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Vibrational Spectrum of HXeSH revisited: Combined computational and experimental study

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Abstract

Vibrational spectrum of HXeSH embedded in low-temperature matrix is experimentally studied. To support the spectrum interpretation, anharmonic vibrational analysis is performed using different models and basis sets and the data is compared with previous experimental and theoretical analyses. Computations of overtones and combination modes allowed for new band assignments. The HXeSH molecule exhibits high anharmonicity similarly as other molecules from the noble-gas hydride family. Comparison of the employed computational methods shows once again that the modelling of the noble-gas compounds faces theoretical challenges to yield quantitatively reliable results.

Keywords: Xenon, noble gas, hydride, computational chemistry, anharmonicity, infrared spectrum, vibrational spectroscopy, matrix isolation

Introduction

The noble-gas chemistry has experienced a steady interest since its renaissance in the 90's when a group of then-novel compounds was synthesized in low-temperature matrices [1–3]. These compounds included HNgY-type (where Ng=noble gas atom, Y= electronegative atom or group) molecules like HXeBr, HKrCl [1], HXeCN [3], HXeOH [4], HXeCCH [5], HArF [6], to name a few. They have been investigated both experimentally and computationally [7,8] and extensively reviewed [9–11]. They are intriguing to chemists not only because they are formed by atoms with full valence shell and they exhibit blue-shifting complexes with other molecules [12–16], but also because they may shed light on many intriguing properties exhibited by noble gases like neuroprotective properties [17,18], anaesthetic properties [19,20] and the puzzling problem of missing xenon [21–23].

Among the fascinating group of noble-gas hydride compounds is the HXeSH molecule first synthesized in 1998 [24]. Being the first example of the Xe–S bond it shows similar features as other molecules in the family. It is formed in a photodissociation and subsequent process of H_2S in xenon matrix. The Xe–S bond exhibits strong ionic character and the SH group bears a significant negative charge, yielding a system that can be approximated as $(HXe)^+(SH)^-$. Its most intense infrared (IR) band is the ν_{Xe-H} stretch ca. 1118 cm^{-1} and its first overtone was tentatively assigned at ca. 2089 cm^{-1} giving the anharmonicity ($\omega_e x_e$) of –74.5 cm^{-1} [25]. In general, the anharmonic effects in HXeSH, and in these HNgY molecules in general, are shown to be important and non-negligible [26,27].

Here, we revisit the infrared spectrum of the HXeSH molecule and provide new assignments of overtones and combination bands. Understanding the IR spectra for noble-gas hydrides is important because it is the main investigation method used to study them and the anharmonicity itself is a subject of interest. For our investigation, we combine experimental measurements in low-temperature matrices with computational predictions. This improves both the understanding of the IR spectrum of HXeSH and the computational methodology used to predict the properties of the noble-gas hydrides.

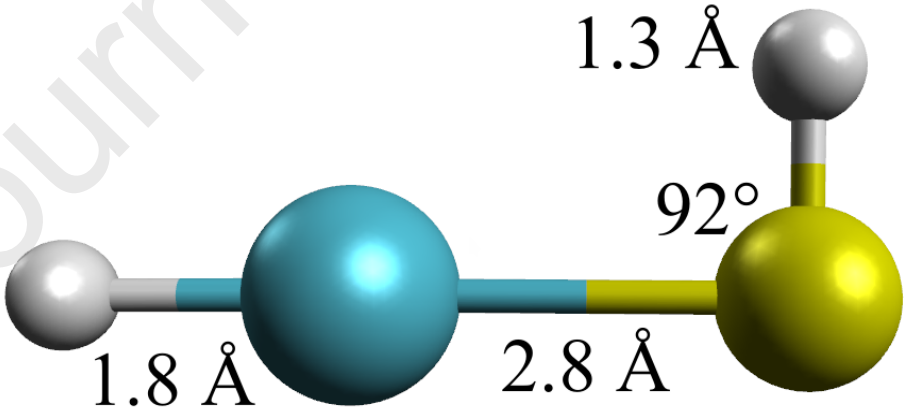

Figure 1. *The structure of the HXeSH molecule. The colours white, yellow and turquoise designate hydrogen, sulfur and xenon atoms, respectively.*

Experimental details

The matrices were deposited onto a MgF_2 substrate placed in a closed-cycle helium refrigerator (Displex DE-202A) at 45 K. The total amount of deposited gas was ~3 mmol. As a matrix film of sufficient thickness was grown, the sample was annealed at 50–55 K in order to minimize changes in the optical characteristics during the actual experiments. All spectral measurements were carried out at ca. 10 K. The temperature of the cold substrate was measured with a silicon diode, and controlled with a LakeShore 330 controller unit. The dilution ratio between the precursor and Xe was typically 1:1000 to 1:500. H_2S of 99.8% purity and Xe of 99.997% purity were obtained from Messer Griesheim and AGA, respectively, and were used without further purification.

The IR absorption spectra were measured with a Nicolet Magna IR 760 spectrometer equipped with a KBr beam splitter and a HgCdTe detector. The MgF_2 substrate, used for subsequent UV measurements reported elsewhere [28], limited the detection window in the IR to the range >1000 cm^{-1}. The samples were irradiated using a 193 nm excimer laser (Lambda Physik, Optex) and a 308 nm excimer laser (Estonian Academy of Sciences, ELI-94). The full details of experimental setup and processes have been published earlier in Refs [28] and [29].

Computational details

To support the analysis of the experimental data, anharmonic vibrational frequencies were computed by the vibrational self-consistent field (VSCF) and its extension by corrections via second-order perturbation theory (CC-VSCF) [30–33]. The correlation-consistent VSCF algorithm is used to calculate the vibrational wave functions and energies. Only interactions between pairs of normal modes are included in the calculations, since interactions of triples and higher were taken negligible [30,31]. Each pair of normal modes were pictured with a 16 × 16 PES grid and the mode-mode couplings were then evaluated by *ab initio* calculations over this grid. A more detailed description of the MP2/CC-VSCF method is given in Refs [31] and [32]. All CC-VSCF calculations in this work were performed in the framework of GAMESS electronic structure program [34]. Electron correlation was considered via Møller-Plesset perturbation theory [35,36] to second order (MP2) and aug-cc-pVDZ-PP basis set was employed which includes the scalar relativistic effect by means of the Effective Core Potentials (ECP) with 8 valence electron shell for xenon [37]. The CC-VSCF calculations were utilized to gain insight of the anharmonicity and overtone spectrum of HXeSH on a computational level used previously for other noble gas hydrides [26,27].

Additional computations on the structure and frequencies of HXeSH were performed using the Gaussian program [38] in order to see the effect of the method and the quality of basis sets used on the harmonic and anharmonic spectrum. Very tight convergence threshold was used throughout the geometry optimization calculations. For H and S atoms, the aug-cc-pVxZ (x=D, T or Q) basis sets were used. For Xe atom, appropriate relativistic variants, i.e. the aug-cc-pVxZ-PP (x=D, T or Q) basis sets. The basis sets are shortly called ‘dz’, ‘tz’ and ‘qz’ in the text. The structures were optimized and vibrational analysis was done using the second order of the Møller-Plesset Perturbation Theory (MP2 variant of MPPT), the fourth order of MPPT including singles, doubles and quadruples (MP4(SDQ)), Density Functional Theory (DFT) with B3LYP potential and Coupled Cluster Singles and Doubles method (CCSD).

MP2 and B3LYP calculations were carried out using the anharmonic analytical algorithm whereas MP4(SDQ) and CCSD calculation were done using the harmonic and numerical approach. Because of the cost of the calculations the latter were not done with the quadruple zeta basis set, i.e. qz.

Results and discussion

Experimental results

The IR absorption spectra of our H_2S/Xe matrix were similar to what is previously reported for H_2S doped Xe matrices [39]. The symmetric (ν_1) and asymmetric (ν_3) stretching modes of H_2S are found at 2596 and 2620 cm^{-1} exhibiting a multiple band structure due to the hindered rotation the molecule undergoes in the matrix [39]. The H_2S bending mode appears as a very weak band at ca. 1180 cm^{-1}.

According to Isoniemi *et al.* [39], the main dissociation channel of H_2S in noble gas matrices employing 193 nm photolysis yields H atom and SH radical with a secondary channel to H_2 molecule and S atom also available. Moreover, SH radicals photodissociate further to S and H atoms [40,41]. Here, upon 193 nm photolysis of the matrix, more than 90% of the total amount of H_2S, including monomers and multimers, was dissociated as evidenced by Figure 2. Parallel to the decrease of the H_2S lines, formation of a photolysis product was indicated by a new line at 2550.5 cm^{-1}. This absorption has previously been assigned as the SH…H_2S complex [39], indicating the formation of SH radicals from the H_2S dimer. The absorption associated with isolated SH radical could not be observed in these experiments.

Annealing of the photolyzed sample at 48 K induced new absorption bands at 1112, 1119, 1136, 1166, and 1181 cm^{-1} due to formation of HXeSH (first three) and HXeH (last two) [2,24]. An additional photolysis at a longer wavelength, 308 nm, bleached the HXeSH absorption bands completely, in accordance with selective photolysis of the noble gas molecules reported previously [42]. This photolysis wavelength coincides with the previously observed electronic transition of HXeSH between 260–325 nm with a maximum at 290 nm [28].

All these processes are found in Fig. 2 including a subsequent photolysis with 193 nm pulses bleaching the formed photoproducts and reproduction of the noble gas molecules upon annealing. These processes take place without notable losses of the forming noble gas molecules HXeH and HXeSH.

Employing the reversible processes of forming and decomposing the noble gas molecules are helping in locating and identifying other vibrational absorptions belonging to the noble gas molecules than the fundamental ones. This is demonstrated in Fig. 2 on the left panel, where bands exhibiting the same appearance and bleaching patterns to the fundamental modes are found. Clearly, vibrational absorptions belonging to studied noble gas molecules are found at 2004, 2070 and 2087 cm^{-1}, as indicated by arrows in Fig. 2. The vibrational absorption at 2004 cm^{-1} is previously known and it has been assigned as the $\nu_1+\nu_3$ combination mode between the symmetric and asymmetric Xe-H stretching modes of HXeH [27]. The two absorptions at 2070 and 2087 cm^{-1} can be associated with HXeSH and are discussed later. There is also a bump in the recorded spectrum around 2100–2110 cm^{-1} that behaves similarly to the other HXeSH absorptions mentioned. This spectral feature is most probable due to

complexes involving HXeSH molecule, i.e. either a dimer $(HXeSH)_2$ or HXeSH-H_2S [16]. Both of these are plausible products following photodecomposition of one or both subunits in $(H_2S)_2$, as demonstrated earlier by Isoniemi *et al*. [39] being able to produce H_2S-SH complex from H_2S dimer. This could also be the origin of the weak broad spectral feature at 1125–1150 cm^{-1}, following the photochemical and thermal behaviour of the HXeSH molecule. Moreover, another vibrational absorption associated with HXeSH appears at 1325 cm^{-1}, which is outside the spectral regions shown in Fig. 2.

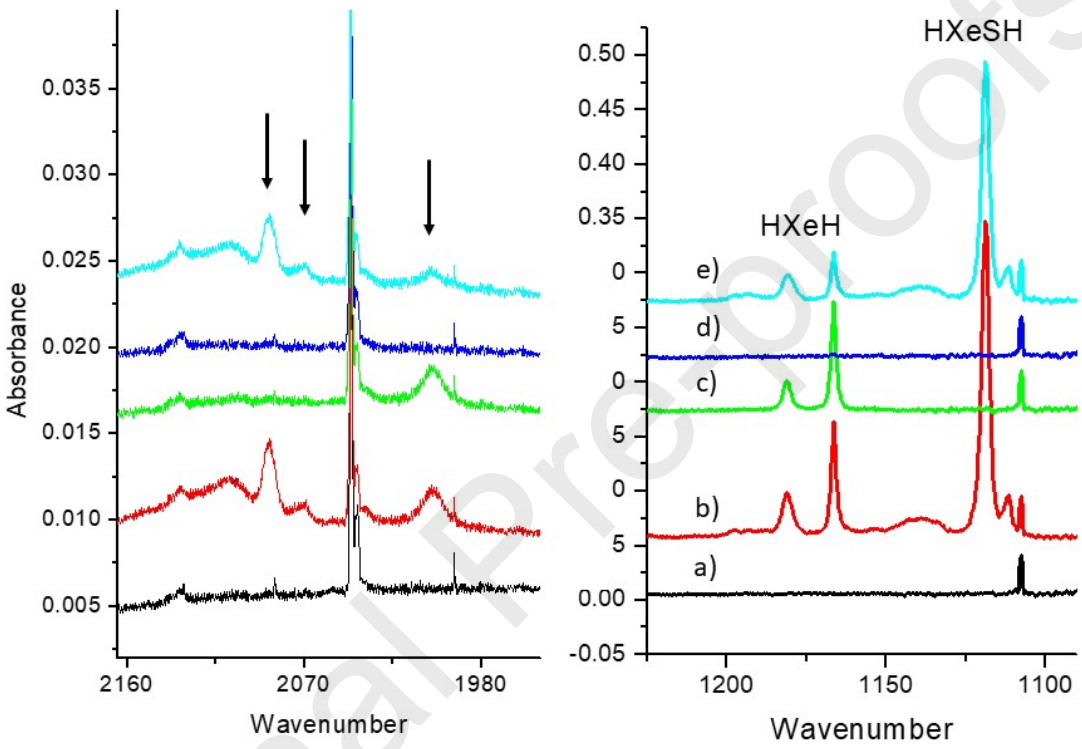

Figure 2. *IR absorption spectra of a H_2S/Xe matrix: (a) after approximately 90% of H_2S was photolyzed with a 193 nm laser, (b) after annealing the photolyzed matrix at 48 K, (c) second photolysis at 308 nm with 100 pulses, and (d) third photolysis at 193 nm with 630 pulses, and e) after reannealing the matrix at 48 K. The arrows indicate the positions of the observed overtone and combination bands of the noble gas compounds HXeH and HXeSH.*

Computational results

The geometry of the HXeSH molecule is presented in Fig. 1 and numerical values of the bond lenghts and the H–Xe–S angle for different methods employed are given in Table 1. The results correspond well to what is established in the literature [24,43] with $r_{Xe–H}$ being ca. 1.7 Å and the α_{HXeS} being close to a right angle. All bond distances and the angle tend to decrease with the size of the basis set within a particular calculation method. There is no

particular trend in this respect when the level of electron correlation increases (e.g. MP2<CCSD<MP4(SDQ)). The B3LYP potential tends to give slightly larger values.

Table 1: The calculated bond distances (in Å) and angles (in degrees) of the HXeSH molecule using different basis sets and methods.

	Basis set	H–Xe	Xe–S	S–H	∠(HXeS)
MP2/CC-VSCF	dz	1.763	2.747	1.353	91.0
MP2	dz	1.765	2.751	1.355	91.1
	tz	1.749	2.694	1.340	90.4
	qz	1.743	2.678	1.338	90.4
B3LYP	dz	1.797	2.756	1.359	92.7
	tz	1.789	2.735	1.347	92.5
	qz	1.788	2.732	1.345	92.4
CCSD	dz	1.784	2.768	1.357	91.8
	tz	1.756	2.709	1.343	91.5
MP4(SDQ)	dz	1.777	2.765	1.356	91.8
	tz	1.753	2.707	1.342	91.6

The values of all the calculated vibrational frequencies, overtones and combinations modes for all the methods are presented in Supplementary Information Tables 1–7, and the selected values which are relevant for the experiment together with the experimental values are presented in Table 2.

Table 2: The chosen experimental and calculated vibrational frequencies in cm^{-1} and the anharmonicities $\omega_e x_e$ for of the ν_2 mode for the HXeSH molecule.

			ν_2 Xe–H	$\nu_2+\nu_6$ Xe–H + Xe–S	$\nu_2+\nu_3$ Xe–H + bend	$2\nu_2$ Xe–H	ν_6 Xe–S	$\nu_2 \rightarrow 2\nu_2$ anharmonicity ($\omega_e x_e$)
	experimental		**1119**	**1325**	**2070**	**2087**	**206**[a]	**–75.5**
	CCSD(T)[b]		1148[b]				218[b]	
	cc-VSCF		1373	1615	1983	2666	244	–40.2
anharmonic + analytical	MP2	dz	1372	1616	1978	2644	248	–50.1
		tz	1448	1708	2069	2807	263	–44.2
		qz	1445	1708	2069	2818	266	–36.0
	B3LYP	dz	1285	1517	1982	2253	234	–158.7
		tz	1245	1479	1935	2129	236	–180.5
		qz	1232	1466	1919	2096	236	–184.1
harmonic + numerical	CCSD	dz	1366				244	
		tz	1495				258	
	MP4(SDQ)	dz	1406				246	
		tz	1514				259	

[a] The number was calculated from the experimental values, see Conclusions.
[b] The harmonic CCSD(T) results are from Ref. [24].

Let us discuss the MP2 computational results. The most intense band, 1445 cm^{-1} on harmonic MP2/qz level is still over three hundred wave numbers off from the experimental result. The experimental H-Xe stretching vibrational mode has been reported to be at 1119 cm^{-1} [24], and this low value has been connected with weak molecular stability [8]. The low energy barrier preventing the molecule to dissociate into a three-body dissociation channel H+Xe+SH also indicates large anharmonicity on the potential energy surface as was demonstrated especially for HArF by Runeberg *et al.* [7]. The molecules, thus, are much more stable in theory than in experiment.

The computed frequencies tend to increase with the size of the basis set, both harmonic and anharmonic ones. For instance, the Xe–H bond oscillation increases from 1372 to 1445 cm^{-1} when going from dz to qz at anharmonic level. This means the bond is predicted to be shorter and stronger with larger basis sets which is evidenced in Table 1 as well.

The methodological anharmonicity, defined here as the difference of the frequency obtained with the harmonic model and the one obtained with the anharmonic model for the same computational method (e.g. $\Delta\nu^{\mathrm{MP2}} = \nu_{\mathrm{anh}}^{\mathrm{MP2}} - \nu_{\mathrm{harm}}^{\mathrm{MP2}}$), is the largest in Xe–H and S–H bonds. This anharmonicity decreases with the basis set size. At the MP2/dz level, it is −128 cm^{-1} for $\nu_{\mathrm{Xe–H}}$, and goes to −95 cm^{-1} at MP2/qz level (see SI Table 1).

This picture is quite different at the pure B3LYP level (see SI Table 1). First, the stretching modes tend to be lower than the respective MP2 values. The bending modes are lower at the harmonic level and higher at the anharmonic level. While the anharmonicity in general is predicted to be much larger using B3LYP, interestingly, it is positive for the bending modes, contrary to the MP2 results. This discrepancy prompted us to attempt to include a higher correlation level by means of Grimme's dispersion corrections [44]. The calculations were done using the GD3 and GD3BJ levels as implemented in Gaussian'16 [45]. All the positive anharmonicity values obtained at the pure B3LYP level became negative upon dispersion inclusion and the overall picture became qualitatively similar to the MP2 results. While the pure B3LYP/qz $\nu_{\mathrm{Xe–H}}$ frequency equal to 1232 cm^{-1} is the closest to the experimental one, this seems to be accidental since the tz results obtained with the D3 and D3BJ approach increased this value by over 100 cm^{-1} compared to pure B3LYP/tz. The effect of dispersion inclusion highlights once again the inadequacies of the pure DFT approach to describe the noble-gas containing molecules [46].

The numerical harmonic CCSD and MP4(SDQ) methods with tz basis set predict $\nu_{\mathrm{Xe–H}}$ to be 1495 and 1514 cm^{-1}, respectively, which is lower than the corresponding harmonic MP2 values (see SI Table 1).

In order to get a better idea of the anharmonicity of the Xe-H stretching vibration of HXeSH, we can deduce the anharmonic constant and anharmonicity from the fundamental and first overtone absorptions. The anharmonicity x_{ij} or $\omega_e x_e$ of vibrational levels can be derived as [47]:

$$G(\upsilon_i\upsilon_j) = \sum_i \omega_i\left(\upsilon_i + \frac{d_i}{2}\right) + \sum_{i<j} x_{ij}\left(\upsilon_i + \frac{d_i}{2}\right)\left(\upsilon_j + \frac{d_j}{2}\right)$$

where $G(\upsilon_i\upsilon_j)$ is the vibrational term value and ω_i is the harmonic vibrational wavenumber. For $i \neq j$ the x_{ij} terms are the coupling constants between normal modes and for $i=j$ the x_{ij} term is the anharmonicity of a particular mode. In this equation, d_i is the degeneracy of the vibration. Using the observed fundamental ν_2 (1119 cm^{-1}) and first overtone $2\nu_2$ (2087 cm^{-1}) frequencies of HXeSH, the experimental anharmonicity x_{22} is –75.5 cm^{-1}. The results for all the computational methods are presented in Table 2. As can be seen, the MP2 results reproduce the anharmonicity better than B3LYP results which are heavily overestimated.

Explicit inclusion of the mode coupling is possible by means of the CC-VSCF method. The obtained CC-VSCF results are presented in Table 2 along the previous studies and in Table 3 the value of the Xe-H stretching mode in HXeSH is compared with other Xe-containing molecules for which the data is available in the literature. The obtained MP2/CC-VSCF value of 1373 cm^{-1} is close to the MP2/dz anharmonic result.

The MP2/CC-VSCF calculated anharmonicity x_{22} for HXeSH is –40 cm^{-1} from which we conclude that the potential surface is slightly steeper in computations compared to the experiment. Moreover, the MP2 potential energy surface for HXeSH seems good in comparison to HXeI [26] and HXeOH [27]. Actually, the anharmonicity computed for HXeSH is almost equal with the one found for HXeOH. Suprisingly, the MP2/dz model seems to reproduce the anharmonicity slightly better than MP2/CC-VSCF, –50.1 vs. –40.2 cm^{-1}.

It must be noted that the computed anharmonicity of HXeH is positive, which means that the first overtone level is above the 3-body dissociation barrier. This was demonstrated computationally by Takayanagi *et al*. [48]. On the other hand, all the other experimentally observed HNgY molecules besides HXeH are found to be bound at the level of the first overtone vibrations.

Table 3. Experimental and MP2/CC-VSCF anharmonicities $\omega_i x_{ii}$ for the Xe-H stretching vibration in some noble gas molecules. All values are given in wavenumbers (cm^{-1}).

	HXeH[a]		HXeBr[a]		HXeI[b]		HXeOH[a]	HXeSH	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Calc.	Exp.	Calc.
$\nu_{\text{Xe-H}}$	1181,1166	1337	1504	1544	1193	1359	1714	1119	1373
$2\nu_{\text{Xe-H}}$		2886	2869	2967	2190	2585	3342	2087	2666
$\omega_e x_e$		+105	-69.5	-60	-98	-66.5	-43	-75.5	-40

[a] The values are from Ref. [27]
[b] The values are from Ref. [26]

Conclusions

Computational and experimental studies have been performed to get a more extensive view on the vibrational spectrum of HXeSH. The Xe-H vibrational mode is a fingerprint vibrational mode for the HXeY molecules, and it gives a good indication on the stability of the HNgY molecules. Anharmonic calculations for the particular vibrational mode are also descriptive whether the molecule is bound upon higher vibrational excitations with respect to the three-body dissociation channel leading to H+Xe+Y fragments. This was demonstrated for HXeH where positive overtone anharmonicities are found suggesting that the first overtone vibration is enough in energy to decompose the molecule. In the case of HXeSH, the computed anharmonicity of the Xe-H vibrational mode is estimated to be –40 cm^{-1}. The experimental value is estimated to be -75,5 cm^{-1} since the first overtone of the Xe-H vibration is located at 2087 cm^{-1} in solid Xe environment. Also, two combination bands at 2070 and 1325 cm^{-1} are identified by CC-VSCF calculations as combination modes between Xe-H + H-Xe-S bend (ν_2+ν_3) and Xe-H + Xe-S (ν_2+ν_6). Moreover, the observation of these new bands allow to estimate the position of the Xe-S stretching mode at ca. 206 cm^{-1} from the difference between ν_2 and ν_2+ν_6. Unfortunately, this vibrational mode can not be directly detected with the experimental setup used here, but the value correlated reasonably well with the various computational methods applied (See Table 2.)

The results obtained by varying the basis set and the computational method are in general agreement with previous studies. However, they vary quite significantly between one another.

The cheapest methods (e.g. MP2 with dz basis set) prove to be closer to experimental values than the more expensive ones (e.g. MP4/tz). As evident from the data presented in Table 2, altering the basis set and computational method used does not give a straightforward way to improve the computational level in order to predict vibrational features for experimentally unknown noble gas hydrides. One way to model the vibrational spectrum of HXeSH would be to use the approach introduced by Lundell *et al.* [27] for several Xe-containing hydrides. Here, however, combining the MP2 methodological anharmonicity (see SI Table 1) with the high level CCSD harmonic calculations yields the values of 1238 and 1384 cm^{-1} at dz and tz level, respectively. This is much better than harmonic calculations but still almost 100 cm^{-1} above the experimental value. The standard anharmonicity $\omega_i x_{ij}$ is much smaller and using it to correct the harmonic results is not much of an improvement.

Because these discrepancies cannot be attributed to the influence of the matrix itself [49], apparently, for the studied systems, it is very hard to obtain a proper balance between correlation level and the size of the basis set. Consequently, the better agreement for MP2 is probably accidental, as it probably was for the referenced CCSD(T)/6-31++G(2d,2p)[H,S]/LJ18-ECP[Xe] value of Xe-H stretch 1148 cm^{-1} [24]. A very large and flexible basis set would be needed in conjunction with extensive electron correlation methods in order to reproduce the actual position of the H-Ng vibrational bands in a reliable, quantitative way [50]. Therefore, this family of compounds still poses a challenge for quantum chemistry computations.

Acknowledgements

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This paper is dedicated to the memory of a good friend and colleague, Dr. Leonid Khriachtchev.

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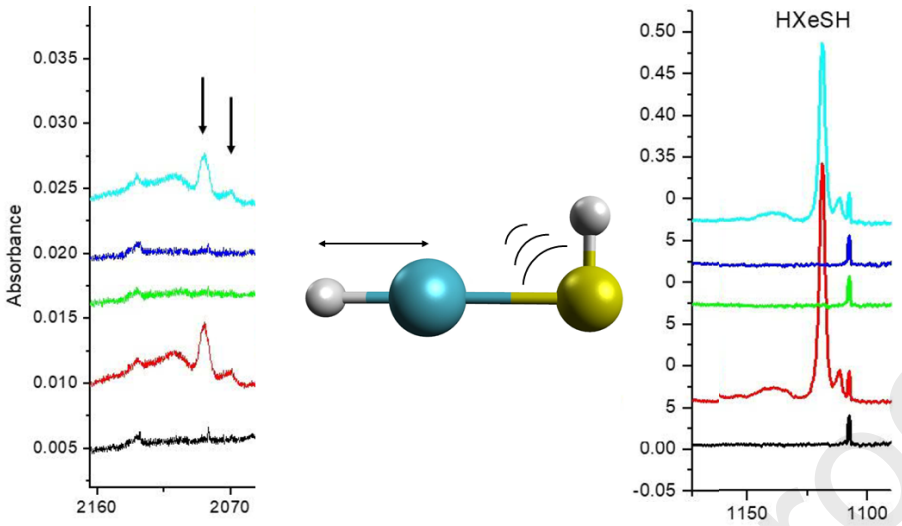

Highlights

- Vibrational spectrum of HXeSH has been studied experimentally and computationally
- New vibrational mode assignments were done for HXeSH
- HXeSH exhibits large anharmonic effects

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Janusz Cukras: Conceptualization, Methodology, Software, Formal analysis, Investigation, Resources, Writing – Original Draft, Writing – Review & Editing, Visualization, Supervision, Project Administration, Funding acquisition Jussi Ahokas: Conceptualization, Methodology, Investigation, Visualization Jan Lundell: Conceptualization, Methodology, Software, Formal analysis, Investigation, Resources, Writing – Original Draft, Writing – Review & Editing, Visualization, Supervision, Funding acquisition