

Article

A Small Neutral Molecule with Two Noble-Gas Atoms: HXeOXeH

Leonid Khriachtchev, Karoliina Isokoski, Arik Cohen, Markku Räsänen, and R. Benny Gerber

J. Am. Chem. Soc., **2008**, 130 (19), 6114-6118 • DOI: 10.1021/ja077835v • Publication Date (Web): 12 April 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009

More About This Article

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

- Supporting Information
- Links to the 5 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](#)

A Small Neutral Molecule with Two Noble-Gas Atoms: HXeOXeH

Leonid Khriachtchev,^{*,†} Karoliina Isokoski,[†] Arik Cohen,[‡] Markku Räsänen,[†] and
R. Benny Gerber^{‡,§}

Laboratory of Physical Chemistry, P.O. Box 55, FIN-00014 University of Helsinki, Finland,
Department of Physical Chemistry, Hebrew University, Jerusalem 91904, Israel, and
Department of Chemistry, University of California, Irvine, California 92697

Received October 12, 2007; E-mail: Leonid.Khriachtchev@Helsinki.Fi

Abstract: A novel noble-gas compound, HXeOXeH, is identified using IR spectroscopy, and it seems to be the smallest known neutral molecule with two noble-gas atoms. HXeOXeH is prepared using, for example, UV photolysis of water in solid xenon and subsequent annealing at 40–45 K. The experimental observations are fully supported by extensive quantum chemical calculations. A large energy release of 8.3 eV is computationally predicted for the decomposition of HXeOXeH into the 2Xe + H₂O global energy minimum. HXeOXeH may represent a first step toward the possible preparation of (Xe–O)_n chains and it may be relevant to the terrestrial “missing xenon” problem.

1. Introduction

Noble-gas chemistry is a fascinating field of research experiencing a renaissance during the past decade.^{1–4} The early noble-gas molecules were mainly prepared using fluorine chemistry. The first Xe-containing compound, XePtF₆, was synthesized by Bartlett in 1962.⁵ The first Kr-containing species (KrF₂) was reported by Turner and Pimentel in the following year.⁶ Argon was harnessed into chemical bonding much more recently, also in a fluorine-containing molecule HARF, made by Khriachtchev et al. in 2000.^{7,8} Fluorine chemistry and direct fluorine noble-gas bonds continue to play dominant and evolving roles in this field. In particular, Brock et al. have recently reported some new fluorine compounds with Xe–O bonds.⁹

However, in recent years there has been growing interest in fluorine-free noble-gas chemistry, and this topic is becoming rich and diverse. In particular, a number of fluorine-free noble-gas hydrides have been reported in low-temperature matrices starting since their discovery in 1995 by Pettersson et al., and the first identified species were HXeCl, HXeBr, HXeI, and HKrCl.¹⁰ These molecules have the general formula HN_gY (N_g

= noble-gas atom and Y = electronegative fragment). To date 22 molecules of this family have been synthesized and characterized, the latest members being HKrC₃N and HXeC₃N.¹¹ The developed preparation procedure is based on UV photolysis of HY precursors in a low-temperature noble-gas matrix and subsequent thermal mobilization of the photogenerated atoms (in most cases hydrogen).¹² For an example relevant to the present work, xenon was reacted by this method with water and an OH radical leading to HXeOH and HXeO species.^{13,14} It has been suggested by Lundell et al. that Xe atoms could be “inserted” into H–C bonds of hydrocarbons,¹⁵ and HXeCCH, HXeCC, and HXeCCXeH molecules were experimentally prepared by photolysis and annealing of C₂H₂/Xe solids.¹⁶ Remarkably, HXeCCXeH was the first noble-gas hydride containing two Xe atoms.

In the present work, we develop these recent achievements and describe the preparation and identification of HXeOXeH. This molecule can be considered as a combination of water and two xenon atoms, and it is probably the smallest molecule with two noble-gas atoms. HXeOXeH contains new features of oxygen bonding to xenon, and at the same time it may have very unusual properties and applications. The HXeOXeH molecule is experimentally identified by IR spectroscopy in a low-temperature matrix using isotope substitution and various

[†] University of Helsinki.

[‡] University of California.

[§] Hebrew University.

- (1) Grochala, W. *Chem. Soc. Rev.* **2007**, *36*, 1632.
- (2) Lehmann, J. F.; Mercier, H. P. A.; Schrobilgen, G. J. *Coord. Chem. Rev.* **2002**, *233*, 1.
- (3) Christe, K. O. *Angew. Chem., Int. Ed.* **2001**, *40*, 1419.
- (4) Brel, V. K.; Pirgulyev, N. S.; Zefirov, N. S. *Uspekhi Khimii* **2001**, *70*, 262.
- (5) Bartlett, N. *Proc. Chem. Soc.* **1962**, 218.
- (6) Turner, J. J.; Pimentel, G. C. *Science* **1963**, *140*, 974.
- (7) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature (London)* **2000**, *406*, 874.
- (8) Khriachtchev, L.; Pettersson, M.; Lignell, A.; Räsänen, M. *J. Am. Chem. Soc.* **2001**, *123*, 8610.
- (9) Brock, D. S.; Bilir, V.; Mercier, H. P. A.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **2007**, *129*, 3598.
- (10) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **1995**, *102*, 6423.

- (11) Khriachtchev, L.; Lignell, A.; Tanskanen, H.; Lundell, J.; Kiljunen, H.; Räsänen, M. *J. Phys. Chem. A* **2006**, *110*, 11876.
- (12) Lundell, J.; Khriachtchev, L.; Pettersson, M.; Räsänen, M. *Low Temp. Phys.* **2000**, *26*, 680.
- (13) Pettersson, M.; Khriachtchev, L.; Lundell, J.; Räsänen, M. *J. Am. Chem. Soc.* **1999**, *121*, 11904.
- (14) Khriachtchev, L.; Pettersson, M.; Lundell, J.; Tanskanen, H.; Kiviniemi, T.; Runeberg, N.; Räsänen, M. *J. Am. Chem. Soc.* **2003**, *125*, 1454.
- (15) Lundell, J.; Cohen, A.; Gerber, R. B. *J. Phys. Chem. A* **2002**, *106*, 11950.
- (16) Khriachtchev, L.; Tanskanen, H.; Lundell, J.; Pettersson, M.; Kiljunen, H.; Räsänen, M. *J. Am. Chem. Soc.* **2003**, *125*, 4696.

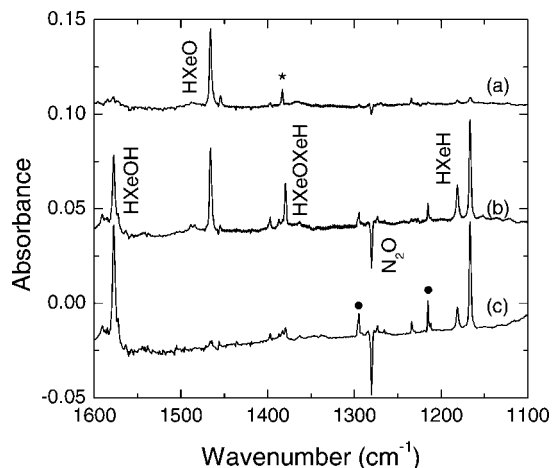


Figure 1. Difference IR spectra demonstrating results of annealing of photolyzed $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{Xe}$ matrices at (a) 33 K and (b) 45 K. Spectrum (c) was obtained by slow warming up to 45 K under global light, which selectively decomposes HXeO radicals. The bands of HOO and HN_2O are marked with asterisk and dots, respectively. The $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{Xe}$ (~1:1:1000) matrix was deposited onto a CsI window at 30 K and photolyzed at 9 K by a VUV xenon lamp (Ophos). The spectra were measured at 9 K.

precursors. The experimental assignment is supported by extensive quantum chemistry calculations including anharmonic approaches.

2. Experimental Results and Assignment

The $\text{H}_2\text{O}/\text{Xe}$, $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{Xe}$, and $\text{HBr}/\text{N}_2\text{O}/\text{Xe}$ solid mixtures were studied in a closed-cycle helium cryostat (APD, DE 202A) at temperatures down to 9 K. The matrices were deposited onto a CsI window at 25–30 K and then cooled down. In most experiments, the matrices were photolyzed by using vacuum ultraviolet light from a xenon lamp (Ophos).¹⁷ The IR spectra were measured at 9 K with a Nicolet 60 SX FTIR spectrometer in the 4000 to 400 cm^{-1} spectral range using a resolution of 1 cm^{-1} .

In a key experiment, a $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{Xe}$ solid mixture is photolyzed by vacuum ultraviolet light at 9 K. Upon photolysis, water and N_2O decompose. Photodecomposition of water leads to H, O, and OH (see refs 13, 18), and N_2O provides reactive O atoms and chemically inert N_2 molecules.^{19,20} Formation of XeHXe^+ is observed during photolysis.²¹ Annealing of the photolyzed sample at 30–35 K mobilizes O atoms^{19,20} and promotes their reactions with neutral H–Xe centers, which forms the HXeO radical with the H–Xe stretching absorption at 1466 cm^{-1} .^{14,20} Some formation of HOO radicals absorbing at 1383.1 and 1095.8 cm^{-1} occurs most probably due to the $\text{O} + \text{OH}$ reaction. This stage of annealing is shown by spectrum (a) in Figure 1.

Additional products are formed upon annealing at 40–45 K, which activates the mobility of H atoms,¹⁸ and the result is presented in spectrum (b) in Figure 1. In particular, these

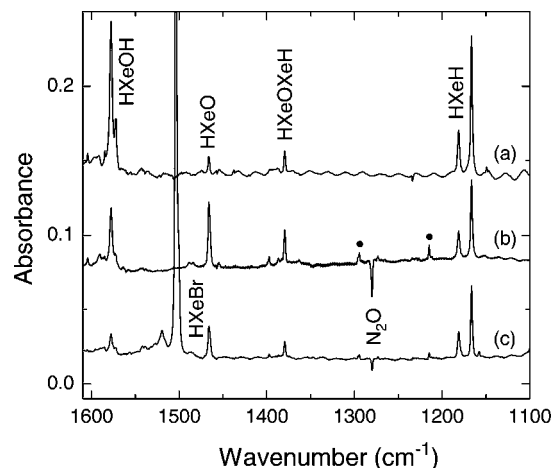


Figure 2. Difference IR absorption spectra demonstrating results of annealing at 45 K of (a) $\text{H}_2\text{O}/\text{Xe}$, (b) $\text{H}_2\text{O}/\text{N}_2\text{O}/\text{Xe}$, and (c) $\text{HBr}/\text{N}_2\text{O}/\text{Xe}$ matrices. The matrices were preliminarily photolyzed with a xenon lamp for 100 min (45 W electrical power), 180 min (35 W), and 60 min (35 W), respectively. The irradiation regimes were chosen to maximize the HXeOXeH concentration. The bands of HN_2O are marked with dots. HXeOH in spectrum (c) is probably contributed by impurity water. The spectra were measured at 9 K.

products are HXeH (1166 and 1180 cm^{-1}),²² HXeOH (1578 cm^{-1}),^{13,18} and HN_2O (1215, 1295, 1629, 3254 cm^{-1} and some other absorptions).²³ One previously unreported band at 1379.7 cm^{-1} systematically appears in the IR spectra, and this is the central observation of the present work. It should be stressed from the beginning that the 1379.7 cm^{-1} band does not originate from the HOO radical in another matrix site or in a complexed form since it is not accompanied with a band near 1100 cm^{-1} and this absorber has a different photolability from that of HOO.²⁴ The 1379.7 cm^{-1} band can be selectively bleached by 488-nm light from an argon-ion laser. Furthermore, no corresponding band with normal matrix shifts appears in similar experiments in argon and krypton matrices, which suggests that this absorber could be due to a novel Xe-containing molecule and the observed band is its H–Xe stretching absorption.

We shall discuss now the experimental assignment of the 1379.7 cm^{-1} absorber. The experiments with different photolysis periods and precursors show that its formation requires only H and O atoms in solid xenon. In fact, this absorber forms after photolysis and annealing of $\text{H}_2\text{O}/\text{Xe}$ matrices (without N_2O) but in smaller amounts as seen in Figure 2. It is interpreted that photolysis of water does not produce sufficient amounts of O atoms due to self-limitation of OH photolysis,²⁵ and the addition of N_2O enhances the 1379.7 cm^{-1} absorber. The 1379.7 cm^{-1} band is quite intense after photolysis and annealing of $\text{HBr}/\text{N}_2\text{O}/\text{Xe}$ matrices as seen in spectrum (c) in Figure 2. Based on these experiments, we assign the 1379.7 cm^{-1} band to the H–Xe stretching mode of HXeOXeH. The known HXeCCXeH molecule absorbs at 1301 cm^{-1} .¹⁶

(17) 193 nm radiation of an excimer laser (MPB, MSX-250) was used in a number of experiments for photolysis; however, the result was less satisfactory.

(18) Khriachtchev, L.; Tanskanen, H.; Pettersson, M.; Räsänen, M.; Feldmam, V.; Sukhov, F.; Orlov, A.; Shestakov, A. F. *J. Chem. Phys.* **2002**, *116*, 5708.

(19) Danilychev, A. V.; Apkarian, V. A. *J. Chem. Phys.* **1993**, *99*, 8617.

(20) Kiviniemi, T.; Pettersson, M.; Khriachtchev, L.; Räsänen, M.; Runeberg, N. *J. Chem. Phys.* **2004**, *121*, 1839.

(21) Karatun, A. A.; Sukhov, F. F.; Slovokhotova, N. A. *High Energy Chem.* **1981**, *15*, 371.

(22) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **1995**, *103*, 205.

(23) Laursen, S. L.; Delia, A. E.; Mitchell, K. *J. Phys. Chem. A* **2000**, *104*, 3681.

(24) In ref 14 this band was mistakenly marked as HOO. Indeed, the absorptions of HOO and HXeOXeH have similar frequencies, and they appear in similar experiments. It took time to understand that these are two different absorbers.

(25) Khriachtchev, L.; Pettersson, M.; Räsänen, M. *Chem. Phys. Lett.* **1998**, *288*, 727.

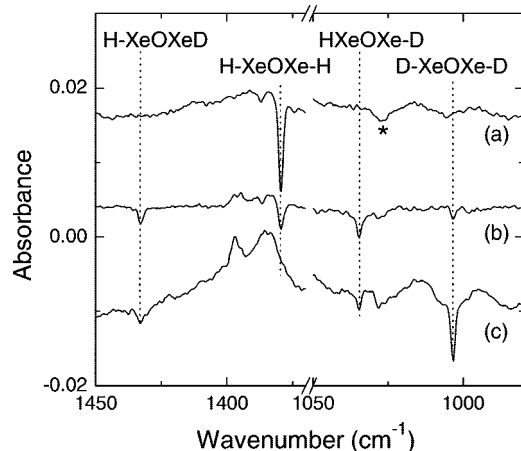


Figure 3. Difference IR absorption spectra demonstrating results of photodissociation of HXeOXeH isotope analogues by 488 nm laser light: (a) without deuteration and with (b) $\sim 55\%$ and (c) $\sim 90\%$ degree of deuteration. The broad bands in spectrum (c) are from a change of substrate absorption. The band marked with the asterisk belongs to ozone.

The assignment of HXeOXeH clearly benefits from the previous experiments with $\text{H}_2\text{C}_2/\text{Xe}$ matrices. In those studies, photolysis and annealing produced in particular HXeCCXeH via the $\text{HXeCC} + \text{Xe} + \text{H}$ reaction.²⁶ In the present case, the analogous reaction is $\text{HXeO} + \text{Xe} + \text{H}$; i.e., the HXeO radical is the precursor for the HXeOXeH formation. This fact allows us to support the assignment. First, in numerous experiments, the 1379.7 cm^{-1} band intensity correlates with the HXeO amount. Second, HXeO is found to decompose under the global light, whereas the 1379.7 cm^{-1} absorber is stable upon this irradiation. If HXeO was the desired precursor, its photodecomposition would prevent the formation of the 1379.7 cm^{-1} absorber even though the latter is stable under this irradiation. This is exactly what was observed. When HXeO radicals are selectively decomposed by IR light after annealing at 35 K and then warming to 45 K is done under global light with a slow ramp (within ~ 2 hours), the 1379.7 cm^{-1} band does not rise [see Figure 1, spectrum (c)]. The other products (HXeH, HXeOH, etc.) are efficiently formed in this experiment. Indeed, HXeO is the precursor of the 1379.7 cm^{-1} absorber, and the latter is formed in the reaction of HXeO with a H atom in solid xenon. This experiment suggests that the 1379.7 cm^{-1} absorber has one oxygen atom and two hydrogen atoms in the structure, and HXeOXeH is the most suitable candidate.

The experiments with deuterated water provide another strong support for our assignment. For HXeOXeD, one can expect two intense bands due to the H–Xe and D–Xe stretching modes, and these bands should be shifted from the corresponding bands of HXeOXeH and DXeOXeD. Upon partial deuteration, the spectra show three additional bands (1432.7 , 1034.7 , and 1003.3 cm^{-1}) after annealing at 45 K (see Figure 3). The 1003.3 cm^{-1} band is assigned to the D–Xe stretching absorption of DXeOXeD, and the H/D frequency ratio of 1.375 is suitable for a noble-gas hydride. For HXeCCXeH, this value was 1.377.¹⁶ The bands at 1432.7 and 1034.7 cm^{-1} are assigned to the H–Xe and D–Xe stretching modes of HXeOXeD, and they are blue-shifted by 53 and 31 cm^{-1} from the corresponding bands of HXeOXeH and DXeOXeD. For HXeCCXeD, the analogous shifts were 41 and 27 cm^{-1} .¹⁶ With a high degree of deuteration, the 1003.3

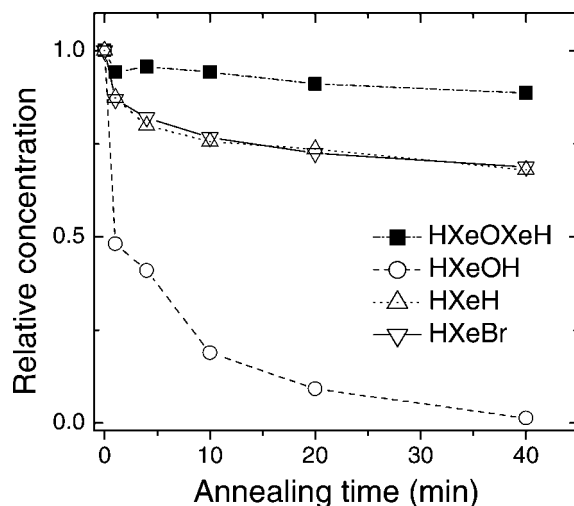


Figure 4. Thermal decay of various noble-gas hydrides at 55 K. The relative concentrations were obtained by integrating the appropriate IR bands.

cm^{-1} band dominates among these bands and the 1379.7 cm^{-1} band nearly disappears. These three bands observed upon deuteration are absent after slow annealing under global irradiation so that they need HXeO and DXeO as precursors.

The noble-gas hydrides are practically absolutely stable at low matrix temperatures ($\sim 10\text{ K}$). However, some of them decay at elevated temperatures ($> 50\text{ K}$ in solid xenon). Figure 4 compares the thermal stabilities of various noble-gas hydrides studied in the present work. The data for HXeOH agree with the previous experiments.²⁷

3. Computational Results

The HXeOXeH molecule and its spectroscopic, structural, and energetic properties were studied by *ab initio* methods, utilizing the GAUSSIAN03 program package.²⁸ Sufficiently high levels of electronic structure methods were used to compute the equilibrium molecular structure on the ground potential energy surface, and the B3LYP,^{29,30} MP2,³¹ and CCSD (ref 32) methods were applied. The calculations were done using the averaged relativistic core potential basis of LaJohn to describe Xe atoms.³³ The basis denoted as LJ-18 is a fully contracted basis set with 18 valence electrons. H and O atoms were described in these calculations by the standard 6–311++G(2d,2p) basis set. For the optimized structures, we obtained all real harmonic vibrational frequencies indicating the true minimum on the potential energy surface. These studies were followed by anharmonic calculations to support the experimental assignments.

The HXeOXeH molecule is *metastable* with respect to the $\text{H}_2\text{O} + 2\text{Xe}$ and $\text{HXeOH} + \text{Xe}$ energy asymptotes, similarly to other noble-gas hydrides.¹² Thus, the molecule decomposition in these channels is exoergic; however, the metastable species is kinetically stabilized by an energy barrier. Such metastable

(26) Tanskanen, H.; Khriachtchev, L.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **2004**, *121*, 8291.

(27) Khriachtchev, L.; Tanskanen, H.; Pettersson, M.; Räsänen, M.; Ahokas, J.; Kunttu, H.; Feldman, V. *J. Chem. Phys.* **2002**, *116*, 5649.

(28) Frisch, M. J., et al. *Gaussian 03*, revision C.02; Gaussian Inc.: Wallingford, CT, 2004.

(29) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(30) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(31) Jensen, J. *Introduction to Computational Chemistry*; Wiley: U.K., 1999.

(32) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F. *J. Chem. Phys.* **1988**, *89*, 7382.

(33) LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812.

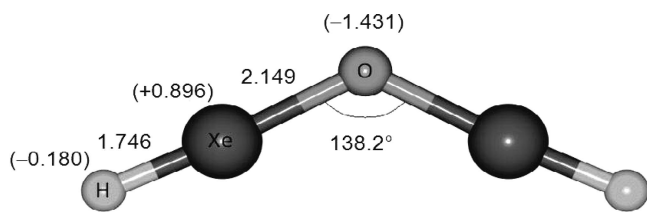


Figure 5. Equilibrium structure of HXeOXeH at the CCSD/6-311++G-(2d,2p), LJ-18 level of theory. The distances are in angstroms, and the Xe–O–Xe angle is in degrees. The partial atomic charges (in parentheses) were computed by NBO. The H–Xe–O angles are close to 180°.

Table 1. Optimized Geometry and Partial Atomic Charges of HXeOXeH Computed at Various Levels of Theory^a

	MP2	B3LYP	CCSD
$r(\text{H–Xe})$	1.764	1.769	1.746
$r(\text{Xe–O})$	2.199	2.153	2.149
$\angle(\text{Xe–O–Xe})$	124.5	139.8	138.2
$q(\text{H})$	–0.171	–0.167	–0.180
$q(\text{Xe})$	+0.762	+0.820	+0.896
$q(\text{O})$	–1.182	–1.306	–1.431

^a The bond distances and the Xe–O–Xe angle are in angstroms and degrees, respectively. The partial atomic charges were computed based on NBO.

species can be made with a suitable preparation strategy provided that the protecting barriers are high enough to prevent their decay to species with lower energies. Exploration of the full multidimensional potential energy surface of the system is not feasible. To test the energetic stability, the potential energy surface was studied for the two-body dissociation path leading from HXeOXeH to Xe + HXeOH. The three-body dissociation path leading from HXeOXeH to H + Xe + OXeH needs time-consuming multiconfigurational methods such as the CASPT2 technique. This work was done for HArF.³⁴ Such a detailed study is not of primary importance in the present case because HXeOXeH is found to be reliably lower in energy than the H + Xe + OXeH asymptote, which allows its annealing-induced formation in experiment. The energy difference between the new compound and its relevant dissociation products was computed at the MP2 and B3LYP levels utilizing the combined basis set described above.

The optimized geometry of the planar HXeOXeH molecule is shown in Figure 5. The geometry parameters and partial charges calculated at the various levels of theory are presented in Table 1. At the CCSD level, the HXeOXeH equilibrium geometry is bent with a Xe–O–Xe angle of 138.2°. On one hand, the H–Xe and Xe–O bond distances found for the new molecule at the CCSD level (1.75 and 2.15 Å) are close to the values obtained for the HXeOH molecule (1.74 and 2.22 Å).¹³ On the other hand, the addition of the second Xe atom seems to open up the Xe–O–Xe angle (~138.2°) compared with the near water-like value found for the Xe–O–H angle in HXeOH (108.7°). Although both MP2 and B3LYP methods show a clear equilibrium structure, the latter method seems to be slightly better in predicting the correct structure and partial atomic charges as judged by the most reliable CCSD technique. At the MP2 level of theory, HXeOXeH is bent with a Xe–O–Xe angle of 124.5°. The H–Xe and Xe–O distances are 1.76 and 2.20 Å, respectively, which is comparable to the corresponding values

Table 2. Computational Harmonic Frequencies (Intensities in Brackets) and Anharmonic Frequencies (in Parentheses) of HXeOXeH at Various Levels of Theory^a

	MP2	B3LYP	CCSD
	1703.3 [333.1] (1593.9)	1722.2[124.6]	1616.1(1512.3)
	1571.8 [5081.5] (1478.4)	1644.1[3744.5]	1454.9(1368.4)
	657.2 [6.3] (630.7)	658.7[24.0]	693.9(665.9)
	627.1 [0.0] (599.5)	637.4[0.0]	659.4(630.35)
	623.9 [19.5] (596.5)	628.5[42.7]	654.9(625.99)
	605.5 [37.29] (579.8)	610.1[37.5]	649.9(622.3)
	529.4 [230.55] (529.5)	543.3[670.1]	500.1(500.1)
	267.9 [11.38] (257.7)	262.5[17.3]	285.5(274.6)
	55.5 [0.50] (52.8)	72.1[2.3]	74.7(71.1)

^a The frequencies and intensities are in cm^{–1} and km/mol, respectively. The anharmonic vibrations at the CCSD level were extrapolated based on the harmonic vibrations at the MP2 and CCSD levels and the anharmonic vibrations at the MP2 level.

for HXeOH (1.72 and 2.21 Å).¹³ In HXeCCXeH, the H–Xe distance (MP2) is 1.78 Å.¹⁵

The NBO partial atomic charges at the CCSD level of theory show that the Xe and O atoms are highly charged by a positive charge of +0.896 and a negative charge of –1.431, respectively. The H atom is slightly negatively charged by –0.180. The charge distributions obtained at different levels of theory are similar, and again the B3LYP results are closer to the CCSD results as compared to MP2. The H–Xe bonds are predominantly covalent, and the Xe–O bonds are mostly ionic with a substantial covalent contribution.

The harmonic and anharmonic vibrational spectra of the HXeOXeH molecule calculated at the various levels of theory are presented in Table 2. The strongest absorption comes from the H–Xe stretching mode similarly to other noble-gas hydrides. The other modes are much weaker in intensity, and they are difficult to use for experimental identification. The MP2 harmonic H–Xe stretching frequency is 1572 cm^{–1} for the strongest asymmetric H–Xe stretching band (intensity 5081 km/mol), and this frequency is larger than the experimental value of 1379.7 cm^{–1}. However, too high H–Ng stretching frequencies obtained with the harmonic approximation are common for noble-gas hydrides.³⁵ The anharmonic calculations using the CC-VSCF method^{36,37} yield 1478 cm^{–1} at the MP2 level and 1368 cm^{–1} at the CCSD level of theory. The latter value practically coincides with experiment. For DXeOXeD, the calculated D–Xe stretching frequency shifts to 1070 cm^{–1} (anharmonic MP2), meaning a reasonable H/D ratio of 1.382 (see Table 3). For HXeOXeD, the anharmonic MP2 calculations predict blue shifts of the H–Xe and D–Xe stretching frequencies by +63 and +36 cm^{–1}, respectively, from the corresponding values of HXeOXeH and DXeOXeD. The observed difference of the corresponding H(D)–Xe stretching vibrations of the HXeOXeH isotope analogues shows a strong coupling between these normal modes even though the terminal H(D)–Xe bonds are “separated” by the –XeOXe– group. In addition to these data, we tested the effect of ¹⁸O isotope substitution. The results in Table 3 show that the ¹⁸O isotope substitution practically does not change the characteristic H–Xe stretching vibration.

Similarly to other noble-gas hydrides, HXeOXeH is a metastable species being 8.3 eV higher in energy than 2Xe +

(34) (a) Runeberg, N.; Lundell, J.; Khriachtchev, L.; Pettersson, M.; Räsänen, M. *J. Chem. Phys.* **2001**, *114*, 836. (b) Chaban, G. M.; Lundell, J.; Gerber, R. B. *Chem. Phys. Lett.* **2002**, *364*, 628.

(35) Lignell, A.; Khriachtchev, L.; Lundell, J.; Tanskanen, H.; Räsänen, M. *J. Chem. Phys.* **2006**, *125*, 184514.

(36) Chaban, G. M.; Jung, J. O.; Gerber, R. B. *J. Chem. Phys.* **1999**, *111*, 1823.

(37) Lundell, J.; Pettersson, M.; Khriachtchev, L.; Räsänen, M.; Chaban, G. M.; Gerber, R. B. *Chem. Phys. Lett.* **2000**, *322*, 389.

Table 3. Harmonic and Anharmonic (in Parentheses) Frequencies (in cm^{-1}) of Various Isotope Analogues of HXeOXeH Calculated at the MP2 Level of Theory

DXeOXeD	DXeOXeH	HXe ¹⁶ OXeH	DXe ¹⁶ OXeD	DXe ¹⁶ OXeH
1211.2 (1155.7)	1643.9 (1541.6)	1703.5 (1593.9)	1210.9 (1155.5)	1643.9 (1541.3)
1116.2 (1069.5)	1157.6 (1105.9)	1571.8 (1478.6)	1116.2 (1069.2)	1157.5 (1102.8)
556.2 (534.1)	640.5 (614.3)	654.8 (628.6)	528.5 (508.2)	637.4 (611.4)
488.4 (472.7)	616.5 (590.5)	627.1 (599.6)	484.2 (468.8)	615.7 (589.8)
449.1 (434.6)	549.5 (525.9)	618.6 (591.7)	449.1 (434.6)	523.6 (501.9)
444.6 (430.9)	450.3 (436.2)	603.6 (578.0)	442.0 (428.4)	446.8 (432.6)
425.4 (412.5)	446.7 (432.3)	505.7 (482.4)	423.8 (410.9)	445.3 (431.0)
260.4 (252.0)	263.9 (254.6)	257.2 (247.7)	251.1 (243.4)	254.0 (245.4)
54.3 (51.8)	54.9 (52.1)	54.9 (52.6)	53.7 (51.4)	54.3 (51.7)

Table 4. Energetic Properties of HXeOXeH at the MP2 and B3LYP Levels of Theory (the Values Are in eV)

	MP2	B3LYP
HXeOXeH (TS) ^a	0.57	–
H + Xe + OXeH	1.38	1.47
HXeOXeH	0.0	0.0
Xe + HXeOH	–4.57	–4.34
2Xe + H ₂ O	–8.28	–8.01

^a Transition state for $\phi = 139$ deg.

H₂O. The bending barrier for decomposition to HXeOH + Xe is 0.57 eV at the MP2 level. It has recently been shown that the DFT method often yields for noble-gas hydrides more reliable energetics than the MP2 method.³⁵ In the present case of HXeOXeH, the energetics obtained by DFT calculations at the B3LYP level of theory is similar to the MP2 results, which makes the energetics more confident. The energetic results obtained at the MP2 and B3LYP levels of theory are summarized in Table 4.

4. Concluding Remarks

Thus, we have identified a new noble-gas hydride HXeOXeH, which is most probably the smallest neutral molecule with two noble-gas atoms. The assignment of the 1379.7 cm^{-1} absorber to the H–Xe stretching mode of HXeOXeH is very solid. This species is produced from H, O, and Xe atoms upon thermal annealing, and different precursors can be used in experiments. The HXeOXeH molecule is formed in the HXeO + Xe + H reaction so that the HXeO radical is an intermediate precursor. The experimental assignment is fully confirmed by extensive quantum chemical calculations at different levels of theory including anharmonic methods. HXeOXeH is lower in energy than HXeO + Xe + H by 1.38 eV, which allows its annealing-induced formation from these neutral constituents. Additionally, this reaction is supported by a large calculated Mulliken electronegativity of HXeO (2.49 eV). The anharmonic H–Xe stretching frequency 1368.4 cm^{-1} obtained at the CCSD level of theory quantitatively agrees with the experimental value 1379.7 cm^{-1} . The theoretical results on the partially deuterated species DXeOXeH show very good agreement with experiment as well. In many respects, the formation and properties of HXeOXeH are similar to those of previously identified HXeCCXeH.^{16,26}

As an important property, one HXeOXeH molecule computationally accumulates a very high energy of 8.3 eV as compared to the global 2Xe + H₂O minimum. Probably, it is a record-breaking value for high-energy materials. The thermal stability

of HXeOXeH should be briefly discussed. Figure 4 shows that HXeOXeH is thermally more stable in solid xenon than HXeOH, HXeBr, and HXeH. Especially remarkable is the improved stability of HXeOXeH with respect to HXeOH, which is caused by an additional Xe atom. Nemukhin et al. reported a bending barrier of 0.41 eV for decomposition of HXeOH to Xe + H₂O,³⁸ which is somewhat lower than the relevant value obtained for HXeOXeH (0.57 eV), and this is in agreement with the present experimental data. Furthermore, interaction with the surroundings can change the decomposition barrier as it was shown for the HXeOH⋯(H₂O)_n system by Nemukhin et al. It is valuable to perform similar studies for HXeOXeH complexes in various surroundings.

Xenon chemistry is particularly important due to the “missing-xenon” problem,^{39,40} and preparation of chemical bonds of xenon with environmental species is a self-contained challenge. In the present work, the HXeOXeH species features a reaction of Xe with a very abundant molecule (water) and environmentally interesting N₂O and HBr. The improved thermal stability of HXeOXeH as compared to HXeOH should be remembered in this respect. Finally, a challenging task concerns the possibility of the polymeric (–Xe–O)_n network. The (XeCC)_n polymers have been recently studied computationally.⁴¹

Acknowledgment. The work was supported by the Academy of Finland through CoE CMS and the INTAS Project Ref. No. 05-1000008-8017. Wojciech Grochala is thanked for useful information on noble-gas compounds.

Note Added after ASAP Publication. Due to a production error, the polymers (XeCC)_n and (–Xe–O)_n were misrepresented in the last paragraph of the Concluding Remarks in the article published on the Web April 12, 2008. The corrected version was reposted on April 16, 2008.

Supporting Information Available: Complete ref 28. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA077835V

- (38) Nemukhin, A. V.; Grigorenko, B. L.; Khriachtchev, L.; Tanskanen, H.; Pettersson, M.; Räsänen, M. *J. Am. Chem. Soc.* **2002**, *124*, 10706.
 (39) Caldwell, W. A.; Nguyen, J. H.; Pfrommer, B. G.; Mauri, F.; Louie, S. G.; Jeanloz, R. *Science* **1997**, *277*, 930.
 (40) Sanloup, C.; Schmidt, B. C.; Perez, E. M. C.; Jambon, A.; Gregoryanz, E.; Mezouar, M. *Science* **2005**, *310*, 1174.
 (41) Brown, E. C.; Cohen, A.; Gerber, R. B. *J. Chem. Phys.* **2005**, *122*, 171101.