement with our assignment, because there will be very few water molecules present. Hence, Cheng et al.[15] failed to reproduce the relative intensities observed by Acquista

et al.[13] and Suzer and Andrews:[14] sometimes the higher-energy band was absent while the lower-energy one was present.

Third, Cheng et al.[15] observed that upon warming their matrices to 25 K, the OH/Ar band at 3548 cm^{-1} suffered irreversible loss of some of its intensity, while the intensity of the 3452-cm^{-1} band increased. These observations, in conjunction with the comments of Suzer and Andrews[14] that H_2O is more mobile in solid argon than OH (since H_2O_2 has not been detected[13,14]), suggest that upon annealing the matrix $H_2O \cdot HO$ is formed as H_2O molecules diffuse and hydrogen bond to trapped OH molecules.

Fourth, Cheng et al.[15] found that irradiation of control H_2O/Ar samples with UV light from a medium-pressure Hg lamp led to increased intensity of a water aggregate band during photolysis. Likewise, they irradiated OH/Ar samples and found that while the absorbance of isolated OH decreased slightly, the bands at 3452 and 3428 cm^{-1} increased in intensity; initially the former was weak and the latter was absent. Such behavior is consistent with expectations for $H_2O \cdot HO$.

Fifth, water dimers, trimers, and multimers form readily even at moderate concentrations when H_2O/Ar matrices are deposited at ~20 K,[22] compared to matrices deposited at 7−8 K.[21] The increased H_2O mobility afforded by a warmer sample temperature, which is responsible for increased dimer yields, will also result in high yields of $H_2O \cdot HO$ when moderate levels of water are present. The binding energies of the H_2O dimer and $H_2O \cdot HO$ are very similar, as noted above. This, along with the much increased transition moment of OH in $H_2O \cdot HO$ (Table 1), may explain why Acquista et al.,[13] Suzer and Andrews,[14] and the present work obtained large $H_2O \cdot HO$ absorption intensities from samples deposited at 20.4, ~12, and ~11.5 K, respectively, even when water concentrations were relatively low.

Sixth, the 3452- and 3428-cm^{-1} bands cannot be attributed to OH complexed to a single Ar atom (OH·Ar)[15,26] because their intensity increases with decreasing Ar concentration (increasing H_2O concentration) and for small H_2O concentrations should show very little concentration dependence. Furthermore, if they were due to OH·Ar, then they should be observed in all OH/Ar experiments, independent of the method used to prepare OH.

Seventh, in a recent paper Gerakines et al.[27] used IR spectroscopy to probe the products of vacuum-UV photolysis of thin layers of H_2O ice (thickness <1 μm). Peaks observed at 3452 and 3428 cm^{-1} were assigned to OH from the early assignment of Acquista et al.,[13] whereas isolated OH/Ar is now known to absorb at 3548 cm^{-1}.[15] Intuitively, one would expect that OH in ice would absorb in the vicinity of the 3452- and 3428-cm^{-1} bands assigned in this work to $H_2O \cdot HO$/Ar, rather than in a region attributed to isolated OH/Ar. Hence we reassign the bands observed by Gerakines et al.[27] to $H_2O \cdot HO$ or higher hydrates of OH. Their results provide further support for the assignment of the 3452- and 3428-cm^{-1} bands to $H_2O \cdot HO$ and account for the absence of the 3548-cm^{-1} band in their work. Interestingly, the observed bands are not shifted on going from an $H_2O \cdot HO$ complex isolated in an Ar matrix to OH formed as a photoproduct in ice. We might conclude that in ice the OH molecule is bound strongly to only one water molecule or that the X $^2\Pi$ ground state of OH is relatively insensitive to the number of water molecules bonded to it.

These seven experimental observations, together with the good agreement between experiment and theoretical calculations[7,8] for the red-shift, strongly support assignment of the bands at 3452 and 3428 cm^{-1} to $H_2O \cdot HO$/Ar.

Now we consider options for individually assigning the 3452- and 3428-cm^{-1} bands. Several possibilities exist. A first option is to assign the 3452-cm^{-1} band to the most stable complex (structure **3**; Figure 1), while assigning the 3428-cm^{-1} band to structure **4** (Figure 1). Upon annealing, structure **4** would be converted into the more stable structure **3**. However, it is unlikely that this is the true assignment. The calculated binding and vibrational energies[7,8] differ little between structures **3** and **4**. Furthermore, since complex **3** is more stable, it would be expected to have the most red-shifted band, while the experimental data[14] show that the 3452-cm^{-1} band actually has higher thermal stability.

As a second option, we might assign the 3428-cm^{-1} band to structure **1** and the 3452-cm^{-1} band to structures **3** and **4**. Such an assignment is most unlikely, because Kim et al.[6] and Wang et al.[7] predict that the OH stretch for structure **1** lies within about 25 cm^{-1} of the isolated OH band, whereas structures **3** and **4** experience much larger shifts (Table 1).

A final option is that the IR bands correspond to two different sites for the $H_2O \cdot HO$ complex in the Ar matrix. Within this assignment, the 3428-cm^{-1} band would be assigned to a thermally less stable site than the 3452-cm^{-1} band. The former is converted to the latter upon annealing the matrix.[14] This assignment is the most likely one. It also successfully accounts for the variable ratio of formation of the two bands observed by Suzer and Andrews[14] and Cheng et al.[15] Slightly different matrix preparation conditions and methods for formation of OH result in different ratios of the two sites. In the present experiments, it appears that the 3428-cm^{-1} band corresponds to $H_2O \cdot HO$ in a less favored site, except at low H_2O concentrations.

Finally, let us consider the other IR bands of the $H_2O \cdot HO$ complex. Theoretical calculations[7,8] predict that the H_2O monomer bands in the complex are not perturbed as greatly as the OH stretch (Table 1). However, no new lines in the H_2O stretching region are observed in the present experiments. This may be due to the lower intensity of the complex H_2O vibrations relative to the OH mode. We note that shifts of this magnitude were predicted for the water bands of the $H_2O \cdot O(^3P)$ complex, while shifts of ~5 cm^{-1} were obtained experimentally.[28] An investigation of the region of the OH···OH$_2$ torsion (a″) and H···OH bend vibrations (Table 1) would be most valuable. These modes should have an intensity of about the same order as the OH stretch of the complex.

Conclusion

We have assigned the bands at 3452 and 3428 cm^{-1} in OH/Ar matrices to the $H_2O \cdot HO$ complex occupying two sites in the argon matrix. The assignment is in agreement with theoretical predictions of the red-shift of the OH stretch upon complexation and gives a good account of the experimental results obtained here and by other workers.

Further work is required to confirm our assignment. In particular, the most convincing evidence for the existence of the $H_2O \cdot HO$ complex would be found between 400 and 650 cm^{-1} in the OH···OH$_2$ torsion (a″) and H···OH bend regions (Table 1), where we are unable to acquire data at present.

We find the absence of consideration of $H_2O \cdot HO$ in biological systems quite surprising, because OH radicals are important oxidants in biology, where their environment is of course aqueous. We believe that $H_2O \cdot HO$ needs to be considered in modeling of both biological and electrochemical oxidation processes.

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Assignments to OH in remote spectra of icy extraterrestrial environments may also need to be reconsidered in the light of the present assignment. The laboratory study by Gerakines et al.,[27] which simulated photolysis of ices in the interstellar medium, is one such example. It is likely that hydrated hydroxyl complexes will exist in the cold, icy environments found in outer space.

Finally, as noted very recently by Aloisio and Francisco,[12] $H_2O \cdot HO$ complexes exist as intermediates in the reaction between OH and H_2O that occurs in Earth's atmosphere. As they point out, laboratory studies of $H_2O \cdot HO$ and other hydrated radicals are of great importance to the understanding of the details of atmospheric chemistry.

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