

A Neutral Xenon-Containing Radical, HXeO

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In 1962, Bartlett reported the first xenon-containing chemical compound, $\text{Xe}^+[\text{PtF}_6]^-$,¹ and a year later a molecule with krypton, KrF_2 , was identified.² It took four decades until argon was conquered by low-temperature synthesis of HArF ,³ and serious activity is obvious nowadays in the field of rare-gas chemistry.^{4–6} The characterization of HArF followed the extensive studies of HRgY molecules where Rg is a rare-gas atom and Y is an electronegative fragment (HXeBr , HXeOH , HKrCN , etc.).⁷ These HRgY molecules are truly chemically bound species with closed-shell electronic configuration.⁸ Here we report the identification of an open-shell species containing xenon, HXeO ($^2\Sigma$), prepared by UV photolysis of $\text{H}_2\text{O}/\text{Xe}$ or $\text{N}_2\text{O}/\text{HBr}/\text{Xe}$ solid mixtures at 7 K and subsequent thermal mobilization of oxygen atoms at ≥ 30 K. The infrared (IR) absorption spectroscopic experiments are supported by extensive ab initio calculations suggesting the intrinsic stability of HXeO .

The $\text{H}_2\text{O}/\text{Xe}$ matrixes ($\sim 1/2000$) were prepared and photolyzed at 193 nm as described elsewhere.⁹ As a result of the irradiation, the matrix mainly contains O and H atoms, OH radicals, and residual H_2O molecules, full spectroscopic evidence for all of them being available.^{9–13} In the previous studies of HXeY molecules, the photolyzed HY/Xe samples were usually annealed at 40–48 K, which mobilized H atoms and led to diffusion-controlled formation of the HXeY molecules in reactions of H atoms with neutral $\text{Xe}-\text{Y}$ centers.¹⁴ The result of such “high-temperature” annealing is presented by the upper trace in Figure 1 for a photolyzed $\text{H}_2\text{O}/\text{Xe}$ sample. In agreement with the previous reports, the obtained IR spectrum shows formation of neutral HXeH and HXeOH molecules.^{7,9,10}

In addition to the known spectral features, we noticed systematic annealing-induced build-up of an unknown band at 1466.1 cm^{-1} (for H_2^{16}O precursor), and this is the key observation of the present work. It was found that this band appears practically alone already under annealing at 30–35 K (see the middle trace in Figure 1), which is characteristic for selective mobilization of atomic oxygen in solid Xe.¹⁵ Moreover, the 1466.1 cm^{-1} band partially decreases under mobilization of H atoms at higher temperatures (≥ 38 K), indicating reaction of the absorber with mobile H atoms. No analogous band with a normal matrix shift is seen upon photolysis and annealing of $\text{H}_2\text{O}/\text{Kr}$ samples, which suggests participation of a Xe atom in this species. Upon deuteration, the analogous band is at 1070.3 cm^{-1} (H/D ratio of 1.370) showing direct participation of a hydrogen atom in the absorbing vibration. It was verified that this absorber does not form from the natural matrix impurities (O_2 and N_2). By analyzing all possible candidates for this absorber and on the basis of our experience in preparation of HRgY molecules,

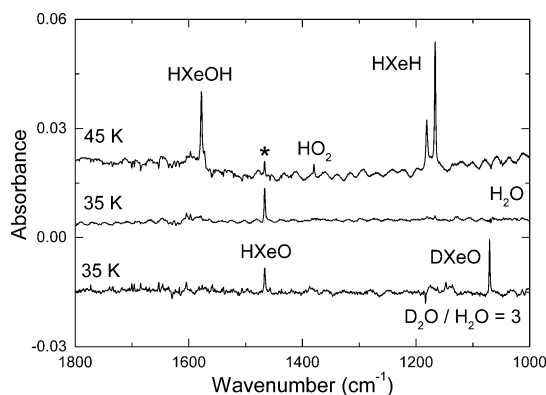


Figure 1. IR absorption bands formed after 193 nm photolysis and posterior annealing of Xe matrixes containing water. The band at 1466 cm^{-1} marked with an asterisk in the upper trace (annealing 45 K) is assigned to HXeO radicals. This species is formed upon annealing at 35 K (the middle and lower traces). Upon deuteration, the band of DXeO is at 1070 cm^{-1} . The spectra in the $4000\text{--}400\text{ cm}^{-1}$ spectral region were measured at 7 K with a Nicolet 60 SX FTIR spectrometer using resolution of 1 cm^{-1} .

we experimentally assign the band at 1466.1 cm^{-1} (1070.3 cm^{-1}) to the H–Xe (D–Xe) stretching mode of the HXeO (DXeO) radical.

The assignment of HXeO was supported by experiments with ^{18}O -substituted water. Small but definite blue shifts of the HXeO bands were found for the heavier oxygen isotope in numerous experiments without any exclusion. Summarizing the data, the band centers are shifted by $(0.27 \pm 0.04)\text{ cm}^{-1}$ for H_2^{18}O and $(0.19 \pm 0.04)\text{ cm}^{-1}$ for D_2^{18}O . In the same experiments, the oxygen-free rare-gas molecules such as HXeD have absorption frequencies independent of oxygen isotope substitution (with accuracy of $\pm 0.02\text{ cm}^{-1}$), which makes the reported oxygen-isotope shifts of HXeO confident. In agreement with our assignment, these data show that oxygen is not involved in the absorbing mode directly but that it participates in the species. The observed oxygen-isotope shift is “anomalous”, meaning blue shift for the larger reduced mass. We have recently found experimentally similar oxygen-isotope shifts for HXeOH and HXeOD molecules and described the effect theoretically in terms of anharmonic coupling between the normal modes.¹⁶ The low sensitivity of our apparatus in the far-IR spectral range ($< 400\text{ cm}^{-1}$) did not allow us to detect the Xe–O stretching vibration that should be more sensitive to oxygen isotope substitution.

According to the proposed image, HXeO is formed in reactions of mobile oxygen atoms with H–Xe centers, i.e., the process needs H and O atoms to be present in a Xe lattice. To verify this model, we performed a series of experiments on Xe matrixes doped with HBr and N_2O . Irradiation at 193 nm efficiently decomposes both HBr and N_2O , producing H and O atoms from the separate sources. Upon annealing of the photolyzed matrixes at 30–35 K, the 1466.1

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cm^{-1} band assigned to HXeO grew similarly to the experiments with water. It was shown that the formation of the 1466.1 cm^{-1} band requires *simultaneous* doping with both HBr and N_2O . The additional species seen in the IR absorption spectra after annealing are HXeH, HXeBr, HO_2 , and O_3 . These experiments with HBr/ N_2O /Xe samples strongly confirm that the species absorbing at 1466.1 cm^{-1} is formed from H and O atoms.

The experimental assignment of HXeO is fully supported by ab initio quantum chemical calculations performed at the MP2/LJ18/6-311++G(2d,2p) and CCSD(T)/LJ18/6-311++G(2d,2p) levels of theory.⁷ HXeO is computationally a true energy minimum exhibiting a linear structure with H–Xe and Xe–O distances of 1.652 and 2.171 Å (MP2) and 1.694 and 2.153 Å [CCSD(T)], respectively. These bond lengths are slightly shorter than the corresponding distances in HXeOH, which are 1.740 and 2.218 Å at the same CCSD(T) level.¹⁰ The H–Xe and Xe–O distances in HXeO are close to the corresponding values in XeH^+ (1.603 Å)¹⁷ and in XeO ($^1\Sigma^+$) (2.06 Å).¹⁸ The natural bond orbital analysis indicates a strong ionic character of HXeO, with a positive charge on the Xe atom (+0.88) and a negative charge on the O atom (–0.90). The H–Xe stretching frequency is 1681 cm^{-1} at the CCSD(T) level of theory. The agreement with the experimental value of 1466 cm^{-1} is very reasonable, taking into account similar overestimates for H–Rg stretching frequencies of other known HRgY molecules by this harmonic theory.⁷ The bending modes are computationally at 580 cm^{-1} , and the Xe–O stretching mode is at 382 cm^{-1} . Estimated at the MP2 theory level, the intensity of the H–Xe stretching mode is 309 km/mol, which is ~5 times smaller than that of HXeOH. This would suggest that the concentrations of HXeO and HXeOH are similar in the $\text{H}_2\text{O}/\text{Xe}$ experiments (see Figure 1), and the formation of HXeO makes an important product channel upon annealing of photolyzed $\text{H}_2\text{O}/\text{Xe}$ samples. The MP2 calculations yield a much smaller intensity for the bending modes (6 km/mol), which explains their invisibility in the experiments similarly to the situation with HXeOH,^{9,10} and the Xe–O stretching has an intensity of 185 km/mol.

The dissociation of HXeO ($^2\Sigma$) to the atomic products correlates with the singlet oxygen (1D) potential surface meaning that the $\text{H} + \text{Xe} + \text{O}$ (1D) reaction can lead to HXeO which is 1.52 eV lower in energy [CCSD(T)]. In contrast, the $\text{H} + \text{Xe} + \text{O}$ (3P) triad is much lower in energy than HXeO (by ~1.01 eV), which suggests that the O (3P) atoms are energetically incapable of forming the HXeO radical. The diffusion-controlled formation of HXeO at 30–35 K indicates the presence of O (1D) atoms in the Xe lattice. It follows that solid Xe can provide storage for the O (1D) atoms, and they move upon thermal annealing at $\geq 30 \text{ K}$. This agrees with the discussions on favorable stabilization of the O (1D) atoms in Xe lattice compared with O (3P).¹⁹

To check the energetic stability of HXeO with respect to the $\text{H} + \text{XeO}$ ($^1\Sigma^+$) channel, computations at the valence MRCISD/aug-cc-pVTZ level of theory were performed. It was found that HXeO is lower in energy than $\text{H} + \text{XeO}$ ($^1\Sigma^+$) by 137 meV, and it is additionally stabilized by 76 meV due to crossing of the neutral and charge-transfer potential surfaces, which means a stabilization barrier of 213 meV (20.6 kJ/mol). This energetics qualitatively corresponds to the computational results on HArF.²⁰

HXeO is an open-shell species ($^2\Sigma$), which makes it rather exceptional among neutral rare-gas compounds. The known open-shell species with rare-gas atoms are mainly radical cations, such as Xe_2^+ ²¹ and XeO^+ .²² A good candidate for a neutral open-shell species containing rare-gas atoms seems to be the XeF complex, which has a dissociation energy of 145 meV and a bond length of

2.31 Å .²³ The exact boundaries between chemical compounds and van der Waals complexes are not absolutely clear, and accurate analysis is always needed.⁴ It is worth noting in this respect that the computational Xe–F distances are 1.904 Å in XeF^+ and 2.146 Å in HXeF,²⁴ which are clearly shorter than in the XeF complex.

The identification of HXeO ($^2\Sigma$) suggests that analogous radicals with other rare-gas elements should be searched for. Both HKrO and HArO are computationally stable species. The H–Ar distance in HArO is 1.343 Å at the CCSD(T) level of theory, which is slightly shorter than the corresponding value of 1.355 Å for HArF,²⁴ and the Ar–O distance is 2.021 Å. In HKrO, the H–Kr and Kr–O distances are 1.490 and 2.087 Å [CCSD(T)]. Direct preparation of HKrO and HArO using the method described here is problematic due to the questionable stability of O (1D) atoms in Kr and Ar solids. However, their probable existence is intriguing, especially for HArO that might be found in the atmospheres.

In conclusion, the presented data allow us to claim the identification of an open-shell triatomic chemical compound containing xenon, HXeO ($^2\Sigma$). The HXeO species is prepared by using UV photolysis of $\text{H}_2\text{O}/\text{Xe}$ or $\text{N}_2\text{O}/\text{HBr}/\text{Xe}$ solid mixtures at 7 K and subsequent thermal mobilization of oxygen atoms at $\geq 30 \text{ K}$. The calculated stabilization barrier is 213 meV at the MRCISD/aug-cc-pVTZ level of theory. The HXeO ($^2\Sigma$) radical forms presumably in the $\text{H} + \text{Xe} + \text{O}$ (1D) reaction, and it is higher in energy (by ~1 eV) than the $\text{H} + \text{Xe} + \text{O}$ (3P) triad.

Acknowledgment. We thank V. Feldman for helpful discussions. The Academy of Finland supported this work. CSC (Espoo, Finland) is thanked for computing resources.

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JA029024R