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Identification of the Water Amidogen Radical Complex

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The gas-phase oxidation of ammonia (NH_3) by a hydroxyl radical (OH) has been the subject of numerous experimental and theoretical investigations.

$$NH_3 + OH \rightarrow NH_2 + H_2O \qquad (1)$$

This prototypical hydrogen abstraction reaction is of great interest because it is a key step in the atmospheric oxidation of NH_3 and is important in the combustion of fossil fuels.[1] Furthermore, the resultant amidogen radical (NH_2) is considered to be involved in both the production and elimination of atmospheric NO_x.[2] Previous theoretical investigations have identified up to five stationary points along the reaction coordinate of eq 1.[3,4] Our calculated relative energies of these stationary points are illustrated in Figure 1. In the present study we identify for the first time the water amidogen radical complex ($H_2O{-}NH_2$) using matrix isolation FT-IR spectroscopy.

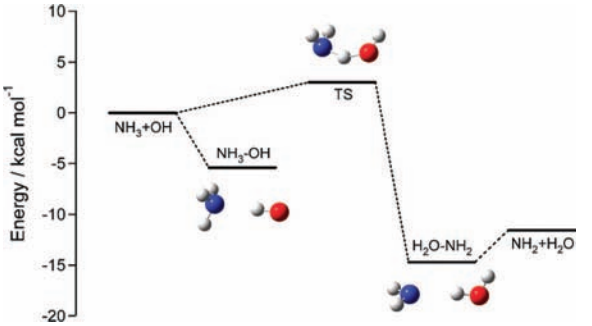

Figure 1. Reaction energetics for eq 1 calculated with the CCSD(T)/aug-cc-pVTZ method including harmonic zero-point vibrational energy correction. The transition state is abbreviated as TS.

The $H_2O{-}NH_2$ complex was prepared using a method similar to that previously described for the water hydroxyl radical complex ($H_2O{-}HO$).[5,6] In brief, separate mixtures of H_2O/Ar and NH_3/Ar were prepared in ratios of 1:150 to 1:500 using high-purity argon. The NH_3/Ar mixture was introduced into the matrix isolation system through a borosilicate glass tube where it was subject to a radio frequency discharge from a Tesla coil. Equal amounts of the discharged mixture and the H_2O/Ar mixture were codeposited onto a KBr sample window cooled to 10.5 ± 0.3 K by a closed-cycle helium refrigerator (APD Displex DE-202). 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.

In Figure 2 we present the global minimum structure of $H_2O{-}NH_2$ optimized using the coupled cluster with singles, doubles, and perturbative triples [CCSD(T)] method. The calculated harmonic frequencies and intensities for $H_2O{-}NH_2$ and the constituent monomers, H_2O and NH_2, are given in Table 1. As expected, the hydrogen bonded OH(b)-stretching mode (υ_2) is significantly perturbed upon complexation, and there are modest changes calculated for the other intramolecular vibrational modes (υ_1, υ_{3-6}).

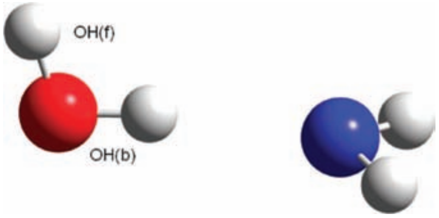

Figure 2. Optimized structure of the $H_2O{-}NH_2$ complex.

Table 1. Calculated Vibrational Frequencies and Intensities for the $H_2O{-}NH_2$ Complex and H_2O and NH_2 Monomers[a]

	$H_2O{-}NH_2$	H_2O	NH_2
υ_1	3888.3 (92)	3919.9 (54)	
υ_2	3711.1 (305)	3810.8 (3)	
υ_3	3479.8 (1)		3454.0 (1)
υ_4	3383.4 (7)		3360.2 (13)
υ_5	1669.8 (44)	1645.9 (70)	
υ_6	1542.0 (20)		1540.0 (25)
υ_7	597.5 (99)		
υ_8	388.8 (123)		
υ_9	201.8 (102)		
υ_{10}	167.8 (11)		
υ_{11}	141.1 (61)		
υ_{12}	39.1 (40)		

[a] Calculated with the CCSD(T)/aug-cc-pVTZ method. Vibrational frequencies are in cm^{-1}, and intensities (in parentheses) are in km mol^{-1}.

In Figure 3 we present FT-IR spectra of the combined NH_3/Ar discharged mixture and H_2O/Ar mixture in the OH(b)- and OD(b)-stretching regions. We observe many vibrational features, but only a few of these are due to radical species (Supporting Information, SI). The strong bands at 3573.5 (2613.9) cm^{-1} and 3435.8 (2517.9) cm^{-1} have been previously assigned to the OH(b)- and OD(b)-stretching modes of $H_2O{-}H_2O$ and $H_2O{-}NH_3$, respectively.[7,8] We assign the band at 3532.1 cm^{-1} to the OH(b)-stretching transition of $H_2O{-}NH_2$, with the equivalent OD(b)-stretching transition of $D_2O{-}ND_2$ assigned to the band at 2588.5 cm^{-1}. In Table 2, we show that the isotopic frequency shift of the OH(b)-stretching frequency for $H_2O{-}NH_2$ is similar to that of $H_2O{-}H_2O$ and $H_2O{-}NH_3$, supporting our assignment.

In general, the frequency of an OH(b)-stretching transition is dependent on the binding energy of a complex, although the trend

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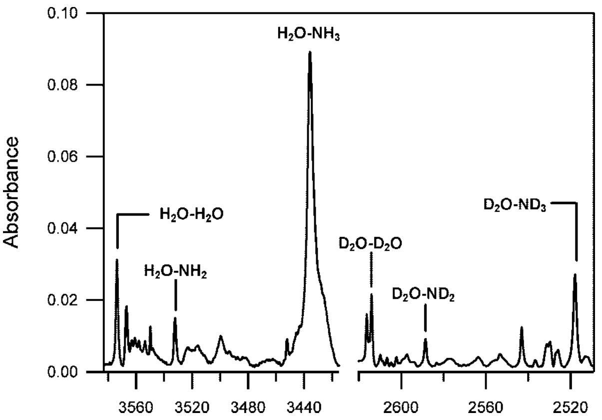

Figure 3. OH(b)-stretching bands for H_2O-H_2O, H_2O-NH_3, H_2O-NH_2, and the deuterated equivalents.

is nonlinear. The binding energy of H_2O-NH_2 is calculated to be 5.1 kcal mol^{-1} at the CCSD(T) complete basis set limit. This value is appreciably less than the binding energy of H_2O-NH_3, and as expected the red shift of H_2O-NH_2 is less than that of H_2O-NH_3 (Table 2).[8,9] The calculated binding energy of H_2O-NH_2 is similar to that of H_2O-H_2O; however the measured red shifts of the two complexes differ by ~40 cm^{-1}.[7,10]

Table 2. Comparison of Measured OH(b)- and OD(b)-Stretching Bands[a] and Binding Energies[b] for H_2O-H_2O, H_2O-NH_3, H_2O-NH_2, and Their Deuterated Equivalents

	H_2O-H_2O	H_2O-NH_2	H_2O-NH_3
E_b	5.0	5.1	6.4
$\upsilon_{OH(b)}$	3573.5	3532.1	3435.8
$\upsilon_{OH(b)}{}^c$	−66.0	−105.9	−203.8
$\upsilon_{OD(b)}$	2613.9	2588.5	2517.9
$\upsilon_{OD(b)}{}^c$	−43.8	−69.2	−140.9
$\upsilon_{OH(b)}/\upsilon_{OD(b)}$	1.37	1.36	1.36

[a] Vibrational frequencies are from the present argon matrix isolation spectra and are expressed in cm^{-1}. [b] Binding energies (E_b) are calculated at the CCSD(T) complete basis set limit and are expressed in kcal mol^{-1}. [c] The experimental OH(b)-stretching frequency minus the experimental symmetric OH-stretching frequency of H_2O monomer.

In Table 3 we compare the observed OH- and OD-stretching frequencies of H_2O-NH_2 and D_2O-ND_2 to results calculated with a harmonically coupled anharmonic oscillator (HCAO) local mode model.[11] The OH(b)-stretching frequency of H_2O-NH_2 is calculated to be 3531.3 cm^{-1}, which is in fortuitously good agreement with the observed band at 3532.1 cm^{-1}. Argon matrices typically red shift OH-stretching frequencies by ~25 cm^{-1}.[7,8] The HCAO calculated OD(b)-stretching frequency is also in good agreement with the observed band at 2588.5 cm^{-1}.

We assign a weak band at 1498.5 cm^{-1} to the HNH-bending transition (υ_6) of H_2O-NH_2 (SI). This vibrational mode is slightly blue-shifted compared to the monomer transition at 1495.0 cm^{-1},[12] in good agreement with the calculated blue shift of the harmonic frequencies (Table 1). The DND-bending transition of D_2O-ND_2 is observed at 1110.3 cm^{-1}, which is again slightly higher than the equivalent monomer transition at 1106.8 cm^{-1}. These transitions are relatively weak; however the region has few other interfering vibrational features.

Table 3. Comparison of Measured and Calculated OH-Stretching Transitions for the H_2O-NH_2 Complex[a]

	experimental[b]	calculated[c]
$\upsilon_{OH(f)}$		3725.5 (71)
$\upsilon_{OH(b)}$	3532.1	3531.3 (369)
$\upsilon_{OD(f)}$		2755.3 (57)
$\upsilon_{OD(b)}$	2588.5	2596.4 (169)

[a] Vibrational frequencies expressed in cm^{-1}, and intensities (in parentheses) expressed in km mol^{-1}. [b] Experimental values are from the present argon matrix isolation spectra. [c] Calculated with an HCAO local mode model. Please see the SI for details.

Of the four remaining intramolecular vibrational modes, the NH-stretching transitions (υ_3 and υ_4) in H_2O-NH_2 are calculated to be very weak (Table 1), and as a result these modes are not observed. The OH(f)-stretching transition in H_2O-NH_2 is relatively strong; however our calculations indicate that this transition is masked by the OH(f)-stretching transitions of H_2O-H_2O and H_2O-NH_3 in the same region.[7−10] The HOH-bending mode of H_2O-NH_3 has been previously observed only in a neon matrix;[8] hence the equivalent HOH-bending mode (υ_5) of H_2O-NH_2 is unlikely to be observed in our present argon matrix.

In summary, we have observed the υ_2 and υ_6 intramolecular vibrational modes of the water amidogen radical complex. We also observe these same absorption features with approximately half the intensity if we discharge the H_2O/Ar mixture (to generate OH radical) instead of the NH_3/Ar mixture, with no sign of the corresponding NH_3-HO complex. We suggest that the OH radical is reacting with NH_3 to form the H_2O-NH_2 complex during codeposition on the sample window.

Acknowledgment. We wish to dedicate this paper to the memory of Dr. Terry I. Quickenden who originated this work before passing away in 2005. C.E. is grateful to the Department of Education, Employment and Workplace Relations (DEEWR) of the Australian Commonwealth Government for an Australian Postgraduate Award, and J.R.L. is grateful to the Foundation for Research, Science, and Technology for a Bright Futures Scholarship. We acknowledge the Marsden Fund administered by the Royal Society of New Zealand for financial support.

Supporting Information Available: Additional experimental spectra and details of the complete basis set limit extrapolation of the binding energies and the HCAO calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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