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Combined ab initio and anharmonic vibrational spectroscopy calculations for rare gas containing fluorohydrides, HRgF

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Abstract

MP2 and CCSD(T) calculations are used to analyse the structures and vibrational spectra of HRgF molecules, where the rare gas atom is He, Ne, Ar, Kr, Xe or Rn. We extend the analysis of the vibrational spectra of these molecules to include anharmonic corrections for the most likely candidates for experimental detection, i.e., HArF, HKrF, HXeF, and their deuterated isotopomers. The anharmonic correlation-corrected vibrational self-consistent-field (CC-VSCF) calculations are used for this, and fundamental, overtone and combination frequencies and their absorption intensities are computed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The rare gas atoms have been regarded as inert due to their stable electron structure unfavorable to the formation of a chemical bond. However, during the last four decades xenon and krypton have lost their nobleness as they have been found to form bonds with usually extremely electronegative substances [1,2]. Recently, also argon has been found to join the group of reactive rare gases, when Khriachtchev and co-workers reported argon fluorohydride, HArF, in low-temperature matrix experiments [3].

A number of rare gas-containing hydrides with a common formula HRgX, where X represents a strongly electronegative species and Rg is Xe, Kr or Ar, have been prepared and identified in rare gas matrices [3–5]. These molecules are formed from neutral atomic or molecular fragments in a concerted reaction $H + Rg + X \rightarrow HRgX$. These molecules obtain their stability from ionic configurations and they are best described as $(HRg)^+X^-$ [4]. The ionic character of the HRgF molecules suggests the existence of strong vibrational transitions that provide effective detection by infrared absorption spectroscopy.

From a computational point of view, the HRgX molecules present a challenging task. The ion-pair nature of these compounds, interaction of different neutral and ionic configurations, relatively weak

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bonds and relativistic effects are very demanding of computational methods. It has already been shown that the equilibrium structure can be obtained at a moderate computational level [4–6], but accurate energetics or vibrational frequencies require higher level multireference or coupled cluster treatments, especially in the case of the weakest bound compounds like HXeH and HXeSH. Among the most strongly bound HRgX molecules are HXeCl and HXeCN for which standard second-order perturbation theory (MP2) works adequately compared with the experimental results. Besides large correlation effects there is evidence for important anharmonic effects for the HRgX molecules [7,8]. Thus, anharmonic vibrational calculations of HRgX molecules are important both because of their usefulness for experimental identification of these molecules, and because of their relevance to dynamical processes in these systems.

The discovery of the first stable covalently bound molecule containing argon, HArF, was reported by Khriachtchev and coworkers [3]. It is also the first experimentally characterized member of the rare gas containing fluorohydrides. The HRgF species containing larger rare gases, i.e., Kr, Xe, and Rn represent an almost untouched territory, even though the previous results on the halogen containing HXeX and HKrX compounds have prompted predictions of strongly bound HRgF species [9,10]. The properties of the lighter rare gas fluorohydrides, especially HHeF, was recently discussed by Wong [11] based on ab initio calculations. Moreover, the other rare gas fluorides containing neon, argon and krypton were also briefly discussed.

In this Letter, we extend the analysis of the halogen containing HRgX molecules from Cl, Br, and I containing rare gas hydrides [7,8] to fluorine containing species, and we present computational results for the whole series HRgF molecules ranging from He to Rn. We also extend the analysis of the infrared spectra of the most likely candidates for experimental detection, i.e., HArF, HKrF and HXeF, which are studied by ab initio vibrational calculations where anharmonicity is taken into account. We believe the present calculations are important for future experimental

studies of HRgF molecules, and especially HKrF and HXeF for which no experimental evidence have been presented yet.

2. Computational methods

The structural and energetical properties, as well as harmonic vibrational frequencies were calculated at the MP2 and CCSD(T) levels of theory. Averaged relativistic core potentials (AREP) [12–14] were used for Kr, Xe and Rn atoms. The underlying d-shell was included in the valence corresponding to 18 valence electrons. The valence basis sets were fully uncontracted. For lighter rare gases, as well as for H and F atoms, the standard 6-311++G(2d,2p) basis set was applied. These calculations were done using the GAUSSIAN 98 [15] package of computer codes running on the SGI Origin 2000 computer at CSC-Center for Scientific Computing (Espoo, Finland).

The vibrational properties of HArF, HKrF and HXeF were studied by first-principles calculations of vibrational spectroscopy, which combines electronic ab initio code GAMESS [16] with the vibrational self-consistent field (VSCF) method and its extension by corrections via second-order perturbation theory [17–20]. This correlation-corrected VSCF (CC-VSCF) method is used to solve the Schrödinger equation within the normal-mode coordinate system to obtain vibrational wave functions and energies. This involves writing the wave function as a product of one-dimensional functions and then solving the resulting equations self-consistently. To make the integrals involved in the CC-VSCF calculation more tractable and to reduce the number of electronic structure computations required, a pairwise coupling approximation is made to the potential in the normal-mode representation [18]. This approximation provides a grid of points in normal-mode coordinates at which the potential energy is calculated. Each pair of normal modes is pictured with a 16×16 potential surface grid and the points are chosen equidistantly over an interval which is defined by the harmonic frequency of a vibrational mode: $Q_{\max} \sim$ the inverse of the square root of the frequency [20]. The same basis sets for all atoms were

used for these calculations as for the MP2 and CCSD(T) calculations.

3. Results

The calculated equilibrium structures and harmonic vibrational frequencies of the linear HRgF molecules are shown in Table 1. Also included are Mulliken charges on each atoms, since as shown previously these numbers are very similar to those derived from more sophisticated analysis of electron densities [3,6,21]. The dissociation energies of the HRgF molecules are estimated according to the neutral atom dissociation limit. For comparison, the computed energy differences between the HRgF molecules and their $\text{Rg} + \text{HF}$ dissociation limits are also shown in Table 1. The HRgX molecules are metastable compared with the global energy minimum $\text{Rg} + \text{HX}$ but it has been experimentally demonstrated that these species decompose producing neutral atoms $\text{H} + \text{Rg} + \text{X}$ [22] in solid rare gases.

The structural properties of HHeF, HNeF, HArF and HKrF calculated here at the MP2 and CCSD(T) levels are in good agreement with those reported earlier [3,9,11,21]. For HXeF and HRnF no previous results are available, but these molecules follow the trends set by the lighter rare gas containing species compared to those of the respective cationic species RgH^+ and RgF^+ . As the size of the rare gas increases, the H–Rg and Rg–F bond distances also increase. At the same time a decreasing trend is observed in the respective vibrational absorptions which are shifting to lower wavenumbers. These trends are demonstrated in Fig. 1, where these mentioned properties of the HRgF molecules are compared with the respective cationic RgH^+ and RgF^+ species. The non-linearity in the figure of HRgF vibrational frequencies is probably due to all-electron basis set representation of HHeF and HArF, whereas for the larger rare gases a pseudopotential is employed. Our CCSD(T)/6-311++G(2d,2p) Rg–H vibrational frequencies are much lower than those calculated at the MP2 level and experimentally observed. The CCSD(T) approach requires more complete and flexible basis sets to reproduce the

experimental data. This is clearly demonstrated for the HRgX molecules by Runeberg and coworkers [21,23], and for example CCSD(T) calculations of HArF using aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets on all atoms shift the harmonic Ar–H stretching vibration from 1865 to 2053 and 2088 cm^{-1} , respectively. In our study, the use of the 6-311++G(2d,2p) basis set is justified by comparison with previous studies, in which the same basis sets were employed to study several HRgX species [4–6].

In analogy with the other rare gas hydrides [4,5] the HRgF molecules have a strong $(\text{HRg})^+\text{F}^-$ charge transfer character in the HRgF electronic structure. It should be stressed that these molecules differ completely from the salts containing a strongly bound $(\text{RgF})^+$ unit [24–27]. As seen in Fig. 1, the calculated bond distances of the RgF^+ are much longer than the Rg–F bond distance found for the HRgF molecules. On the other hand, the bond distances of isolated RgH^+ cations are much shorter than the respective Rg–H bond distances in the HRgF molecules, and this suggests that the complete ionic limit $(\text{HRg})^+\text{F}^-$ is dominating but some covalent character is also present. As recently suggested [28], the HRgF molecules can be described as a resonance hybrid between several possible structures, the most important being obviously HRg^+F^- . The other important structures are neutral H–Rg–F and ionic HRg^-F^+ configurations. The ionic structures tend to stabilise the compound and the neutral structure destabilises it. In general, these hybrid structures can be approximated to contribute with a ratio of 60%/20%/20% [28], i.e., the electronic structure of HRgF molecules is mainly ionic but with a non-negligible fraction of a covalent character. This picture is in good agreement with the simple model derived by Pettersson and coworkers [4] which predicts the existence of these type of molecules based on the ionization potential of the rare gas atom, electron affinity of the electronegative fragment, in this case fluorine, and the dissociation energy of the RgH^+ cation. These three properties give the characteristics of the ratio between two potential energy surfaces: an ionic surface corresponding to the equilibrium structure of the HRgF molecule with a dissociation limit $\text{HRg}^+ + \text{X}^-$.

Table 1
Calculated bond distances, Mulliken charges, dipole moments, and vibrational frequencies for the HRgF molecules. The numbers in the parentheses are the IR intensities (in km mol^{-1})

	$r(\text{Rg-H})$ (Å)	$r(\text{Rg-F})$ (Å)	$q(\text{H})$	$q(\text{Rg})$	$q(\text{F})$	μ/D	ω_1 (cm^{-1})	ω_2 (cm^{-1})	ω_3 (cm^{-1})	$D_e(\text{H} + \text{Rg} + \text{F})$ (eV)	$D_e(\text{Rg} + \text{HF})$ (eV)
HHF											
MP2	0.7930	1.4134	0.330	0.226	-0.556	5.40	1006.3 (509)	829.4 (37)	2701.6 (2952)	+0.792	+6.917
CCSD(T)	0.8247	1.4217					963.6	778.9	2110.1	+0.415	+6.931
HNeF											
MP2	1.0188	1.9594	0.375	0.405	-0.780	9.32	437.7 (561)	374.4 (136)	1740.8 (8742)	+2.508	+8.634
CCSD(T)	—	—					—	—	—	—	—
HArF											
MP2	1.3262	1.9957	0.128	0.525	-0.652	7.19	481.2 (267)	743.4 (26)	2148.9 (1149)	-0.070	+6.056
CCSD(T)	1.3550	2.0048					478.9	781.1	1793.1	-0.510	+6.007
HKrF											
MP2	1.4229	2.1336	-0.222	0.957	-0.735	7.72	396.1 (196)	695.2 (2)	2315.9 (988)	-0.948	+5.178
CCSD(T)	1.4388	2.1382					396.8	673.7	2173.8	-1.366	+5.151
HXeF											
MP2	1.6655	2.1461	-0.191	0.865	-0.674	5.89	438.9 (195)	657.8 (4)	2068.9 (598)	-1.956	+4.169
CCSD(T)	1.6808	2.1497					433.2	643.6	1954.7	-2.395	+4.122
HRnF											
MP2	1.8677	2.8094	0.235	0.399	-0.635	8.59	312.6 (139)	601.2 (6)	1575.0 (1374)	+0.411	+6.537
CCSD(T)	1.9424	2.8494					293.9	544.9	1124.4	-0.026	+6.490

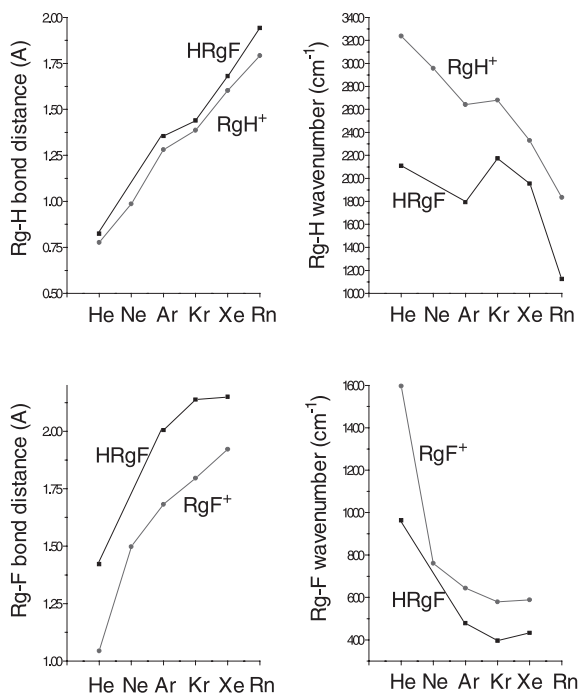


Fig. 1. Comparison of the bond distances and harmonic frequencies for the cationic species and the HRgF molecules. All results were obtained at the CCSD(T) level.

However, when the HRgX molecule is stretched along the molecular axis the ionic adiabatic surface is crossed by a repulsive surface corresponding to the neutral fragments $H + Rg + X$. The dissociation limit of the HRgF molecules correspond to the neutral fragments due to the avoided crossing between the neutral and ionic potential surfaces. The existence of such avoided crossing explains also the strange results found for HNeF. At the B3LYP [11] and MP2 levels, the equilibrium structure is easily found since the search proceeds only on the strongly bound ionic surface. However, as found also by Wong, the CCSD(T) calculations take perturbatively into account also the neutral potential surface. The optimisation of HNeF at the CCSD(T) level is quite quickly driven towards the neutral atom limit, which indicates that the crossing between the two potential surfaces occur very close to the minimum of the ionic surface and that there is no barrier for the dissociation of HNeF to $H + Ne + F$. However, more

detailed computational investigations of the HNeF molecule must be left for future studies employing preferably multi-reference (MRCI) approaches to study the interplay between the ionic and neutral potential energy surfaces. On the other hand, the lighter HHeF molecule is computed to be ca 0.4 eV above the neutral atom dissociation limit at the CCSD(T)/6-311++G(2d,2p) level of theory but Wong [11] reported a barrier of 0.34 eV (CCSD(T)/aug-cc-pVQZ) towards the $HHeF \rightarrow He + HF$ dissociation channel. The CC-VSCF calculations give the following vibrational frequencies for HHeF: 2059, 966, and 518 cm^{-1} corresponding to He–H stretching, He–F stretching and H–He–F bending modes, respectively. The small barrier for the dissociation of HHeF (keeping in mind that the vibrational zero-point energy is 0.22 eV) casts doubts on the existence of this system and further higher-level (MRCI) computational studies would be helpful.

HKrF and HXeF represent extremely stable molecules compared with their neutral atom dissociation limit, and ongoing low-temperature matrix isolation experiments indicate that both of these compounds are preparable [29]. To aid these experiments we will address the anharmonic vibrational properties of these molecules in the following. The HRnF molecule appears quite weakly bound and multireference computational methods combined with more flexible basis sets should be applied to obtain more conclusive results [30,31]. Nevertheless, increasing electron correlation from MP2 to CCSD(T) level lowers the HRnF molecule below the $H + Rn + F$ dissociation limit, and the similarity of this molecule to the other HRgX molecules suggests a non-negligible barrier for the $HRnF \rightarrow H + Rn + F$ dissociation process.

3.1. HArF and DArF

Results of the ab initio vibrational spectroscopy calculations for HArF and DArF, and comparison with experiment, are shown in Table 2. These molecules are the first in the family of rare gas containing hydrides for which all vibrational modes have been experimentally observed. The Ar–H stretch ($\nu(\text{Ar–H})$) is found at 1969.5 cm^{-1} , the bending absorption is at 687.0 cm^{-1} , and the

Table 2

MP2/CC-VSCF calculated anharmonic frequencies^a for HArF and DArF (in cm⁻¹)

Mode ^b	ArH ⁺ ^c		ArF ⁺ ^d		HArF			DArF	
	MP2 (harmonic)	CC-VSCF	MP2 (harmonic)	CC-VSCF	MP2 (harmonic)	CC-VSCF	Exp. ^e	CC-VSCF	Exp. ^e
3ν ₃		7286.9 (0)				5259.5 (2)		3984.3 (0)	
2ν ₃		4961.1 (4)				3643.0 (2)		2739.8 (0)	
ν ₂ + ν ₃						2557.1 (1)		1915.3 (0)	
ν ₁ + ν ₃						2393.3 (3)		1895.3 (2)	
3ν ₂						2109.7 (0)		1578.8 (0)	
ν ₃	2650.6 (580)	2535.7 (693)			2148.9 (1149)	1911.8 (88)	1969.5	1416.7 (55)	1466.3
2ν ₂						1407.1 (7)		1052.5 (2)	
3ν ₁				2289.3 (0)		1402.0 (0)		1399.1 (0)	
ν ₁ + ν ₂						1173.6 (0)		995.4 (0)	
2ν ₁				1532.3 (0)		940.6 (5)		938.6 (5)	
ν ₂					743.4 (26)	703.9 (42)	687.0	526.3 (13)	513.0
ν ₁			775.0 (2)	769.1 (17)	481.2 (267)	473.3 (276)	435.7	472.2 (275)	435.0

^a The numbers in parentheses are the IR intensities (in km mol⁻¹), and they were obtained from Hartree–Fock wave functions for the CC-VSCF calculations.

^b ν₁ is ν(Ar–F); ν₂ is δ(H–Ar–F); ν₃ is ν(Ar–H).

^c The optimized Ar–H bond distance is 1.281 Å.

^d The optimized Ar–F bond distance is 1.636 Å.

^e From Ref. [3].

heavy atom stretching absorption ν(Ar–F) is at 435.7 cm⁻¹ [3]. The anharmonic CC-VSCF calculations reproduce these band positions quite well predicting the three absorptions at 1912, 704 and 473 cm⁻¹, respectively. Similarly, the three bands experimentally observed for DArF at 1466.3, 513.0 and 435.3 cm⁻¹ are all well reproduced by the anharmonic CC-VSCF calculations. The Ar–D stretch is computed to be at 1417 cm⁻¹, which is slightly below the experimentally observed position for this band similarly to the Ar–H band. This can partly be explained by matrix effects in the experiments compared to the gas phase calculation. In fact, calculations by Runeberg and co-workers including six additional argon atoms in octahedral configuration produced an upward shift of 38 cm⁻¹ for the Ar–H stretching [21]. The bending and heavy atom stretching modes are calculated to lie at 526 and 472 cm⁻¹, respectively, and they are in good agreement with the experimental values.

As a real advantage of the present calculations, we can estimate the combination and overtone bands from the ab initio calculated potential energy surface. Experimentally no overtones or

combinations for HArF or DArF have been reported. The CC-VSCF calculations predict weak first overtones and combinations involving the strong ν(Ar–H) fundamental band, and these could be searched for experimentally. Similarly, for DArF the first overtone of each fundamental band is predicted to have a low intensity (ca. 2 km mol⁻¹).

3.2. HKrF and DKrF

The anharmonic vibrational frequencies of HKrF and DKrF are shown in Table 3. The Kr–H stretching (ν₃) is predicted at 2316 cm⁻¹ by the harmonic MP2 calculation. Including anharmonicity in the calculation shifts this band to 2180 cm⁻¹, which is almost the same position to the one predicted by the harmonic CCSD(T) calculation. It can be concluded that both electron correlation and anharmonicity seem important and that these values are slightly overestimated compared to the experimental position of this band. The calculated position of the ν(Kr–H) can be compared with the experimental value of ν(Kr–H) in KrH⁺, which is 2710 cm⁻¹ [32] being much

Table 3

MP2/CC-VSCF calculated anharmonic frequencies^a for HKrF and DKrF (in cm⁻¹)

Mode ^b	KrH ⁺ ^c		KrF ⁺ ^d		HKrF		DKrF
	MP2 (harmonic)	CC-VSCF	MP2 (harmonic)	CC-VSCF	MP2 (harmonic)	CC-VSCF	CC-VSCF
3ν ₃		7650.1 (0)				6107.6 (1)	4532.4 (0)
2ν ₃		5186.6 (1)				4210.8 (2)	3094.6 (0)
ν ₂ + ν ₃						2757.2 (0)	2031.5 (0)
ν ₁ + ν ₃						2550.7 (1)	1968.9 (1)
ν ₃	2725.0 (413)	2636.7 (554)			2315.9 (988)	2179.7 (122)	1584.0 (64)
3ν ₂						1919.6 (0)	1439.5 (0)
2ν ₂						1303.6 (7)	968.5 (0)
3ν ₁				2025.3 (0)		1175.8 (0)	1175.6 (0)
ν ₁ + ν ₂						1057.5 (0)	882.5 (0)
2ν ₁				1355.8 (0)		787.9 (3)	787.7 (3)
ν ₂					695.2 (2)	664.0 (10)	488.7 (2)
ν ₁			688.7 (2)	680.7 (12)	396.1 (196)	396.0 (216)	395.9 (216)

^a The numbers in parentheses are the IR intensities (in km mol⁻¹), and they were obtained from Hartree–Fock wave functions for the CC-VSCF calculations.

^b ν₁ is ν(Kr–F); ν₂ is δ(H–Kr–F); ν₃ is ν(Kr–H).

^c The optimized Kr–H bond distance is 1.382 Å.

^d The optimized Kr–F bond distance is 1.757 Å.

higher than in HKrF. Upon deuteration this band is computed to display a typical deuterium shift and the CC-VSCF computed position of the Kr–D stretching absorption is at 1584 cm⁻¹.

The HKrF bending (ν₂) and Kr–F stretching (ν₁) modes appear much less anharmonic than the Kr–H stretching. The bending mode is reduced by ca. 30 cm⁻¹ to 664 cm⁻¹ from its value in the harmonic approximation. The heavy atom stretch ν(Kr–F) is insensitive to the inclusion of anharmonicity and the vibration is found at ca. 396 cm⁻¹. Even though this band is predicted to be the most intense in the HKrF vibrational spectrum it is already below the edge of detection in standard FTIR-measurements.

The overtone and combination bands of HKrF and DKrF are quite weak and only the first overtone of the HKrF bending could appear as a serious candidate for experimental detection. This band is predicted to lie at 1304 cm⁻¹ and be of similar intensity as the bending fundamental absorption.

3.3. HXeF and DXeF

The results of the anharmonic CC-VSCF calculations for HXeF and DXeF are collected in Table 4. HXeF is the last member of the family of

HXeX molecules containing a halogen atom which has not been experimentally characterized. HXeI is the weakest bound of this family and these molecules become more tightly bound with the decreasing size of the halogen atom. The Xe–H stretching vibration is a fingerprint of these molecules, as well as for all the Xe-containing hydrides, and the Xe–H bond distance reflects directly the fraction of stabilising ionic contribution in the molecule [4,5]. The Xe–H stretching absorption frequency increases in the order HXeI(1193 cm⁻¹) < HXeBr (1504 cm⁻¹) < HXeCl (1648 cm⁻¹), and already for HXeCl the anharmonic vibrational calculations similar to those in this study gave almost perfect agreement with the experimental value [8]. For HXeF the CC-VSCF calculations predict the ν(Xe–H) to lie at 1982 cm⁻¹. It must be noted that again the absorption is lower in the spectrum compared to the vibrational absorption of the XeH⁺ cation (2270 cm⁻¹ [33]). The deuterated counterpart of the ν(Xe–H) band is computed to be at 1426 cm⁻¹.

It is interesting that the anharmonic calculations predict the ν(Xe–H) band to be equally intense compared to the Xe–F stretching band. For the lighter rare gases this absorption band was estimated to be weaker than the Rg–F band, even though the harmonic approximation indicate that

Table 4

MP2/CC-VSCF calculated anharmonic frequencies^a for HXeF and DXeF (in cm⁻¹)

Mode ^b	XeH ⁺ ^c		XeF ⁺ ^d		HXeF		DXeF
	MP2 (harmonic)	CC-VSCF	MP2 (harmonic)	CC-VSCF	MP2 (harmonic)	CC-VSCF	CC-VSCF
3ν ₃		6710.7 (0)				5720.5 (0)	4162.3 (0)
2ν ₃		4546.5 (0)				3888.1 (2)	2812.9 (1)
ν ₂ + ν ₃						2563.3 (0)	1866.1 (0)
ν ₁ + ν ₃						2402.9 (1)	1857.6 (1)
ν ₃	2384.3 (241)	2310.0 (337)			2068.9 (598)	1981.9 (270)	1425.5 (141)
3ν ₂						1879.8 (0)	1389.4(0)
3ν ₁				1888.8 (0)		1308.2 (0)	1309.6 (0)
2ν ₂						1266.3 (3)	931.6 (1)
ν ₁ + ν ₂						1077.6 (1)	907.4 (0)
2ν ₁				1265.1 (1)		876.4 (3)	877.4 (3)
ν ₂					657.8 (4)	639.7 (2)	468.4 (3)
ν ₁			643.3 (7)	635.4 (1)	438.9 (195)	440.3 (263)	440.8 (263)

^a The numbers in parentheses are the IR intensities (in km mol⁻¹), and they were obtained from Hartree–Fock wave functions for the CC-VSCF calculations.

^b ν₁ is ν(Xe–F); ν₂ is δ(H–Xe–F); ν₃ is ν(Xe–H).

^c The optimized Xe–H bond distance is 1.597 Å.

^d The optimized Xe–F bond distance is 1.904 Å.

the Xe–H stretching band is the strongest one. Clearly, the decreasing intensity of the bending mode correlates with the increasing size of the rare gas atom. For HXeF, the bending mode has very low intensity which will make it difficult to measure this vibrational band experimentally.

The heavy-atom stretch of HXeF is at 440 cm⁻¹ and this band could be observed experimentally. In the case of HArF, the ν(Ar–F) was experimentally found at 435.7 cm⁻¹ [3] when the CC-VSCF predicted it to occur at 473 cm⁻¹. Therefore, for the Xe-compound the heavy-atom stretching might be found experimentally above 400 cm⁻¹.

The overtone and combination spectrum of HXeF is quite sparse and the only candidates to appear in the experimental spectrum are the first overtones of each fundamental band. For DXeF the situation is even worse and only possible candidates for experimental exploration are the first overtones of the two stretching modes.

4. Conclusions

We have investigated the structural and vibrational properties of the HRgF molecules, where

Rg is a rare gas atom (He, Ne, Ar, Kr, Xe, Rn) at the MP2 and CCSD(T) levels of electronic structure theory. Calculations show that the HArF, HKrF, and HXeF molecules are stable compared with their dissociation limit to neutral atoms H + Rg + F by up to 2.4 eV. HRnF is very weakly bound and it is calculated to be only 0.03 eV below the neutral atomic limit at the CCSD(T) level. HHeF and HNeF are both calculated to be above the neutral atomic limit at the CCSD(T) level. The most prominent candidates for experimental detection are HArF, HKrF and HXeF, the first of which has recently been reported by Khriachtchev and coworkers [3] and work on the other two are in progress. In order to help the experimental efforts, we have extended the vibrational studies of these three molecules by including anharmonic effects. The computational approach combines the electronic structure codes with algorithms that compute vibrational states at a level of high accuracy, including anharmonic effects and coupling between vibrational modes. For the HRgX molecules especially, the characteristic and experimental fingerprint vibration ν(Xe–H) involves large anharmonic effects, which is evident when we compare the calculated anharmonic frequencies with the harmonic ones and those derived from

low-temperature matrix experiments (HArF). In addition to the fundamental absorptions, we make predictions for combination and overtone absorptions, which could be used to help experimental studies by providing additional fingerprints for the HRgF molecules.

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