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HXeSH, the First Example of a Xenon−Sulfur Bond

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Quite recently, we have reported a number of novel rare-gas compounds of type HXY (X = Xe or Kr, and Y is a fragment with a large electron affinity). The compounds obtained so far include HXeH, HXeCl, HXeBr, HXeI, HXeCN, HXeNC, HKrCl, and HKrCN.[1−4] They are prepared in rare-gas matrices at low temperatures (<50 K) by photolyzing a suitable precursor HY, which yields isolated hydrogen atoms and Y-fragments. After photolysis, thermal mobilization of hydrogen atoms leads to their reactions with the rare-gas atoms surrounding the Y-fragments. The resulting novel HXY rare-gas compounds are detected by IR spectroscopy mainly via extremely intense X−H stretching absorptions. In this report we introduce a new member of this family, HXeSH. This molecule expands the number of elements capable of making chemical bonds with xenon and represents the first compound with a xenon−sulfur bond.

The electronic structure calculations for HXeSH were carried out with the Gaussian 94 package of computer codes.[5] The relativistic effective core potential (ECP) by LaJohn et al. was used on Xe.[6] This ECP includes the d-subshell in the valence space resulting in 18 valence electrons and was used in a decontracted form. The standard split-valence 6-311++G(2d,-2p) basis set was used for hydrogen and sulfur.

The calculated structural parameters of HXeSH at different computational levels are given in Table 1. Like H_2S, HXeSH is also a bent molecule with an H−S−Xe angle near 90 degrees. The calculated S−H bond distance of 1.34 Å in HXeSH is essentially the same as the experimental value in H_2S.[7] The Xe−H distance (1.84 Å at the CCSD(T)-level) is somewhat larger than the value of free XeH^+ (1.60 Å)[8] but much smaller than the van der Waals distance of neutral Xe−H (3.95 Å).[9] The calculated length of the Xe−H bond compares well with XeH_2 and HXeI molecules, which both have experimental Xe−H stretching absorptions in the 1200 cm^{-1} region of the spectrum.[1,2,10] The calculated Xe−S bond distance of 2.77 Å can be compared with the recently calculated values for the excited states of Xe−S. For the $1^1\Sigma^+$ state (Xe+ S(^{1}D)) and the lowest charge-transfer (Xe^+S^-) state $2^3\Pi$, 2.62 and 3.32 Å were obtained for the R_e-values, respectively.[11] Also, our Xe−S bond distance is near the I−S bond distance of 2.67 Å for the linear S−I−S unit in $[(S_7I)_2I)]^{3+}$.[12] The calculated charge distribution indicates significant ion-pair character as in all the other HXY molecules observed thus far.[1−4] Xenon carries a relatively large positive charge, and the SH group is negatively charged.

Table 1. Calculated Geometries, Mulliken Charges, and Dipole Moment of HXeSH

	MP2	CCSD(T)
H−Xe (Å)	1.7740	1.8443
S−Xe (Å)	2.7285	2.7748
H−S (Å)	1.3342	1.3386
∠H−S−Xe (deg)	91.02	90.34
∠S−Xe−H (deg)	180.0	180.0
E_{el} [au]	−524.970935	−525.007726
q (H)[a]	−0.009	
q (S)	−0.435	
q (Xe)	0.671	
q (H)[b]	−0.226	
μ [D]	4.4579	

[a] S-bonded hydrogen. [b] Xe-bonded hydrogen.

Table 2. Calculated Vibrational Wavenumbers (in cm^{-1}) of HXeSH[a]

mode	MP2	CCSD(T)	exp.
S−H stretch	2729.9 (8)	2666.9	
Xe−H stretch	1520.6 (3149)	1147.8	1118.6
asym bend	652.6 (2)	607.1	
H−Xe−S bend	546.6 (4)	483.2	
sym bend	472.5 (11)	437.1	
Xe−S stretch	251.4 (37)	218.3	

[a] The numbers in the parentheses are the infrared intensities (in km mol^{-1}).

The calculated harmonic wavenumbers are given in Table 2. HXeSH possesses a strong Xe−H stretching absorption, the other modes being much weaker. The wavenumbers are very sensitive to the level of correlation, but the CCSD(T) result should be rather reliable.

H_2S was typically prepared at H_2S/Xe matrix ratio of 1/1000, and highly monomeric sample was confirmed by different deposition temperatures and mixing ratios.

Both 193 and 235 nm irradiations were found to dissociate H_2S. As a result of the photodissociation, H-atoms, SH-radicals, and S-atoms were produced. H-atoms were probed by detecting the Xe−H exciplex emission around 250 nm with excitation at 193 nm.[13] SH-radicals were excited by 337.5 nm irradiation, and their emission was detected around 427 nm.[14] S-atoms were excited by 466.4 nm, and the emission was detected around 808 nm.[14] During photolysis, the infrared spectra showed a weak band at 2550 cm^{-1} and the characteristic spectrum of Xe_2H^+ in the 1100−700 cm^{-1} region.[15]

After most of the H_2S was dissociated, the sample was slowly annealed at 50−60 K and cooled back to 7.5 K. Around 45 K, several IR-bands were generated which are shown in Figure 1. The bands at 1166 and 1180 cm^{-1} are known to belong to XeH_2.[2]

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(1) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys*. **1995**, 102, 6423−6431.

(2) Pettersson, M.; Lundell, J.; Räsänen, M. *J. Chem. Phys*. **1995**, 103, 205−210.

(3) Pettersson, M.; Nieminen, J.; Khriachtchev, L.; Räsänen, M. *J. Chem. Phys*. **1997**, 107, 8423−8431.

(4) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Räsänen, M. *J. Chem. Phys*. **1998**, *109*, 618−625.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

(6) LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys*. **1987**, 87, 2812−2824.

(7) Greenwood, N. N.; Earnshaw, A. Chemistry of the Elements; Pergamon Press: Oxford, 1994; p 806.

(8) Rogers, S. A.; Brazier, C. R.; Bernath, P. F. *J. Chem. Phys*. **1987**, 87, 159−162.

(9) Bickes Jr, R. W.; Lantzsch, B.; Toennies, J. P.; Walschewski, K. *Discuss. Faraday Soc*. **1973**, 55, 167−178.

(10) Runeberg, N.; Seth, M.; Pyykkö, P. *Chem. Phys. Lett*. **1995**, 246, 239−244.

(11) Yamanishi, M., Hirao, K., Yamashita, K. *J. Chem. Phys*. **1998**, *108*, 1514−1521.

(12) Passmore, J-, Sutherland, G., White, P. *J. Chem. Soc., Chem. Commun*. **1979**, 901−902.

(13) Creuzburg, M.; Wittl, F. *J. Mol. Struct*. **1990**, 222, 127−140.

(14) Khriachtchev, L.; Pettersson, M.; Isoniemi, E.; Räsänen, M. *J. Chem. Phys*. **1998**, 108, 5747−5754.

(15) Kunttu, H.; Seetula, J.; Räsänen, M.; Apkarian, V. A. *J. Chem. Phys*. **1992**, 96, 5630−5635.

S0002-7863(98)01032-4 CCC: $15.00

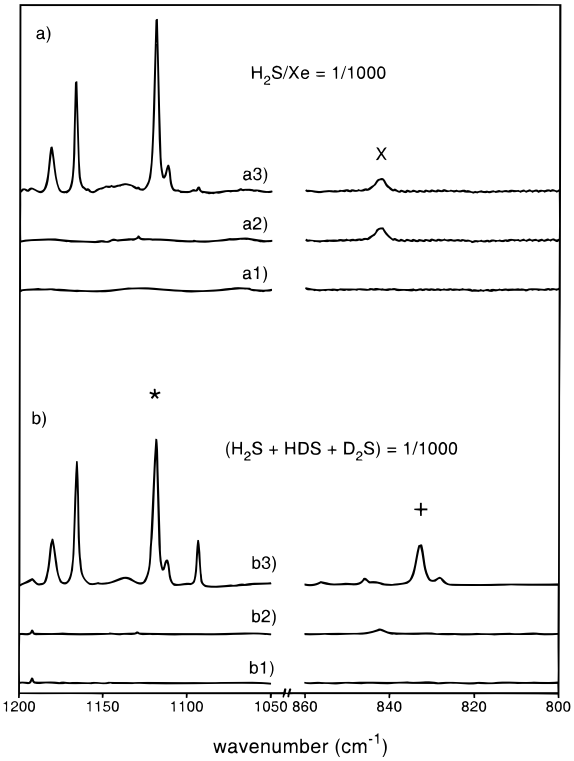
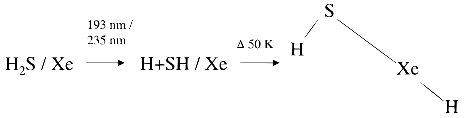


Figure 1. IR spectra of (a) $H_2S/Xe = 1/1000$ and (b) $(H_2S + D_2S + HDS)/Xe = 1/1000$ samples recorded at 7.5 K. Traces a1 and b1 represent the situation after deposition, a2 and b2 after photolysis, and a3 and b3 after annealing at 50 K. The strongest absorptions of HXeSH(D) and DXeSH(D) are marked with * and +, respectively. The band marked with X is due to the $\nu_3 + \nu_1$ absorption of Xe_2H^+ (see ref 15). The bands at 1166, 1180, and 1093 cm^{-1} belong to XeH_2 and XeHD (see Table 3).

Scheme 1



Upon deuteration, HXeD was observed at 1093 and 753 cm^{-1} and smaller amounts of XeD_2 at 846 and 856 cm^{-1}.[2]

In addition to these known bands, new absorptions at 1118.6 and 1112.0 cm^{-1}, together with a broad sideband centered at 1136 cm^{-1}, were observed in the experiments with H_2S (Figure 1a). Upon deuteration, the sharp bands were shifted to 832.8 and 828.3 cm^{-1} (see Figure 1b) giving a H/D ratio of 1.343. This value is near 1.336 found for HXeI in previous studies.[1] The broad sideband is less prominent in the deuterated form and overlapped by XeD_2, and it is centered around 843 cm^{-1}. These new absorptions are assigned to different isotopomers of the novel rare-gas molecule HXeSH (Scheme 1). The absorptions appearing in annealing are presented in Table 3.

The stability of HXeSH under glowbar irradiation was tested, and no changes were observed after overnight irradiation. The threshold for the photodecomposition in the visible region was determined by irradiating the sample for 5 min at various wavelengths and recording the IR spectrum after each irradiation. The threshold was determined to be between 700 and 750 nm. Irradiation by 700 nm light for 5 min resulted in a 50% decomposition, but 750 nm did not decompose the HXeSH molecules at all. Thermally, HXeSH is quite stable, and its absorption was still visible after cycling the matrix to 100 K.

Table 3. Observed Absorptions Appearing in Annealing the H_2S/Xe or $(H_2S + HDS + D_2S)/Xe$ Matrices After Photolysis[a]

wavenmbr	assgnmnt	wavenmbr	assgnmnt
700	XeH_2, bend	1093	XeHD, Xe−H stretch
753	XeHD, Xe−D stretch	1112.0 m	HXeSH(D), Xe−H stretch
828.3 m	DXeSH(D), Xe−D stretch	1118.6 s	HXeSH(D), Xe−H stretch
832.8 s	DXeSH(D), Xe−D stretch	1136 br	HXeSH(D), Xe−H stretch
843 br	DXeSH(D), Xe−D stretch	1166	XeH_2, asym stretch
846	XeD_2, asym stretch	1181	XeH_2, asym stretch
856	XeD_2, asym stretch		

[a] m = medium strength, s = strong.

The assignment of the new absorptions to different isotopomers of HXeSH is based on several facts. First, the new absorptions are produced only in Xe-matrix, and no similar absorptions were detected in other rare-gas matrixes. This suggests that Xe is a constituent of the absorbing molecule. Second, deuteration shows that the hydrogen atom is connected with the strong observed absorption, and the deuteration shift is typical for the anharmonic hydrogen stretching vibration. Only one new band per each observed absorption of the H-form appears upon deuteration. This is expected in the case of HXeSH because the reduced mass for the Xe−H stretching vibration is strongly affected by the deuteration of the XeH but very little affected by the deuteration of the SH. In the latter case, the deuteration induces so small a shift to the Xe−H stretching absorption position that it cannot be resolved under our conditions. Thus, the Xe−H stretching absorptions of both HXeSH and HXeSD are observed in the same position, and similarly, the Xe-D stretching absorptions of DXeSD and DXeSH are unresolved. Third, the calculations predict HXeSH to be a stable species, and the calculated position of the Xe−H stretching absorption is in perfect agreement with the experiments. Also, the general appearance of the spectrum of HXeSH is very similar to the other HXeY species observed so far possessing a strong sharp absorption which is accompanied by a weaker absorption at the lower wavenumber and a broad sideband at higher wavenumbers.[1,3,4] Finally, no other candidates can be thought of which would have similar absorptions in this region. On this basis, the assignment of the new absorptions to HXeSH is very plausible.

Since HXeSH has a Xe−H stretching absorption located in the same region as those of XeH_2 and HXeI, the stability should be similar in all of these compounds because the strength of the Xe−H bond reflects the depth of the potential well of the molecule under question. On this basis, we can estimate the D_e of HXeSH with respect to dissociation into H + Xe + SH to be about 0.4 eV, similar to those in HXeI and XeH_2.[3,10] The thermodynamically most stable products would naturally be H_2S + Xe. The bond strengths of Xe−H and Xe−S are really the same because if one of them is broken, the other one is no longer bound except in a van der Waals sense. In the other words, both bonds break simultaneously.

In conclusion, the first rare-gas compound with a Xe−S bond has been synthesized. This molecule, HXeSH, possesses a strong characteristic Xe−H stretching absorption at 1118.6 cm^{-1}. Ab initio calculations support the existence of this molecule.

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