Infrared Measurements and Calculations on H$_2$O-HO

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The OH radical is a very important species in the biological, environmental, and physical sciences. The hydration of OH is important in the biological sciences because the effect on OH by complexation with a single water molecule may change the oxidation potential of the radical. Hydrated OH may also be important as an intermediate species in the reaction between OH and H$_2$O in the atmosphere and as a species formed in the radiolysis and photolysis of H$_2$O ice. The reinterpretation by Langford et al. of the work by Gerakines et al. on the vacuum-UV photolysis of H$_2$O ice has indeed shown that a hydroxyl-water complex (H$_2$O-HO) was formed within the lattice of their laboratory ices. This complex might also be relevant to the interpretation of the spectra of outer solar system bodies that are often ice-covered.

Recent work has provided the first assignment of infrared absorption bands at 3452 and 3428 cm$^{-1}$ to an H$_2$O-HO complex in an Ar matrix. To confirm this assignment, the present study investigates the H$_2$O-HO complex by comparing calculated isotopic shifts of the OH stretching vibration with those observed experimentally. We also compare the measured decrease in intensity of the OH stretching vibration upon isotopic substitution (OD) with the decrease predicted from calculations. The OH stretching band at 3442 cm$^{-1}$ is assigned to the OH radical of the complex in a third site.

Structures 1–3 (Figure 1) represent three true minima on the H$_2$O-HO potential energy surface. All three structures were optimized with the quadratic configuration interaction including single and double excitations (QCISD) method and the 6-311++G(2d,2p) basis set in Gaussian. The calculated harmonic frequencies are given in Table 1, and the lack of imaginary frequencies confirms the structures as minima. Structures 1 and 2 have very similar geometries, but belong to different electronic states, 2$^\text{A''}$ and 1$^\text{A''}$ respectively. The QCISD/6-311++G(2d,2p) calculated energy difference between 1 and 2 is only 0.32 kcal mol$^{-1}$. The calculated harmonic frequencies of the symmetric and asymmetric stretches in the H$_2$O unit and of the stretch in the OH unit of 1 and 2 are very similar. It is therefore likely that different sites within the matrix, and not different structures, are the cause of the multiplet peaks observed by Langford et al.

H$_2$O-HO was prepared using a method similar to that described by Langford et al. In brief, H$_2$O:Ar mixtures in ratios of 1:100 to 1:500 were prepared from distilled water and high-purity argon. The H$_2$O:Ar mixture (~5–8 mmol h$^{-1}$) was introduced into the matrix isolation system through a borosilicate glass tube where it was subjected to a radio frequency discharge from a Tesla coil. The discharged mixture was then deposited on to a KBr sample window cooled to 11.5 ± 0.5 K by a closed-cycle helium refrigerator (CTI-Cryogenics 8300 compressor and a 350CP displacer). A Lakeshore DT-470 silicon diode sensor measured the sample temperature. The spectra of the matrices were obtained at 0.5 cm$^{-1}$ spectral resolution with a Mattson Sirius 100 FTIR spectrometer.

Table 2 shows the experimental and calculated isotopic shifts of the OH radical stretch of structure 1. These calculations were performed using an anharmonic oscillator local mode model. The calculated isotopic shifts agree well with those we have measured experimentally. The calculated scaled frequencies for the OH and OD stretch agree well with the experimental values, especially if matrix shifts are considered.

Langford et al. assigned the bands at 3452.2 and 3428.0 cm$^{-1}$ seen by previous workers to the OH radical stretch, red-shifted from the free OH radical stretch of 3549 cm$^{-1}$ by complexation to a water molecule. The two bands were attributed to the complex present in two different sites within the argon matrix. It is clear from the similar isotopic shifts in Table 2 that the three bands arise
Table 2. Comparison of Calculated and Measured Frequencies and Isotopic Shifts (cm⁻¹) of the Hydroxyl OH-Stretching Band in H₂O-HO Structure 1 (°A)

<table>
<thead>
<tr>
<th></th>
<th>experimental</th>
<th>calculated¹</th>
<th>unscaled</th>
<th>scaled²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν₁ (cm⁻¹)</td>
<td>3452.2</td>
<td>3428.0</td>
<td>3442.1</td>
<td>3546.1</td>
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<tr>
<td>ν₂ (cm⁻¹)</td>
<td>2542.9</td>
<td>2524.6</td>
<td>2536.4</td>
<td>2643.6</td>
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<td>isotopic shift</td>
<td>909.3</td>
<td>903.4</td>
<td>905.7</td>
<td>902.5</td>
</tr>
<tr>
<td>% difference</td>
<td>0.75</td>
<td>0.10</td>
<td>0.35</td>
<td>1.88</td>
</tr>
</tbody>
</table>

¹ Anharmonic oscillator local mode model with a Morse potential fit to a QCISD/6-311++G(2d,2p) calculated 15 point grid (−0.3 to 0.4 Å) about the equilibrium OH bond length. ² Scaling factors (α) by 0.9719 and (ω) by 0.8154 are obtained from comparing calculated ω and α to experimental values for the OH radical. Experimental values found from a Birge–Sponer fit to the ΔνOH = 1 − 6 from HITRAN 2000 database.

Figure 2. The absorption bands of H₂O-HO and D₂O-DO in the OH/OD stretch infrared region.

Table 3. Comparison of the Band Intensity Ratios of the Hydroxyl OH-Stretching Band of H₂O-HO and Its Deuterated Isotopomer

<table>
<thead>
<tr>
<th></th>
<th>site 1</th>
<th>site 2</th>
<th>site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>OD/OH ratio</td>
<td>0.51</td>
<td>0.62 ± 0.10e</td>
<td>0.56 ± 0.27e</td>
</tr>
<tr>
<td>OD/ν₁-OH ratio</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν₁-OH ratio</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The signal intensities remain steady for many hours, suggesting that there is no subsequent migration of either OH or H₂O through the matrix. Assuming that they each occupy a substitutional site in what will be a fairly rigid face-centered cubic argon lattice at 11.5 K, one can readily calculate the probability of randomly depositing a water molecule next to an OH radical. Thus, in a 1:150 H₂O:Ar mixture, ca. 7.4% of the OH radicals have a nearest-neighbor water molecule to which they can complex. Anharmonic local mode calculations predict that the ratio of the IR intensities of the isolated OH stretch infrared region to the OH stretch in the complex is 0.028. Our experimentally measured value is 0.032 ± 0.007 after correction for the 7.4% nearest-neighbor percentage from above.

Structure 1 has the singly occupied molecular orbital perpendicular to the C₁ symmetry plane, while structure 2 has this molecular orbital in the symmetry plane. The ν₁ and ν₂ modes of structures 1 and 2 involve the motion of the hydroxyl hydrogen in and out of the C₁ plane, respectively. As a result, these two modes are most useful for spectroscopic identification of structures 1 and 2 (Table 1). Unfortunately, in the present work we were unable to acquire data below ca. 580 cm⁻¹ and we did not observe any absorptions from the ν₃ mode above this limit.

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References

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