

A Chemical Compound Formed from Water and Xenon: HXeOH

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Xenon is the most reactive stable rare gas, and its chemical properties have been widely explored since the discovery of the first xenon-containing compound by Bartlett in 1962.^{1,2} Usually, extremely electronegative substances are required to make a Xe-containing compound, and such reagents are seldomly found in nature, thus, allowing xenon chemistry only in the laboratory.

Recently, we have shown that Xe and Kr can form neutral ground state HXY compounds, where X = Xe or Kr and Y is a fragment with a relatively large electron affinity.³ One of the most profound examples is HXeSH synthesized in a low-temperature Xe matrix.⁴ The successful preparation of this compound prompted the search of its oxygen analogue, HXeOH. Here we report the preparation of HXeOH in a Xe matrix. This compound is unique because its preparation needs in addition to xenon only water, which is very abundant in nature, thus, shifting Xe chemistry from laboratory conditions toward environmental reality.

In experiments, water vapor was mixed with xenon in a vacuum line roughly in a ratio Xe:H₂O = 1000 or larger. The gas mixture was deposited on a CsI substrate held at 30 K, which resulted in a highly monomeric matrix with respect to water. After deposition, the substrate was cooled to 7.5 K.

Water molecules were dissociated in the matrix with a 193 nm ArF laser as demonstrated in Figure 1. The H₂O → H + OH channel and subsequent permanent trapping of H atoms and OH radicals were confirmed by the observation of LIF (laser induced fluorescence) from H⁻Xe_n⁺ exciplexes and OH radicals.^{5,6} In addition, an IR band appeared at 3531.3 cm⁻¹ which can be assigned to OH radicals in agreement with the assignment in ref 7. The OH concentration started to decay slowly after achieving a maximum, indicating that 193 nm photolyzes it to oxygen and hydrogen atoms. The rise of O atoms was monitored by LIF as well.⁸

After the decomposition of H₂O and formation of H atoms and OH radicals, the matrix was annealed at two stages. First, the matrix was warmed to 35 K, and at this temperature O atoms are mobilized,⁹ as witnessed by appearing bands at 1383 and 1096 cm⁻¹ (HO₂), and ~1027 cm⁻¹ (O₃). No changes in the water-bending region appear at this stage as seen in Figure 1.

At the second stage, the matrix was warmed to about 48 K to mobilize H atoms. At this temperature XeH₂¹⁰ appeared indicating global diffusion of H atoms. In addition to known bands of XeH₂ at 1166 and 1180 cm⁻¹, a new strong absorption appeared at 1577.6 cm⁻¹ after annealing at 48 K, as shown in Figure 1. This band does not belong to a water molecule, and it appears only after 193 nm photolysis and annealing at >40 K.

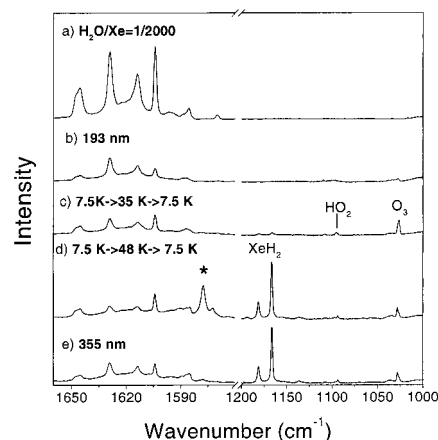


Figure 1. Photolysis and annealing of a H₂O/Xe = 1/2000 matrix: (a) situation after deposition showing the vibration-rotation bands of monomeric water; (b) situation after 10⁴ pulses of 193 nm radiation showing the decomposition of ~70% of water; (c) annealing of the matrix at 35 K mobilizes O atoms, which is evidenced by formation of ozone and HO₂; (d) annealing at 48 K mobilizes H atoms, which is evidenced by formation of XeH₂ and a new product marked with *; (e) selective bleaching of the band at 1577.6 cm⁻¹ by irradiation with 355 nm for 5 min. All of the spectra are recorded at 7.5 K with 1 cm⁻¹ resolution.

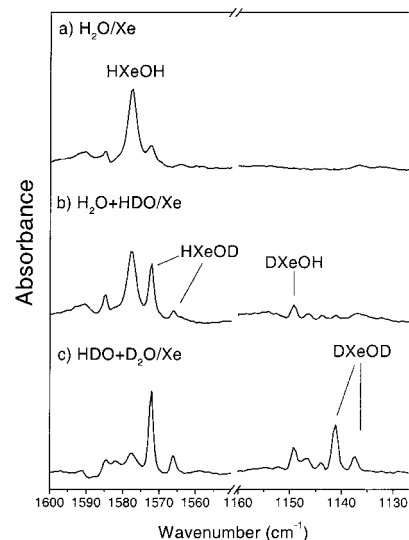


Figure 2. Formation of different isotopomers of HXeOH in H₂O/HDO/D₂O/Xe matrixes: (a) Difference spectrum between the situation after 35 K annealing and 48 K annealing after 193 nm photolysis of H₂O showing the formation of HXeOH only; (b) same as in (a) but with H₂O + HDO/Xe yielding mainly HXeOH, HXeOD, and DXeOH; (c) same as in (a) but with HDO + D₂O/Xe yielding mainly HXeOH, HXeOD, DXeOH, and DXeOD. All of the spectra are recorded at 7.5 K with 1 cm⁻¹ resolution.

Comparative experiments with H₂O, HDO, and D₂O were performed to identify the species responsible for the new absorptions, and the results are presented in Figure 2. Two different shifts for the new compound were observed. A new band at 1141.2 cm⁻¹ indicates a D-shift for a hydrogen stretch with a H/D ratio of 1.382 from 1577.6 cm⁻¹. The second band appeared at 1572.2 cm⁻¹, suggesting that the molecule contains another hydrogen atom. Consistent with this, the strongly shifted band at 1141.2 cm⁻¹ also had another slightly shifted counterpart at 1149.3 cm⁻¹. When the H₂O:HDO:D₂O ratio was changed, the relative intensities of the four bands changed accordingly. For example, in a matrix with mostly HDO and D₂O, the band at 1577.6 cm⁻¹ was almost invisible. All four absorptions have smaller sidebands as seen in Figure 2. These bands are collected in Table 1.

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Table 1. Calculated Vibrational Wavenumbers (in cm^{-1}) of Different Isotopomers of HXeOH Using the LJ18/6-311++G(2d,2p) Basis Set Compared with the Observed Wavenumbers^a

approx mode	HXeOH		HXeOH CCSD(T)	HXeOD		DXeOH		DXeOD	
	MP2	exp ^b		MP2	exp ^b	MP2	exp ^b	MP2	exp ^b
A' O-H stretch	3842.4 (51)		3835.6	2797.6 (31)		3842.3 (54)		2797.4 (37)	
A' Xe-H stretch	1822.7 (1456)	1577.6	1677.9	1820.8 (1462)	1572.2	1297.5 (745)	1149.3	1294.0 (750)	1141.2
		1572.4			1566.1		1146.7		1137.5
		1591.3			1581.9		1144.0		
					1584.6				
A' H-Xe-O-H antisymmetric bend	818.6 (8)		812.1	726.8 (12)		766.1 (4)		607.8 (5)	
A'' H-Xe-O oop bend	652.4 (7)		629.5	651.1 (9)		474.5 (4)		472.8 (7)	
A' H-Xe-O-H symmetric bend	584.1 (10)		574.5	492.6 (36)		454.4 (34)		444.7 (99)	
A' Xe-OH stretch	436.4 (126)		419.2	418.9 (93)		434.5 (102)		402.2 (31)	

^a Numbers in parentheses are the calculated IR intensities (in km mol^{-1}). Numbers in bold are the observed main absorptions. ^b Determined from a difference spectra between the situation before and after 355 nm induced decomposition of H(D)XeOH(D). This method resolves well even very small sidebands which are not easily observable in Figure 2.

The photodecomposition threshold of the new molecule was determined by irradiating the sample with different wavelengths with an OPO (optical parametric oscillator) and then detecting decomposition of the product. The threshold was located between 400 and 375 nm. Photobleaching with 355 nm radiation is shown in trace (e) of Figure 1. This experiment clearly demonstrates that the species under question is not complexed water because the photodissociation threshold is well below the dissociation energy of water. After the photodecomposition, the compound could be partially regenerated in the subsequent annealing.

On the basis of these observations, the new bands are assigned to HXeOH. The compound is formed from the decomposition products of water at the temperature of hydrogen-atom mobilization. The observed strong band at 1577.6 cm^{-1} is assigned to the Xe-H stretch. The smaller shift to 1572.2 cm^{-1} induced by deuteration is explained naturally by the deuteration of the OH group and, accordingly, the band at 1572.2 cm^{-1} is assigned to HXeOD. Similarly, the bands at 1141.2 and 1149.3 cm^{-1} are assigned to DXeOD and DXeOH, respectively. The photodecomposition at around 375 nm fits perfectly the known trend of related compounds.³

Our ab initio calculations fully agree with these conclusions. The calculations were done with the Gaussian98 package of computer codes.¹¹ The relativistic effective core potential by LaJohn et al.¹² (LJ18) was used on Xe, and the valence basis set was decontracted. The standard 6-311++G(2d,2p) basis set was used for oxygen and hydrogen.

The calculated structure for HXeOH is shown in Figure 3, and the calculated vibrational spectra of different isotopomers of HXeOH are presented in Table 1 together with the observed bands. The Mulliken charges for the atoms at the MP2 level are -0.24 , $+0.82$, -0.81 , and $+0.23$ for H (Xe-bound), Xe, O, and H (O-bound), respectively. This indicates a substantial ion-pair character as in the other similar compounds.³ The Xe-H distance is near free (Xe-H)⁺ bond distance of 1.602 \AA ¹³ being in line with a (HXe)⁺(OH)⁻ ion-pair character. The Xe-O-H angle is 108.7° at the CCSD(T) level, and this value is near 104.5° of

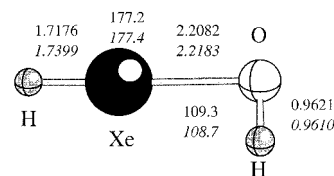


Figure 3. Calculated equilibrium structure of HXeOH. Bond distances are given in ångströms, and bond angles are given in degrees. The calculations were performed at the MP2 and CCSD(T) (lower values) levels using the LJ18/6-311++G(2d,2p) basis set.

water. Interestingly, the H-Xe-O angle deviates slightly from linearity which is different from the other related molecules which were predicted to have linear HXeY groups.³ It is notable that F-Xe-O angle in FXeOSO₂F is about 177.5° ,¹⁴ bearing some similarity to the H-Xe-O group. The O-H distance is just typical for a O-H group. The Xe-O distance in HXeOH is similar to the experimental Xe-O distance of 2.16 \AA in FXeOSO₂F.¹⁴

The calculations at the CCSD(T) level give 0, 4.69, and 5.26 eV for the relative electronic energies for H₂O + Xe, HXeOH, and H + Xe + OH, respectively. Therefore, HXeOH is a high-energy compound with respect to the global minimum (H₂O + Xe), but it is still bound with respect to the (H + Xe + OH) asymptote by about 0.6 eV. Taking into account the computational zero-point energies, the binding energy is reduced to about 0.3 eV at this level of theory.

The calculated spectrum supports strongly the experimental assignment. The calculations predict a strong Xe-H stretching band and the other modes to be much weaker. Experimentally, the Xe-H stretch is the only strong band, and the other bands above 450 cm^{-1} are presumably too weak to be observed. At the MP2 level the calculated wavenumber of the Xe-H stretch is rather higher than that of the experimental, but at the CCSD(T) level the agreement is fairly good. A similar trend was observed, for example, for HXeSH.⁴ The calculations predict the HXeOH-HXeOD splitting to be 1.9 cm^{-1} and the DXeOD-DXeOH splitting to be 3.5 cm^{-1} and this is in reasonable agreement with the observed shifts, which are 5.4 and 8.1 cm^{-1} , respectively.

In summary, our experiments and computations strongly suggest that HXeOH has been prepared in a low-temperature Xe matrix. It represents a chemical compound formed from a rare gas atom and a naturally very abundant and relatively inert molecule, and it prompts for search of this molecule in nature. Although HXeOH is predicted to have a D₀ of only about 0.3 eV with respect to (H + Xe + OH) asymptote it may be strongly stabilized by electrostatic solvation and H-bonding effects, and its formation, for example, in ice, under UV radiation seems realistic.

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