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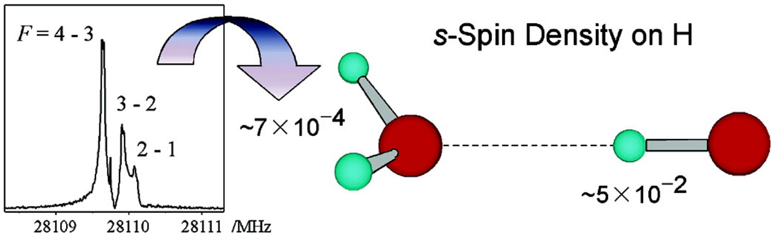

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Rotational Spectrum and Hydrogen Bonding of the H_2O−HO Radical Complex

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The hydroxyl radical, OH, plays a key role as a reactive intermediate in elementary reactions occurring in various fields of chemistry.[1−3] Detailed knowledge on mutual interaction of the radical with other molecules is crucial in microscopic description of such fundamental processes. Furthermore, interaction with nearby partners may substantially alter the reactivity of the radical through a charge rearrangement, in particular, of the unpaired electron orbital. Hydrated OH is a prototypical system to address the issue, since it serves as an attractive well in the entrance channel to the simple identity hydrogen abstraction reaction, OH + H_2O → H_2O + OH,[4] and has also been predicted to behave as a stronger oxidant than free OH.[5] In this respect, the complex is regarded to have possible significance in chemical processes in the Earth's atmosphere,[6] crystalline and amorphous ices,[7] and aqueous environments including biological systems.[3]

Theoretical calculations have revealed two different hydrogen-bonding topologies for the minimum-energy structure of hydrated hydroxyl (Figure 1).[8,9] The more stable form, **1**, is of C_s symmetry, where hydroxyl acts as a proton donor and the unpaired electron orbital lies in the reflection plane (thus in a $^2A'$ state). Matrix isolation infrared spectra of several isotopic variants of the radical complex have been reported to assign the observed bands to the geometry **1**.[10,11] Here we report the first identification of H_2O−HO in the gas phase via microwave spectroscopy. The present study confirms the geometry in isolated condition. In addition, the inherently high spectral resolution of the method provides quantitative information on the electronic rearrangement by hydrogen bond (H-bond) formation.

The rotational spectrum of H_2O−HO was recorded by utilizing a Fourier transform microwave (FTMW) spectrometer combined with a pulsed-discharge nozzle source. Details of the experimental setup have been described elsewhere.[12] The OH radical was generated by a DC discharge of H_2O diluted in Ar or Ne, and the radical was subsequently cooled to form the hydrated complex in a supersonic expansion. Three successive R-branch transitions ($N = 1-0$ to $3-2$) within the $K_a = 0$ manifold of a near-prolate top have been observed in 5−40 GHz, of which assignment to the H_2O−HO complex was confirmed by examining chemical composition, paramagnetic behavior, and the observed magnetic hyperfine structure due to the H nuclei. The spectrum is represented as that of a doublet molecule (i.e., $S = {}^1/_2$) in Hund's case (b),[13] in which the electronic angular momentum of OH($^2\Pi$) is effectively quenched by complex formation. However, the spectrum exhibits extremely large spin doubling between the $J = N + {}^1/_2$ and $N - {}^1/_2$ components. This is a signature of deviation from the case (b)-limit representation and approach to the case (a)-limit one.

Magnetic hyperfine structure that appeared in each of the observed rotational transitions was characteristic of a radical with two nonzero nuclear spins with $I_1 = {}^1/_2$ and $I_2 = 1$, causing larger (~MHz) and smaller (<MHz) splitting, respectively. The I_1 spin is that of the H atom in hydroxyl, while I_2 is the composite angular momentum of two H spins in water. Since rotational states with $K_a = 0$ are coupled with $I_2 = 1$ but not with $I_2 = 0$, Pauli's exclusion principle restricts the complex structure to be of two-fold symmetry around the *a* principal axis and the vibronic wave function to be anti-symmetric to the C_2 rotation. The restriction concludes that the complex geometry is planar (C_{2v}) as the zero-point vibrational average because the flipping of the water H atoms above and below the molecular plane is feasible (Figure 1). This conclusion is fully compatible with the theoretical results, which have predicted a marginal energy difference from the minimum to the planar structure which corresponds to a saddle point in the $^2B_1$ state (~17 cm^{-1} with the CISD(Q)/TZ2P calculations[8] and ~240 cm^{-1} with the CCSD(T)/aug-cc-PVTZ calculations by using the MOLPRO package[14]).

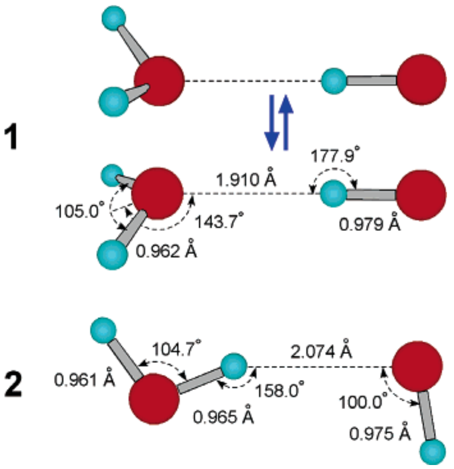

Figure 1. Two stable H-bonding forms of H_2O−HO. Structures **1** and **2** are those in the $^2A'$ state (global minimum) and the $^2A''$ state, respectively, derived by CCSD(T)/aug-cc-PVTZ calculations.

A total of 60 observed hyperfine split transitions have been subjected to a least-squares fitting with a standard Hamiltonian for an asymmetric-top doublet radical, including centrifugal distortion, spin rotation, and magnetic hyperfine interactions.[15] Spectroscopic constants thus determined are listed in Tables 1 and 2. The rms of the fit was 12 kHz, in reasonable agreement with the measurement accuracy of ~10 kHz.

The experimental value of $(B + C)/2$ differs only <3% from that calculated for the CCSD(T)/aug-cc-PVTZ geometry of **1** in $^2A'$. The difference further decreases to <2% for the planar ($^2B_1$) theoretical geometry. When we assume the C_{2v} geometry and no perceptible change in structure of the monomer units from free molecules,[13,16] the H-bond distance is calculated to be 1.945 Å from the experimental $(B + C)/2$. This is somewhat longer than that in the analogous system H_2O−HF (1.745 Å)[17] and slightly shorter

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Table 1. Rotational Constant of $H_2O{-}HO$ (in GHz)

		ab initio[b]	
	exptl[a]	C_s ($^2A'$)	C_{2v} ($^2B_1$)
$(B + C)/2$	6.57813(7)	6.77	6.70

[a] 1σ uncertainty (in parentheses) is in the units of the last significant digit. The best-fit centrifugal-distortion and spin-rotation constants (in MHz) are $\Delta_N = 0.05110(13)$, $(\epsilon_{bb} + \epsilon_{cc})/2 = 3607.64(14)$, $\epsilon_{bb} - \epsilon_{cc} = 4246(23)$, and $^s\Delta_N = 0.280(3)$. The following constants are fixed to the calculated values from the ab initio geometry: $A = 428.7$ GHz and $B - C = 104.5$ MHz. [b] Derived from the CCSD(T)/aug-cc-PVTZ geometries.

Table 2. Magnetic Hyperfine Constants Due to Hydrogen Nuclei in $H_2O{-}HO$ and Free OH (in MHz)

	$H_2O{-}HO$[a]		
	H_2O side	OH side	free OH[b]
a_F	0.940(5)	−8.226(6)	−74.04
T_{aa}	4.447(8)	126.159(9)	88.08

[a] 1σ uncertainty (in parentheses) is in the units of the last significant digit. [b] From ref 19.

than that in $(H_2O)_2$ (2.019 Å).[18] For the less stable form **2**, $(B + C)/2$ is estimated to be substantially smaller (6.2−6.4 GHz) because of the longer H-bond distance (∼2.1 Å).[8,9]

The spin-rotation constants, ϵ_{bb} and ϵ_{cc}, are extremely large, almost comparable to $(B + C)/2$. This indicates the existence of a low-lying excited state that is coupled with the ground state ($^2A'$ as C_s or $^2B_1$ as C_{2v}) via the spin−orbit interaction. A candidate is the $^2A''$ (or $^2B_2$) state, in which the unpaired electron orbital lies in the molecular plane. This and the ground states correlate with the $^2\Pi$ state of free OH, the degeneracy of which is removed by the interaction with nearby water. We adopt the monomer spin−orbit coupling constant,[19] and secular determinants of a Hamiltonian matrix constructed for the two coupled states are calculated to fit the observed spin-rotation doubling, resulting in a $^2A'/^2A''$ (or $^2B_1/^2B_2$) interval of ∼150 cm^{-1}. This estimate agrees remarkably well with the CCSD(T)/aug-cc-PVTZ calculations (120 cm^{-1} at C_s geometry and 140 cm^{-1} at C_{2v}). Previous calculations have given similar results.[8,9,10b,11]

The magnetic hyperfine constants in hydroxyl are substantially altered from the free OH values[19] by microscopic hydration (Table 2). The negative value of the Fermi contact constant, a_F, in free OH is solely due to the spin polarization by the unpaired electron in the $p\pi$ orbital of the adjacent O atom.[19] The extent of the polarization is proportional to the spin density on the $p\pi$(O) orbital.[20] If a_F in the complex is also entirely a result of the polarization, reduction of the spin density by the H-bond formation amounts to 1/9, apparently too large. Instead, most of the difference should come from the direct contact to the H nucleus of the unpaired electron by occupation in an *s*-type orbital. Comparison with the atomic hyperfine constant for H (^2S)[21] sets the *s*-spin density at the radical H to be 4.6%. It is noted that, in the rigid C_{2v} geometry, the unpaired electron resides in the out-of-plane $p\pi$ orbital, which vanishes at the molecular plane by symmetry. The large-amplitude flipping mentioned before should contribute to sample nonplanar configurations, where the direct contact becomes possible.

The spin−spin dipolar coupling constant, T_{aa}, is proportional to $\langle(3\cos^2\theta - 1)/r^3\rangle$, where r is the distance from the H nuclei to the unpaired electron and θ denotes the angle between the r vector and a axis.[15] More than a 40% increase in T_{aa} of OH indicates the significant deformation of the unpaired electron orbital, which implies a considerable withdraw of the unpaired electron around O toward H through the H-bond formation.

Nonzero hyperfine constants for water H nuclei evidence the unpaired electron orbital extending over the entire complex. In particular, the small but positive value for a_F proves the ∼0.07% of *s*-spin density at the position of H atoms. Again, contribution from nonplanar geometry seems to be substantial. In addition, if the unpaired electron resides exclusively in the $p\pi$(O) orbital of OH, the $T_{aa}(H_2O)/T_{aa}(OH)$ ratio should be ∼0.02 by considering the $1/r^3$ dependence. The experimental ratio (0.035) is of the same order, and the excess may be caused by some occupation of the unpaired electron in the water $p\pi$(O) orbital. It means that a small portion of the electron density is transferred from water to the OH radical through the H-bond formation, $H_2O^{\delta+}{-}HO^{\delta-}$. Such a charge transfer has also been reported for a molecular complex containing a stable radical, NO−HF,[22] where the radical is a proton acceptor and is subjected to the electron removal.

To obtain more details on the electronic rearrangement and internal dynamics of $H_2O{-}HO$, further investigation will be important. Studies on other isotopic species, in particular with ^{17}O ($I = {}^1/_2$), will experimentally establish the electronic-state symmetry via hyperfine constants. Observation of the $I_2 = 0$ state (with $K_a = 1$ or out-of-plane bending excitation) will provide a finer depiction of the floppiness of the complex. Judging from the fairly high S/N achieved in the present observation for $H_2O{-}HO$, the experimental method adopted herein should be applicable for radical−molecule complexes with OH and other important reactive intermediates, e.g., SO, ClO, and HOO.

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