

Infrared Measurements and Calculations on HO·HO

Paul D. Cooper, Henrik G. Kjaergaard, Vaughan S. Langford,
Allan J. McKinley, Terence I. Quickenden, and Daniel P. Schofield

J. Am. Chem. Soc., **2003**, 125 (20), 6048-6049 • DOI: 10.1021/ja034388k • Publication Date (Web): 26 April 2003

Downloaded from <http://pubs.acs.org> on March 26, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 7 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



Infrared Measurements and Calculations on H₂O·HO

Paul D. Cooper,[†] Henrik G. Kjaergaard,[‡] Vaughan S. Langford,^{†,§} Allan J. McKinley,[†]
Terence I. Quickenden,^{*,†} and Daniel P. Schofield[‡]

Chemistry, M313, School of Biomedical and Chemical Sciences, The University of Western Australia,
35 Stirling Highway, Crawley, WA 6009 Australia, and Department of Chemistry, University of Otago, PO Box 56,
Dunedin, New Zealand

Received January 29, 2003; E-mail: tiq@chem.uwa.edu.au

The OH radical is a very important species in the biological, environmental, and physical sciences. The hydration of OH is important in the biological sciences¹ because the effect on OH by complexation with a single water molecule may change the oxidation potential of the radical.² Hydrated OH may also be important as an intermediate species in the reaction between OH and H₂O in the atmosphere³ and as a species formed in the radiolysis⁴ and photolysis^{4,5} of H₂O ice. The reinterpretation by Langford et al.⁶ of the work by Gerakines et al.⁷ on the vacuum-UV photolysis of H₂O ice has indeed shown that a hydroxyl–water complex (H₂O·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 and subjected to strong fluxes of radiation.⁴

Recent work has provided the first assignment of infrared absorption bands at 3452 and 3428 cm⁻¹ to an H₂O·HO complex in an Ar matrix.⁶ To confirm this assignment, the present study investigates the H₂O·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 H₂O·HO potential energy surface.⁸ 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 Gaussian98.⁹ 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, ²A' and ²A'' 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 H₂O 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 multiple peaks observed by Langford et al.⁶

H₂O·HO was prepared using a method similar to that described by Langford et al.⁶ In brief, H₂O:Ar mixtures in ratios of 1:100 to 1:500 were prepared from distilled water and high-purity argon. The H₂O: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

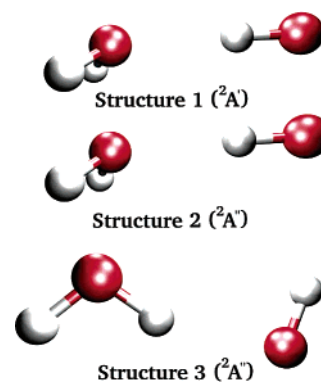


Figure 1. QCISD/6-311++G(2d,2p) optimized structures for the H₂O·HO complex.

Table 1. Calculated Binding Energies, Vibrational Frequencies, and Intensities (in parentheses) for H₂O·HO Structures^a

	1 (² A')	2 (² A'')	3 (² A'')
<i>E_b</i>	5.69	5.37	3.51
<i>v</i> ₁	165.6 (122)	168.4 (22.5)	87.0 (187.3)
<i>v</i> ₂	174.4 (1.07)	186.5 (0.0005)	105.9 (219.6)
<i>v</i> ₃	184.4 (64.6)	199.3 (174.2)	161.0 (73.6)
<i>v</i> ₄	427.0 (197)	525.0 (170.2)	310.8 (178.8)
<i>v</i> ₅	621.2 (149)	526.2 (167.3)	369.9 (4.1)
<i>v</i> ₆	1685.1 (70.3)	1688.9 (69.5)	1697.2 (51.4)
<i>v</i> ₇	3697.7 (250)	3694.3 (235.5)	3758.6 (23.7)
<i>v</i> ₈	3877.3 (13.8)	3875.1 (13.8)	3853.3 (94.1)
<i>v</i> ₉	3978.6 (82.3)	3974.4 (79.1)	3967.3 (116)

^a Calculated with the QCISD/6-311++G(2d,2p) method. Binding energies in kcal mol⁻¹. Vibrational frequencies in cm⁻¹. Intensities in km mol⁻¹.

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.^{10–12} 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.⁶ assigned the bands at 3452.2 and 3428.0 cm⁻¹ seen by previous workers^{13,14} 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

[†] Chemistry, The University of Western Australia.

[‡] Department of Chemistry, University of Otago.

[§] Presently Research Fellow, University of Canterbury, Christchurch, New Zealand.

Table 2. Comparison of Calculated and Measured Frequencies and Isotopic Shifts (cm^{-1}) of the Hydroxyl OH-Stretching Band in $\text{H}_2\text{O}\cdot\text{HO}$ Structure **1** ($^2\text{A}'$)

	experimental			calculated ^a	
	site 1	site 2	site 3	unscaled	scaled ^b
ν_{OH}	3452.2	3428.0	3442.1	3546.1	3479.0
ν_{OD}	2542.9	2524.6	2536.4	2643.6	2586.8
isotopic shift	909.3	903.4	905.7	902.5	892.2
% difference				0.75, 0.10, 0.35	1.88, 1.24, 1.51

^a 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. ^b Scaling factors (ω by 0.9719 and ωx by 0.8154) are obtained from comparing calculated ω and ωx to experimental values for the OH radical. Experimental values found from a Birge–Spencer fit to the $\Delta\nu_{\text{OH}} = 1-6$ from HITRAN 2000 database.

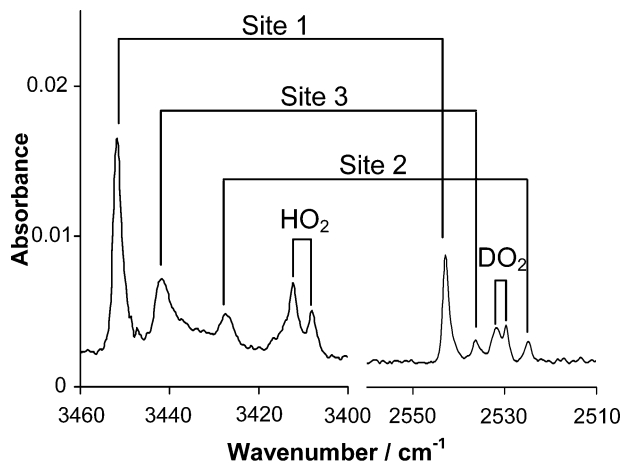


Figure 2. The absorption bands of $\text{H}_2\text{O}\cdot\text{HO}$ and $\text{D}_2\text{O}\cdot\text{DO}$ in the OH/OD stretch infrared region.

Table 3. Comparison of the Band Intensity Ratios of the Hydroxyl OH-Stretching Band of $\text{H}_2\text{O}\cdot\text{HO}$ and Its Deuterated Isotopomer

calculated ^a	site 1	site 2	site 3
OD/OH ratio	OD/OH ratio	OD/OH ratio	OD/OH ratio
0.51	0.62 ± 0.10^a	0.56 ± 0.27^a	0.33 ± 0.27^a

^a Anharmonic oscillator local mode calculation. ^b Errors estimated at the 95% confidence level.

from OH stretching vibrations and the previously unassigned 3442.1 cm^{-1} band⁶ originates from the OH radical stretch of the complex in a third site (Figure 2). The intensity of the band at 3442.1 cm^{-1} shows a dependence on H_2O concentration similar to that previously observed⁶ for the 3452.2 cm^{-1} band, whereas the 3428.0 cm^{-1} band intensity is independent of H_2O concentration over the range measured.

In Table 3 we show the intensity ratios of the OD/OH radical stretching vibration of the complex. Our calculations predict a decrease in the OH radical stretching intensity by 0.51 upon deuteration. The agreement is good, especially when the problems of slightly overlapping bands and low intensities are considered.

It is assumed that prior to deposition, the kinetic energies of the gaseous OH and H_2O molecules will be too high for the formation of the $\text{H}_2\text{O}\cdot\text{HO}$ complex. In these circumstances the OH and H_2O molecules should deposit randomly on the cold surface. At 11.5 K

the signal intensities remain steady for many hours, suggesting that there is no subsequent migration of either OH or H_2O through the matrix. Assuming that they each occupy a substitutional site in what will be a fairly rigid face-centered cubic argon lattice¹⁵ 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 $\text{H}_2\text{O}:\text{Ar}$ 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 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 C_s symmetry plane, while structure **2** has this molecular orbital in the symmetry plane. The ν_4 and ν_5 modes of structures **1** and **2** involve the motion of the hydroxyl hydrogen in and out of the C_s 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 ν_5 mode above this limit.

Acknowledgment. The following sources of funds are gratefully acknowledged. The Australian Government for a Postgraduate Scholarship for P.D.C.; The University of Otago for a Postgraduate Scholarship for D.P.S.; The University of Western Australia and The Marsden Fund, NZ, for Research Grants. T.I.Q. and P.D.C. thank Professor R. E. Johnson of the University of Virginia for helpful discussions.

References

- (1) Hamad, S.; Lago, S.; Mejías, J. A. *J. Phys. Chem. A* **2002**, *106*, 9104–9113.
- (2) Hobza, P.; Zahradník, R. *J. Theor. Biol.* **1977**, *66*, 461–474.
- (3) Aloisio, S.; Francisco, J. S. *Acc. Chem. Res.* **2000**, *33*, 825–830.
- (4) Johnson, R. E.; Quickenden, T. I. *J. Geophys. Res.* **1997**, *102*, 10985–10996.
- (5) Langford, V. S.; McKinley, A. J.; Quickenden, T. I. *Acc. Chem. Res.* **2000**, *33*, 665–671.
- (6) Langford, V. S.; McKinley, A. J.; Quickenden, T. I. *J. Am. Chem. Soc.* **2000**, *122*, 12859–12863.
- (7) Gerakines, P. A.; Schutte, W. A.; Ehrenfreund, P. *Astron. Astrophys.* **1996**, *312*, 289–305.
- (8) Xie, Y.; Schaefer, H. F., III. *J. Chem. Phys.* **1993**, *98*, 8829–8834.
- (9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*; Gaussian Inc.: Pittsburgh, PA, 1998.
- (10) Henry, B. R. *Acc. Chem. Res.* **1987**, *20*, 429–435.
- (11) Kjaergaard, H. G.; Turnbull, D. M.; Henry, B. R. *J. Chem. Phys.* **1993**, *99*, 9438–9452.
- (12) Low, G. R.; Kjaergaard, H. G. *J. Chem. Phys.* **1999**, *110*, 9104–9115.
- (13) Acquista, N.; Shoen, L. J.; Lide, D. R., Jr. *J. Chem. Phys.* **1968**, *48*, 1534–1536.
- (14) Suzer, S.; Andrews, L. *J. Chem. Phys.* **1988**, *88*, 916–921.
- (15) Jodl, H. J. In *Chemistry and Physics of Matrix-Isolated Species*; Andrews, L., Moskovits, M., Eds.; Elsevier Science Publishers: Amsterdam, 1989; p 362.

JA034388K