ELSEVIER

A study on stabilization of HHeF molecule upon complexation with Xe atoms

Antti Lignell [a,*], Leonid Khriachtchev [a], Markku Räsänen [a], Mika Pettersson [b]

[a] *Laboratory of Physical Chemistry, Department of Chemistry, P.O. Box 55, A. I. Virtasen aukio 1, FIN-00014, University of Helsinki, Finland*
[b] *Department of Chemistry, P.O. Box 35, FIN-40014, University of Jyväskylä, Finland*

Abstract

In the present work, we computationally study energetic stabilization of HHeF by its complexation with Xe atoms. For the studied HHeF$\cdots$Xe$_n$ systems ($n = 1$–$4, 6$), we found a large complexation-induced decrease of energy of HHeF with respect to its dissociation into atoms. As a working hypothesis, we assume that this stabilization effect continues for the larger systems ($n > 6$) as well. This suggests that dissociation of HHeF via the H–He stretching coordinate might be suppressed and its lifetime might be increased by inserting it into large Xe clusters or matrices.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Since Bartlett's discovery of the first rare gas compound $Xe^+[PtF_6]^-$ in 1962 [1], the reactivity of rare gases has been a fascinating subject for chemists [2,3]. During the last decade, a number of HRgY (H = hydrogen atom, Rg = rare gas atom, and Y = electronegative fragment) molecules have been prepared in rare gas matrices including the first argon containing compound HArF [4–7]. This leaves helium and neon as the only elements in the periodic table without known chemical compounds. Several computational studies have considered the metastable HHeF molecule [8–12]. According to the computational predictions, it decomposes along the stretching and bending coordinates to the H + He + F and HF + He fragments, respectively. Its lifetime, limited by tunnelling, is predicted to be in the femto–picosecond range [9,10]. It has also been suggested that solid high-pressure (over 23 GPa) He matrix may extend the lifetime of the HHeF molecule sufficiently for its detection, but such studies are experimentally very demanding [11]. In addition, HHeCl and HNeCl molecules are stable at some levels of theory, but

at higher level of electron correlation they become unstable [13]. Thus, HHeF molecule is presently the only serious candidate for a He-containing chemical compound.

The first study on HRgY complexes was computationally performed on the HXeH$\cdots$H$_2$O system [14]. Later, computational and experimental works on the N$_2$ complexes of HKrCl, HKrF, and HArF and the HXeOH$\cdots$(H$_2$O)$_n$ systems were done [15–17]. McDowell has also calculated various complexes of rare gas molecules including the HArF$\cdots$N$_2$, HArF$\cdots$CO, and HArF$\cdots$HF systems [18–21]. In our recent experimental and computational study of the HRgY complexes, we suggested that complexation could be a way to energetically stabilize unstable molecular systems [16]. In that work, we proposed that the lifetime of HHeF could increase upon complexation with another molecule, e.g. in the HHeF$\cdots$N$_2$ complex. Very recently, Wang et al. [22] have found computationally that the He, CO, and N$_2$ complexes of HHeF are stable at the MP2/cc-pVDZ level of theory. The main focus of their work was the vibrational blueshift (shift to higher frequency) of the H–Rg stretching mode upon complexation, as it was found for some other HRgY molecules earlier [15–21]. In the present work, we explore the complexation-induced stabilization of HHeF and present a computational study

* Corresponding author. Fax: +358-9-19150279.
E-mail address: lignell@csc.fi (A. Lignell).

of HHeF interaction with up to six Xe atoms. A large decrease of energy of the HHeF$\cdots$Xe$_n$ ($n \leqslant 6$) system is found, which suggests that tunneling-induced dissociation of HHeF might be slowed by inserting HHeF into large Xe clusters or matrices.

2. Computational details and results

The ab initio calculations were performed using the GAUSSIAN 98 (Revision A.11) program package on an IBM eServer Cluster 1600 and SGI Origin 2000 computers [23]. The electron correlation method was the second order Møller-Plesset perturbation theory (MP2). The standard split valence basis set 6-311++G(2d,2p) was used for the lighter atoms (H, He, F) and the Stuttgart/Dresden effective core potentials (SDD) were used for the description of Xe atoms. The partial charges of atoms were obtained using the Mulliken population analysis because the NBO charges could not be obtained for this system by our computational method. The full interaction energy of the complexes was found as difference between energies of the complex and the monomers ($E_{int} = E(complex) - E(HHeF) - n \cdot E(Xe)$, where n is the number of Xe atoms), and the BSSE correction was not involved into the calculations for $n > 1$. The interaction energy between Xe atoms in the supermolecular cluster $[E_{Xe–Xe} = E(Xe_n) - n \cdot E(Xe)]$ was also calculated. For the computation of $E(Xe_n)$, we used optimized coordinates of Xe atoms in the corresponding HHeF$\cdots$Xe$_n$ complexes (without HHeF molecule). The interaction energy corrected with the Xe–Xe components was estimated as $E_{int}^{(corr)} = E_{int} - E_{Xe–Xe}$. The HHeF$\cdots$Xe$_n$ systems for $n = 0$–$4, 6$ were calculated. The case of $n = 5$ was not done because it was very time-consuming due to the lack of symmetry. For $n = 1$, we calculated the counterpoise BSSE correction by taking into account deformation energy correction [24]. The approximate tunnelling path for the bending motion of HHeF, both in monomeric and complexed ($n = 1$) forms, was calculated by keeping coordinates of He, F, and Xe atoms frozen and varying the H–He–F angle simultaneously optimising the H–He distance. We failed to scan the bending coordinate of HHeF$\cdots$Xe$_n$ for $n > 1$.

For all studied complexes, we found minima on the intermolecular potential energy surface. Some of the systems ($n = 2, 4, 6$) had very low imaginary frequencies ($<10i$ cm^{-1}) with normal optimisation criteria because of flatness of the intermolecular potential energy surface. Further optimisation with the tight convergence criteria eliminated imaginary frequencies for $n = 2$ and decreased the imaginary frequencies for $n = 4, 6$ showing that the minima were true. The optimized structures of the studied complexes are presented in Fig. 1. The H–He distances (r), the partial charges (q) of the (HHe) entity,
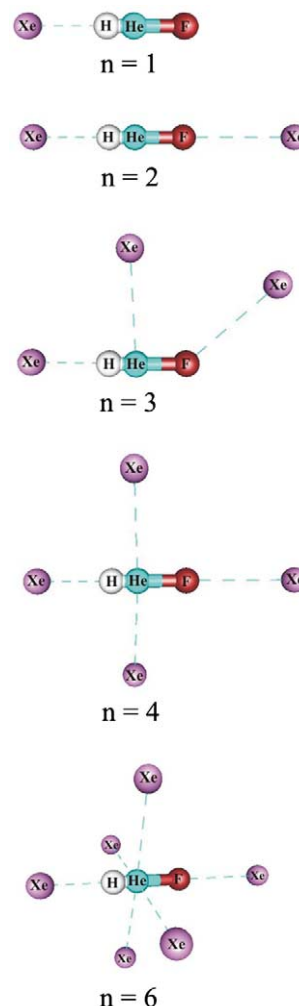

Fig. 1. Optimised structures of the HHeF$\cdots$Xe$_n$ complexes. The structural parameters are presented in Table 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the H–He stretching frequencies, the full interaction energies E_{int}, and the stabilization energies $E_{int}^{(corr)}$ corrected with Xe–Xe interactions are given in Table 1. For $n = 1$, the interaction energy is found to be -1099 cm^{-1} when the BSSE correction and the deformation energy are taken into account, showing a 3-fold decrease of interaction energy compared with the uncorrected value. We did not investigate the effect of BSSE for the $n > 1$, retaining this question open. The HHeF monomer was also calculated, and our HHeF structure and the vibrational properties agree well with the existing data [8–12]. The energy of HHeF at the present level of theory was ~ 6500 and $55\,800$ cm^{-1} higher than the H + He + F and HF + He asymptotes, respectively, showing its metastability with respect to these dissociation channels. In particular, the metastability with respect to the H + He + F asymptote makes impossible the diffusion-controlled formation of HHeF from the atomic frag-

Table 1
H–He and He–F distance (r), HHe Mulliken charge (q), H–He stretching frequency (v), and interaction energy (E_{int}) for the HHeF$\cdots$Xe$_n$ ($n = 0$–4, 6) complexes

	r (H–He) (Å)	r (He–F) (Å)	q (HHe)$^+$ (e)	v (H–He) (cm^{-1})	E_{int} (cm^{-1})	$E_{int}^{(corr)}$ (cm^{-1})
HHeF monomer	0.7931	1.4138	0.5561	2698.5 (2962)	–	–
HHeF$\cdots$Xe	0.7892	1.4716	0.5923	2842.3 (181)	3309.0	3309.0[a]
HHeF$\cdots$Xe$_2$	0.7886	1.4817	0.6320	2855.5 (121)	3715.6	3702.9
HHeF$\cdots$Xe$_3$	0.7895	1.4911	0.6009	2846.5 (16)	4543.8	4080.0
HHeF$\cdots$Xe$_4$	0.7909	1.5022	0.6178	2831.5 (0)	5053.5	4406.7
HHeF$\cdots$Xe$_6$	0.7951	1.5274	0.6237	2772.6 (89)	7366.5	5207.2

$E_{int}^{(corr)}$ is the corrected stabilization energy where the energy of Xe–Xe interactions are subtracted from the total interaction energy E_{int}. The level of theory was MP2 with basis sets 6-311++G(2d,2p) for HHeF and SDD for Xe atoms. BSSE correction was not included in the values of interaction energy. IR-absorption intensities (in km mol^{-1}) are given in parentheses after the vibrational frequency.

[a] The BSSE corrected value is -1100 cm^{-1} when the deformation energy is taken into account.

ments, i.e. using the preparation method of all HRgY molecules known by now [4–7].

In order to discuss energetics of the species in a Xe matrix (see later), a number of energy estimates were considered. The interaction energy of a He atom in Xe matrix (-190 cm^{-1}) was calculated by using He–Xe pair potential in the substitutional matrix site geometry and multiplied by 12, the number of surrounding Xe atoms [25]. The effect of the He atom on the surrounding matrix site geometry was not taken into account. This simplification most probably has a minor effect on the interaction energy of the substitutional He atom, as compared with the relaxed system, similarly to a substitutional oxygen atom in a Xe matrix [26]. The repulsive interaction energy of H atom in a relaxed octahedral interstitial matrix site (500 cm^{-1}) was taken from [27]. The energy of F atom in Xe lattice was estimated with the interaction energy of the Xe–F dimer because of its relatively strong bonding (-1170 cm^{-1}) [28].

3. Discussion

For the HHeF$\cdots$Xe$_n$ ($n = 1, 2$) systems, the complexation induces contraction of the H–He bond and elongation of the He–F bond with respect to the monomer (see Table 1). For $n \geqslant 3$, the H–He bond starts to elongate with respect to the case of $n = 2$. The shortening of the H–He bond leads to a blueshift (shift to the higher frequency) of the H–He stretching frequency accompanied with a decrease of its absorption intensity. This blueshift is attributed to the enhancement of the (HHe)$^+$F$^-$ ion-pair character of the molecule upon complexation [15,16]. For the complexes of HRgY molecules, a blueshift of the H–Rg stretching frequency seems to be a usual effect [15–22]. The only known redshifted H–Rg stretching frequency was computationally found in the HArF$\cdots$P$_2$ complex [19].

The complex with one Xe atom has interaction energy of -3310 cm^{-1} before the BSSE correction, and -1100 cm^{-1}

after the correction. This value is larger than the interaction energies of the other reported HHeF complexes. For instance, the interaction energy of the HHeF$\cdots$N$_2$ complex is computationally only -686 cm^{-1} [22]. The strong attractive interaction is most probably dominated by dispersion and polarization forces. The addition of further Xe atoms ($n > 1$) yields additional interaction energies (see solid symbols in Fig. 2). The energy of HHeF$\cdots$Xe$_6$ (without BSSE correction) is below the fully dissociated atomic asymptote (H + He + F + 6·Xe). However, the interaction energies of the Xe–Xe pairs, present in the HHeF$\cdots$Xe$_n$ clusters, are not included in this fully atomic asymptote. In order to describe the energetics of the HHeF molecule itself, the HHeF$\cdots$Xe$_n$ energy was corrected with the Xe–Xe interactions ($E_{int}^{(corr)}$). As seen in Fig. 2 (open circles), this corrected value decreases obviously more slowly compared with E_{int}. Additional decrease of the computed interaction energy arises from the BSSE correction.
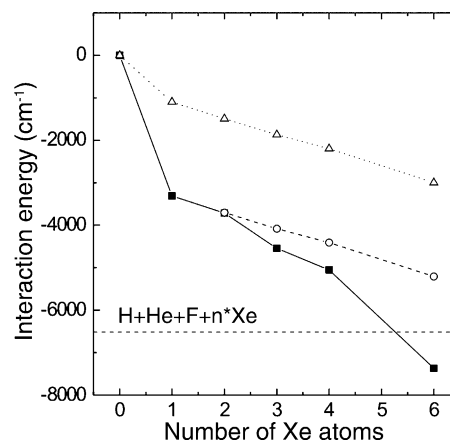

Fig. 2. Interaction energies of the HHeF$\cdots$Xe$_n$ systems (solid symbols). The stabilization energy, corrected with Xe–Xe interactions, is shown by open circles (see text for details). Triangles show the stabilization energy with subtraction of the BSSE correction obtained for the 1:1 complex. The horizontal line represents the fully atomic asymptote.

As a working hypothesis, the found stabilization effect of the HHeF$\cdots$Xe$_n$ complex is assumed to continue for larger Xe clusters ($n > 6$) as well. It is interesting to consider the situation in solid bulk Xe. Because the Xe lattice has the face-centered cubic (fcc) coordination with 12 closest neighbours, it is possible that HHeF in a large Xe cluster or in a Xe matrix is lower in energy than the ''true'' atomic asymptote $H + He + F + Xe_n$ where the Xe–Xe interactions are taken into account. The energy of HHeF$\cdots$Xe$_n$ possibly decreases even for $n > 12$, even though the effect of the second solvation shell should be smaller.

The energetic position of the system below the atomic asymptote would have two important consequences. First, the low energy of HHeF in a Xe matrix makes possible its experimental preparation via the diffusion-controlled $H + He + F$ reaction, i.e. similarly to other HRgY molecules prepared so far [4–7]. Second, the energetic position of HHeF below the atomic asymptote suppresses tunnelling dissociation along the stretching coordinate. This fact is important because according to the results of Takayanagi and Wada, tunnelling along the stretching coordinate limits mostly the lifetime of the HHeF molecule [10]. The interaction energies between the free atoms and surrounding Xe matrix should be taken into account in these estimates. Let us assume that upon deposition of a sample, a He atom is trapped in a substitutional site and HF is trapped interstitially. Photolysis of the HF precursor to the $H + F$ fragments gives a large excess energy to the hydrogen atom making possible its trapping in the (repulsive) interstitial matrix site. Global mobility of hydrogen atoms in Xe solids, which controls the formation of HRgY molecules, occurs between the octahedral interstitial sites [27]. The total energy of the atoms in a Xe matrix prior to annealing can be estimated as $E(F_{Xe-F}, He_{subst.}, H_{interst.}) = -860 \text{ cm}^{-1}$. This means that if the hydrogen atom is trapped in an octahedral interstitial site, formation of HHeF$\cdots$Xe$_n$ upon the diffusion-controlled reaction of H atom with a substitutionally trapped He$\cdots$Fe–Xe center becomes energetically somewhat less favourable. It is also notable that HHeF molecule has harmonic vibrational zero-point energy (ZPE) of 2700 cm^{-1} that should be taken into account when considering its experimental preparation in bulk. The ZPE of atomic fragments in matrices is more difficult to estimate quantitatively, but it partially compensates the effect of ZPE of HHeF.

The stability of HHeF is limited also by tunnelling along the bending coordinate [9,10]. This process is quite difficult to be described quantitatively. Even for isolated HHeF, the literature shows large deviations between the predicted tunnelling rates [9,10]. We do not believe that the methods used in our study can give adequate estimates for tunnelling of the HHeF$\cdots$Xe$_n$ system either along the stretching or bending coordinates. However,
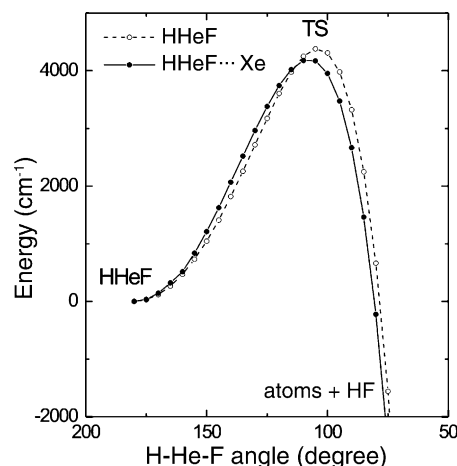

Fig. 3. Bending barriers of the HHeF monomer (open symbols) and the 1:1 HHeF$\cdots$Xe complex (solid symbols) along the tunnelling path of hydrogen atom. The 1:1 complexation induces a decrease of the barrier height. The effect for the larger Xe cluster is unclear.

we scanned the bending barrier for the 1:1 HHeF$\cdots$Xe complex (see Fig. 3). The computations show a slight decrease of the bending barrier height ($\sim5\%$) when compared with the HHeF monomer. In agreement, it has been noted previously that complexation can decrease the bending barrier due to the changed charge separation of molecule upon complexation [17]. However, it is still possible that HHeF in a large Xe cluster can be stabilized with respect to tunnelling through the bending barrier. This stabilization might occur due to the repulsive interaction between H and Xe atoms close to the transition state of HHeF in the Xe$_n$ cluster. Evaluation of this subject is beyond the scope of the present work.

4. Concluding remarks

We presented a computational study of the HHeF molecule interacting with Xe atoms. The HHeF$\cdots$Xe interaction is quite large (-3310 cm^{-1} without BSSE correction and -1100 cm^{-1} after the BSSE correction). Addition of further complexing Xe atoms yields smaller additional interaction energies, but with the increasing number of Xe atoms the total interaction energy increases steadily. We proposed a working hypothesis that the stabilization of HHeF still continues for larger Xe clusters ($n > 6$). This stabilization possibly increases the lifetime of the He-containing molecule in Xe clusters or matrices and might help its experimental preparation and detection. In future, it is interesting to study the HHeF complexes with different partners in order to find even stronger stabilization effects. The lifetime of deuterated and tritiated HHeF molecules, both in monomer and complex forms, should be calculated. It is important

to note, that there might be a possibility to stabilize some other new short-lived or unstable, particularly He and Ne containing HRgY molecules using complexation.

References

[1] N. Bartlett, Proc. Chem. Soc. London (1962) 218.
[2] V.K. Brel, N.Sh. Pirkuliev, N.S. Zefirov, Russ. Chem. Rev. 70 (2001) 231, orig. Usp. Khim. 70 (2001) 262.
[3] J.F. Lehman, H.P.A. Mercier, G.J. Schrobilgen, Coord. Chem. Rev. 233–234 (2002) 1.
[4] M. Pettersson, J. Lundell, M. Räsänen, Eur.J. Inorg. Chem. (1999) 729.
[5] J. Lundell, L. Khriachtchev, M. Pettersson, M. Räsänen, Low Temp. Phys. 26 (2000) 680.
[6] L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, M. Räsänen, Nature (London) 406 (2000) 874.
[7] L. Khriachtchev, M. Pettersson, A. Lignell, M. Räsänen, J. Am. Chem. Soc. 123 (2001) 8610.
[8] M.W. Wong, J. Am. Chem. Soc. 122 (2000) 6289.
[9] G.M. Chaban, J. Lundell, R.B. Gerber, J. Chem. Phys. 115 (2001) 7341.
[10] T. Takayanagi, A. Wada, Chem. Phys. Lett. 352 (2002) 91.
[11] Z. Bihary, G.M. Chaban, R.B. Gerber, J. Chem. Phys. 117 (2002) 5105.
[12] T. Takayanagi, Chem. Phys. Lett. 371 (2003) 675.
[13] S.A.C. McDowell, Chem. Phys. Lett. 342 (2001) 631.
[14] J. Lundell, M. Pettersson, Phys. Chem. Chem. Phys. 1 (1999) 1691.
[15] A. Lignell, L. Khriachtchev, M. Pettersson, M. Räsänen, J. Chem. Phys. 117 (2002) 961.
[16] A. Lignell, L. Khriachtchev, M. Pettersson, M. Räsänen, J. Chem. Phys. 118 (2003) 11 120.
[17] A.V. Nemukhin, B.L. Grigorenko, L. Khriachtchev, H. Tanskanen, M. Pettersson, M. Räsänen, J. Am. Chem. Soc. 124 (2002) 10 706.
[18] S.A.C. McDowell, Chem. Phys. Lett. 368 (2003) 649.
[19] S.A.C. McDowell, Phys. Chem. Chem. Phys. 5 (2003) 808.
[20] S.A.C. McDowell, Chem. Phys. Lett. 377 (2003) 143.
[21] S.A.C. McDowell, Mol. Phys. 101 (2003) 2261.
[22] J.T. Wang, Y. Feng, L. Liu, X.S. Li, Q.X. Guo, Chem. Lett. 32 (2003) 746.
[23] M.J. Frisch, G.W. Trucks, H.B. Schlegel et al., GAUSSIAN 98, Revision A.11, Gaussian, Inc., Pittsburgh, PA, 1998.
[24] F.B. van Duijneveldt, J.G.C.M. van Duijneveldt-van de Rijdt, J.H. van Lenthe, Chem. Rev. 94 (1994) 1873.
[25] K.T. Tang, J.P. Toennies, J. Chem. Phys. 118 (2003) 4976.
[26] A.V. Danilychev, V.A. Apkarian, J. Chem. Phys. 100 (1994) 5556.
[27] L. Khriachtchev, H. Tanskanen, M. Pettersson, M. Räsänen, V. Feldman, F. Sukhov, A. Orlov, A.F. Shestakov, J. Chem. Phys. 116 (2002) 5708.
[28] V. Aquilanti, E. Luzzatti, F. Pirani, G.G. Volpi, J. Chem. Phys. 105 (1988) 6165.