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Anharmonic Vibrational Spectroscopy Calculations for Novel Rare-Gas-Containing Compounds: HXeH, HXeCl, HXeBr, and HXeOH

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A first-principles calculation of vibrational spectroscopy of HXeH, HXeCl, HXeBr, and HXeOH molecules is performed by combining ab initio codes with the vibrational self-consistent field (VSCF) method, and with its extension by perturbation theory (CC-VSCF). The MP2/CC-VSCF method is anharmonic, and it is able to reproduce the experimentally observed spectral features of HXeH, HXeCl, HXeBr, and HXeOH. The most intense bands of the HXeY molecules, the Xe−H stretching modes, are found to be highly anharmonic. In general, the other fundamental modes presented anharmonic effects to a lesser extent. New predictions of overtone and combination vibrations are made to help experimental investigations of these molecules. It is shown that vibrational spectroscopy calculations are reliable and useful for analyzing the spectral features of rare-gas-containing molecules. While the results of the MP2/CC-VSCF calculations are in much better agreement with experiments than the corresponding harmonic frequencies, substantial discrepancies remain. These are mostly due to the large electronic correlation effects in these systems, which are not sufficiently well presented at the MP2 level.

1. Introduction

The inertness of rare gas atoms toward chemical bond formation has been attributed to the octet rule picturing full electron shells. The nobility of rare gases started to deteriorate after the first xenon compound was found by Bartlett in 1962.[1] Thereafter, xenon has been found to form bonds with usually extremely electronegative substances[2] and numerous Xe-containing compounds are currently known.[3] Chemistry related to the lighter rare gases is much more sparse than that on Xe, and some compounds involving Kr−F, Kr−O, Kr−C, and Kr−N bonds have been synthesized in a laboratory,[2,3] but no neutral ground state chemically bound molecules of helium, neon, or argon have been reported so far.

Recently, a new group of rare-gas molecules, krypton and xenon hydrides HRgY, where Y is an electronegative fragment, have been identified in low-temperature matrices.[4] The first observed HRgY compounds were triatomic HXeY (Y═H, Cl, Br, I) and HKrCl molecules.[5,6] These molecules obtain their stability from ionic configurations and they are best described as HRg^+Y^-. After the mechanism of their formation from neutral fragments was understood,[7] these ideas have been used to prepare and characterize more complex compounds HXeCN,[8] HXeNC,[8] HKrCN,[8] HXeSH,[9] HXeOH,[10] and HXeNCO.[11]

From the computational point of view the HRgY molecules present a challenging task. The ion-pair nature of these compounds, interaction of different neutral and ionic configurations, and relatively weak bonds and relativistic effects present severe tests for computational methods. It has already been shown that the equilibrium structure can be achieved at a moderate level,[4] but accurate energetics or vibrational properties require high-level multireference or CCSD(T) treatments.[12] However, the highly correlated quantum chemical calculations are quite unfeasible beyond triatomic Rg species. Moreover, extensive benchmark calculations on XeH_2 by Runeberg et al.[12] indicated a highly anharmonic potential energy surface for this molecule. This is an important aspect since potential energy surfaces determine the dynamics of nuclear motions. This prompted us to study the anharmonic properties of these novel Rg-containing molecules and in this paper we will present anharmonic vibrational spectroscopy calculations on HXeH, HXeCl, HXeBr, and HXeOH. The importance of anharmonic vibrational calculations on these systems is 2-fold. First, vibrational spectroscopy is the main technique used to identify these compounds and characterize their properties. Computed harmonic frequencies deviate strongly from experiment for these systems, so anharmonic calculations are essential. Further, the strongly anharmonic structure of the potential energy surfaces is in itself of considerable interest. Anharmonic spectroscopy calculations for polyatomic systems require treatment of coupling between the different modes, since beyond the harmonic approximation the states are no longer separable in the various modes. To carry out the anharmonic, coupled mode calculations, we will employ the vibrational self-consistent field (VSCF) method, and its extension the correlation-corrected VSCF (CC-VSCF).[13−18] A major advantage of this method for our purpose here is that recently an algorithm was introduced that combines

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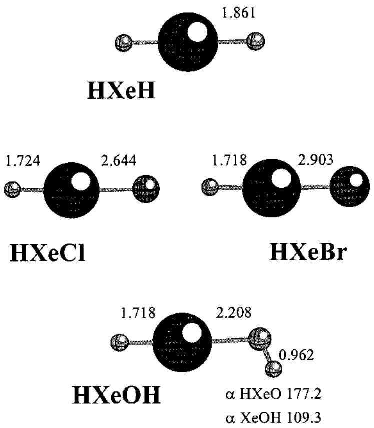

Figure 1. MP2-calculated equilibrium structures of HXeH, HXeCl, HXeBr, and HXeOH.

electronic structure codes with VSCF and CC-VSCF.[19,20] The combined algorithm thus provides a scheme which directly computes anharmonic vibrational wave functions and spectroscopy from ab initio electronic structure methods. Recently, we combined this approach with experimental matrix isolation studies to study HXeI[21] and we were able to find and assign several new combination and overtone bands. We believe the present calculations will be important for future computational and experimental studies of HRgY molecules, and make new contributions also on the HRgY species observed in low-temperature matrix isolation experiments.

2. Calculations

All ab initio calculations in this work were performed in the framework of the GAMESS electronic structure program.[22] Electron correlation was considered via Møller−Plesset perturbation theory[23,24] to second order (MP2). Averaged relativistic core potentials (AREP) were used for xenon and halogen atoms. On Xe, an 18-electron valence space including the d-subshell was used with the LaJohn effective core potential (ECP).[25] The 4s4p4d valence basis set was completely decontracted. For Br, a similar 17-VE ECP was used,[26] and the 4s4p4d valence basis set was fully decontracted. An 7-VE ECP by Christiansen was applied on chlorine,[27] and it was combined with a balanced atomic basis set by Wallace et al.[28] The valence 4s4p1d basis on Cl was contracted as [2s2p1d]. For oxygen and hydrogen standard 6-311++G(2d,2p) basis set including multiple diffusion and polarization functions were used.[29−31]

The anharmonic vibrational frequencies were derived from the vibrational self-consistent field (VSCF) and its extension by corrections via second-order perturbation theory (CC-VSCF).[17,19,20,32] 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 are negligible as we have determined numerically.[17,19] Each pair of normal modes is pictured with a 16 × 16 PES grid and the mode−mode couplings are then evaluated by ab initio calculations over this grid. A more detailed description of the MP2/CC-VSCF method is given in refs 19 and 20.

3. Results

The calculated structural parameters for the various HXeY molecules at the MP2 level are shown in Figure 1. For all of these molecules, the Xe−H bond distance is shorter than 2 Å, showing an almost 2-fold decrease compared to the equilibrium distance between Xe and H derived from van der Waals pair potential (3.8 Å).[33] The Xe−H distance in HXeH is calculated to be 1.861 Å and in all other molecules it is even shorter, ca. 1.72 Å. The properties of the HRgY molecules have been shown to be highly sensitive toward the choice of the basis set and the electron correlation,[4,12] as can be seen from Table 1, where computational results of HXeH have been collected. The LJ18 basis set is the one used in this study. Increasing electron correlation elongates the Xe−H bond so that the longest bond is found at the CCSD(T) level. This correlates directly with the calculated harmonic vibrational frequencies, since too large force constant gives also too high vibrational frequency. The MP2/LJ18 calculation predicts the Xe−H antisymmetric stretch to be at 1385 cm^{-1}, which is almost 200 cm^{-1} too high compared to the experimental doublet at 1166/1181 cm^{-1} found in Xe-matrix experiments. Increasing electron correlation reduces the harmonic frequency by almost 100 cm^{-1}. The best harmonic vibrational frequencies for HXeH have been published by Runeberg and co-workers.[12] Their CCSD(T) calculations using a 8-VE ECP on Xe and a huge H-basis, including also BSSE and spin−orbit corrections, result in an almost perfect agreement with the experimental values. However, in their study Runeberg and co-workers[12] stress that the vibrational modes of HXeH are extremely anharmonic which casts a doubt on the good agreement between the experimental and computational frequencies. In the following we will tackle the question of anharmonicity first on HXeH, then the halogen-containing molecules HXeCl and HXeBr, and finally we will discuss the vibrational properties of HXeOH.

TABLE 1: Calculated Bond Lengths (Å) Compared with Calculated and Experimental Vibrational Frequencies (cm^{-1}) of HXeH[a]

	r(H−Xe)	$\omega_1(\sigma_g)$ [int]	$\omega_2(\pi_u)$[b] [int]	$\omega_3(\sigma_u)$ [int]
MP2/LJ18[c]	1.8608	1558.7 [0]	875.5 [69]	1384.6 [2503]
MP3/LJ18[c]	1.8834	1436.4 [0]	850.0 [60]	1341.7 [1982]
MP4(SDTQ)/LJ18[c]	1.8944	1349.1	812.6	1336.8
QCISD/LJ18[c]	1.8982	1316.2 [0]	809.5 [62]	1308.1 [1849]
QCISD(T)/LJ18[c]	1.9177	1197.4	770.9	1285.8
CCSD/LJ18[c]	1.8976	1319.3	810.9	1315.3
CCSD(T)/LJ18[c]	1.9184	1189.2	769.7	1283.2
CCSD(T)/LJ18[d]	1.892	1281	777	1272
CCSD(T)/LJ18 + BSSE + SO[d]	1.916	1216	773	1279
CCSD(T)/N8[e]	1.929	1028	735	1199
CCSD(T)/N8 + BSSE + SO[e]	1.958	1018	708	1187
experimental[f]			701	1181,1166

[a] The numbers in parentheses are the calculated IR intensities (km mol^{-1}). [b] Doubly degenerate. [c] 18-VE ECP on Xe and 6-311++G(2d,2p) on H. [d] Modified 18-VE ECP on Xe and aug-cc-pVTZ+f on H (ref 12). [e] Modified 8-VE ECP on Xe and aug-cc-pVTZ+f on H (ref 12). [f] From ref 6.

HXeH. The Xe−H stretching motion is an essential part of the vibrational calculation of the HRgY molecules, not least because this band appears as the most intense band in the observed spectrum.[4] Table 2 shows the results of anharmonic vibrational spectroscopy calculations for the fundamental, first and second overtones, and combination bands of HXeH with the corresponding experimental results. The MP2/CC-VSCF calculations predict the antisymmetric Xe−H stretching mode to be an extremely intense band similar to the harmonic calculations. The frequency of ν_{as}(Xe−H) decreases from 1385 to 1338 cm^{-1} when the anharmonicity is accounted for, indicating a surprisingly small anharmonic shift. On the contrary, the symmetric Xe−H stretch shifts from 1559 to 1470 cm^{-1},

TABLE 2: MP2/CC-VSCF Calculated Anharmonic Frequencies for HXeH

	assignment	freq (cm^{-1})	exptl freq^{a} (cm^{-1})	IR int^{b} (km mol^{-1})
$3\nu_1$		4264.3		0.0
$3\nu_3$		3933.2		82.7
$2\nu_1$		2885.5		0.0
$\nu_1 + \nu_3$		2755.1	2003	227.3
$2\nu_3$		2648.6		0.0
$3\nu_2$		2480.7		0.0
$\nu_1 + \nu_2$		2295.1		0.7
$\nu_2 + \nu_3$		2142.4		0.0
$2\nu_2$		1666.4		0.0
ν_1	sym H−Xe str	1469.5	(840)	0.0
ν_3	asym H−Xe str	1337.5	1181, 1166	4594.1
ν_2	H−Xe−H bend^{c}	839.5	701	69.0

[a] From refs 4 and 6. [b] Calculated using dipole moments obtained from Hartree−Fock wave functions. [c] Doubly degenerate.

TABLE 3: MP2/CC-VSCF Calculated Anharmonic Frequencies for HXeCl

assignment	MP2 harmonic freq (cm^{-1})	CC-VSCF freq (cm^{-1})	exptl^{a} freq (cm^{-1})	CC-VCSF IR intens^{b}
3ν(H−Xe)		4663.5		0.0
2ν(H−Xe)		3194.9		20.1
ν(H−Xe) + δ(H−Xe−Cl)		2187.7		1.5
ν(H−Xe) + ν(Xe−Cl)		1884.6		4.3
3δ(H−Xe−Cl)		1692.4		0.0
ν(H−Xe)	1751.3	1641.8	1648	1288.1
2δ(H−Xe−Cl)		1143.3		0.0
δ(H−Xe−Cl) + ν(Xe−Cl)		836.2		0.3
3ν(Xe−Cl)		777.7		0.0
δ(H−Xe−Cl)^{c}	599.1	577.4		1.6
2ν(Xe−Cl)		519.3		0.6
ν(Xe−Cl)	263.6	260.1		91.9

[a] From refs 4 and 5. [b] Calculated using dipole moments obtained from Hartree−Fock wave functions and given in km mol^{-1}. [c] Doubly degenerate.

indicating an anharmonicity twice that of the antisymmetric mode. This can be related to the fact that the symmetric mode corresponds to the dissociation channel of HXeH producing neutral atomic fragments H + Xe + H. The bending mode is at ca. 700 cm^{-1}, and it appears as almost harmonic with a very small anharmonicity.

Clearly, the anharmonicity is not the only reason for the discrepancy between the anharmonic and experimental vibrational frequencies for the antisymmetric Xe−H stretch. Partly the inaccuracy of the electronic structure theory at the MP2 level is to blame. As seen in Table 1, the increase of the electron correlation reduces the vibrational frequency. Unfortunately, we are not yet able to do a similar CC-VSCF calculation beyond the MP2 level, but combining CCSD(T) calculations with the VSCF method would result to a more correct vibrational picture of HXeH. The CCSD(T) calculations are extremely expensive and a different strategy can be adopted: the harmonic frequencies can be calculated using the CCSD(T) theory and thereafter “corrected” by the anharmonicity calculated at the MP2 level. This should give a rough but still improved estimate of the vibrational frequencies compared to the harmonic calculations. This can be demonstrated for the antisymmetric Xe−H stretch of HXeH. The correction from the CCSD(T) theory is ca. 100 cm^{-1} compared with the MP2 result, and the anharmonicity for ν_{as}(Xe−H) is about 50 cm^{-1} from the CC-VSCF calculation Therefore, we can give an approximate estimation for the position of the Xe−H antisymmetric stretch which is about 1235 cm^{-1}. Indeed, the experimental position of this band is only 50 cm^{-1} lower than the estimated value. It can be noted that the inclusion of highly sophisticated electron correlation methods is especially important when the HRgY molecule is relatively weakly bound (like HXeH), and the potential energy surface near the dissociation limit is not described accurately enough with modest methods like the perturbation theory. The MP2 level appears to be much better when the HRgY molecules are more strongly bound like in the cases of HXeCl and HXeBr discussed below.

As a real advantage of the present MP2/CC-VSCF calculations, we can also estimate combinations and overtones from the ab initio calculated potential energy surface. Experimentally a band at 2003 cm^{-1} has been identified in matrix experiments to belong to HXeH but no conclusive assignment has been given.[4,34] Due to basic group theory this experimental band cannot be the first overtone of ν_{as}(Xe−H), but instead a combination of the antisymmetric and symmetric Xe−H stretching modes. Moreover, this gives us an indirect measure of the IR-inactive Xe−H symmetric stretch, which should be around 840 cm^{-1}, but it must be remembered that the anharmonicity of this mode is not known. In the case of HXeI, the anharmonic constant for the $\nu_1 + \nu_3$ band was estimated to be about 20 cm^{-1}, and this suggests that for HXeH this combination band could be around 900 cm^{-1}. Nevertheless, this number is much lower than the predicted harmonic MP2 (1559 cm^{-1}), anharmonic MP2 (1470 cm^{-1}), and harmonic CCDSD(T) (1189 cm^{-1}) numbers. Another band that has a significant calculated IR intensity is $3\nu_{as}$(Xe−H) predicted to lie at ca. 3930 cm^{-1}. However, taking into account the mismatch between the calculated and experimental values for the fundamental band, this estimate must be regarded to be several hundreds of wavenumbers too high and the actual position of this overtone could be around 3400 cm^{-1}.

HXeCl. Results of the ab initio vibrational spectroscopy calculations for HXeCl, and comparison with experiment,[4,5] are shown in Table 3. Experimentally, only the Xe−H stretch of HXeCl has been assigned in solid Xe (1649 cm^{-1}),[5] Kr (1664 cm^{-1}),[4] and Ne (1612 cm^{-1})[35] with their respective deuterium isotopic species. The harmonic MP2 calculation predicts this mode to be at 1751 cm^{-1}, and the inclusion of anharmonicity reduces this by ca. 100 cm^{-1}. The CC-VSCF calculated value 1642 cm^{-1} is extremely close to the experimental value in Xe. This ensures that the more strongly bound HRgY molecules could be decribed reasonably well already at the MP2 level and that inclusion of anharmonicity results in a qualitatively correct picture of the vibrational properties of the molecule. However, the experimental band positions indicate also a large perturbation of the molecular electron structure due to the polarizable environment. It is interesting, however, that going from Xe to Kr matrix the Xe−H band position of HXeCl increases but the neon matrix represents the least perturbative environment of the three matrices and the band position is much lower than in Xe. The CC-VSCF value for a gas phase molecule is overestimated by a few tens of wavenumbers compared to the neon matrix value, and this could be mostly attributed to both small deficiences in the lack of extensive electron correlation in the calculation.

Our CC-VSCF calculations predict the heavy atom stretch Xe−Cl to be quite harmonic, the harmonic (264 cm^{-1}), and anharmonic (260 cm^{-1}) values are almost equal. The Xe−Cl

TABLE 4: MP2/CC-VSCF Calculated Anharmonic Frequencies for HXeBr

assignment	MP2 harmonic freq (cm^{-1})	CC-VSCF freq (cm^{-1})	exptl[a] freq (cm^{-1})	CC-VSCF IR intens[b]
3ν(H−Xe)		4291.0		0.8
2ν(H−Xe)		2967.4	2869	15.3
ν(H−Xe) + δ(H−Xe−Br)		2016.2		0.4
ν(H−Xe) + ν(Xe−Br)		1705.4		1.6
3δ(H−Xe−Br)		1470.8		0.0
ν(H−Xe)	1684.5	1544.0	1504	1445.2
2δ(H−Xe−Br)		996.5	965	33.1
δ(H−Xe−Br) + ν(Xe−Br)		685.5		0.1
3ν(Xe−Br)		537.4		0.0
δ(H−Xe−Br)[c]	527.06	506.3	489	1.8
2ν(Xe−Br)		359.0		0.2
ν(Xe−Br)	181.7	179.9		47.7

[a] From refs 4 and 5. [b] Calculated using dipole moments obtained from Hartree−Fock wave functions and given in km mol^{-1}. [c] Doubly degenerate.

stretch appears to have a noticeable intensity which would warrant the assignment in the far-infrared region. The degenerate bending fundamental is predicted to be quite weak. Among the overtones and combinations the first overtone of the H−Xe stretch at 3195 cm^{-1} is predicted to have some intensity as well as the combination between H−Xe and Xe−Cl stretching modes at 1885 cm^{-1}, and these could be searched for experimentally.

HXeBr. Table 4 shows the results of ab initio vibrational spectroscopy calculations for the transitions of HXeBr with the corresponding experimental results. The experimental spectrum of HXeBr in solid Xe has been found to be richer than that of HXeCl. The most intense band is again the H−Xe stretch, which is observed at 1504 cm^{-1} in a pure Xe matrix.[5] The position of this experimentally observed band is nicely reproduced by the CC-VSCF calculations lowering the harmonic value by 140 cm^{-1} to 1544 cm^{-1}. Another observed fundamental band of HXeBr is the H−Xe−Br bending mode found at 489 cm^{-1} in solid Xe.[5] This mode is much less anharmonic than the H−Xe stretch, and already the harmonic calculation gives a reasonable estimate of 527 cm^{-1}. The CC-VSCF value 506 cm^{-1} can be regarded as extremely good. The heavy atom stretch ν(Xe−Br) is predicted to be also highly harmonic, and is computed to be at ca. 180 cm^{-1} at both harmonic and anharmonic levels.

Experimentally, two additional bands at 965 and 2869 cm^{-1} have been observed to belong to HXeBr in solid Xe.[4,5] The first band at 965 cm^{-1} is in good agreement with the CC-VSCF calculations being the first overtone of the bending mode. It is interesting that the calculated intensity of the 2δ(HXeBr) is much larger than that of the fundamental. The CC-VSCF calculated position of 2ν(H−Xe) is ca. 100 cm^{-1} above the experimental value (2967 cm^{-1}), and the calculated intensity is about 1% of the fundamental intensity. We note here that the intensities were calculated using dipole moments obtained from the Hartree−Fock wave functions. This means that quantitatively the results are probably in doubt, but the calculations should be reliable enough for predicting a given transition to be weak or strong.

In order to get an idea of the anharmonicity of the Xe−H stretching vibration of HXeBr, we can deduce the anharmonic constant from the fundamental and first overtone absorptions. The anharmonicity of vibrational levels of a linear triatomic molecule was derived in the usual way[36]

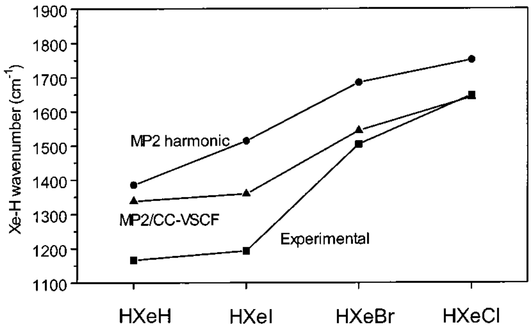

Figure 2. Experimental,[4,21] harmonic, and anharmonic Xe−H stretching vibrational frequencies for linear HXeH, HXeCl, HXeBr, and HXeI molecules.

$$G(v_1v_2v_3) = \sum_i \omega_i\left(v_i + \frac{d_i}{2}\right) + \sum_{i<j} x_{ij}\left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right) \quad (1)$$

where $G(v_1v_2v_3)$ is the vibrational term value and ω_i is the harmonic vibrational wavenumber. For $i = j$ the x_{ij} terms are the coupling constants between normal modes. In this equation, d_i is the degeneracy of the vibration.

Using the observed fundamental ν_3 (1504 cm^{-1}) and first overtone 2ν_3 (2869 cm^{-1}) frequencies of HXeBr, the anharmonic constant x_{33} is −69.5 cm^{-1}. Computationally, we find that the potential surface is slightly steeper than the experimental one, and the MP2/CC-VSCF calculated anharmonic constant x_{33} for HXeBr is −60.5 cm^{-1}. The MP2-calculated potential energy surface for HXeBr is, therefore, quite good compared to more weakly bound molecules like HXeH and HXeI. For the latter, the calculated anharmonic constant was ca. 30% too small compared with the one derived from experiments.[21]

The improvement of the MP2 calculations from the linear HXeY molecules from the weakest (HXeH) to the strongest (HXeCl) bound included in this study is shown in Figure 2. The Xe−H stretching vibration is a fingerprint of the HXeY molecules and the Xe−H bond distance reflects directly the fraction of stabilizing ionic contribution in the molecule.[4] As seen in Figure 2 the Xe−H vibrational frequencies of HXeCl and HXeBr are well reproduced by the anharmonic CC-VSCF calculations, whereas much larger discrepancies exist for HXeH and HXeI. This trend can be used to estimate that the fluorine-containing compound HXeF should be even more strongly bound than the molecules studied here, and computational work on fluorine-containing rare gas molecules is currently in progress.

HXeOH. This molecule represents the first chemical compound formed from a rare-gas atom and the water molecule. It is conceivable that it may be found in nature. HXeOH differs from the other HRgY molecules in this study, being nonlinear, even though the molecule is planar. The Xe−O−H angle resembles the precursor water molecule, and the MP2-calculated bending angle is 109.3°. Also, the H−Xe−O is not exactly linear as in the other molecules but it is slightly bent (by 2.8°). This bears some similarity with the F−Xe−O angle for example in FXeOSO$_2$F, where the angle is tilted from linearity by 2.5°.[37] The tilt of the H−Xe−O group appears to be a general property of this group since preliminary calculations on larger systems predict similar configurations as well.[38]

The results of the anharmonic vibrational calculations of HXeOH are collected in Table 5, and are compared with harmonic MP2, CCSD(T), and Xe-matrix results. The most intense vibration of HXeOH is again the Xe−H stretch, which is in fact the only mode assigned for this molecule at the time

TABLE 5: MP2/CC-VSCF Calculated Anharmonic Frequencies for HXeOH

mode	assignment	MP2 harmonic freq (cm^{-1})	CC-VSCF freq (cm^{-1})	CCSD(T) harmonic freq (cm^{-1})	exptl^{a} freq (cm^{-1})	CC-VSCF IR intens^{b}
$3\nu_1$	3ν(OH)		10462.6			0.2
$2\nu_1$	2ν(OH)		7123.2			4.9
$\nu_1 + \nu_2$	ν(OH) + ν(HXe)		5289.1			1.9
$3\nu_2$	3ν(HXe)		4896.1			0.0
$\nu_1 + \nu_3$	ν(OH) + δ_{as}(HXeOH)		4370.6			0.9
$\nu_1 + \nu_4$	ν(OH) + δ(HXeO)		4224.2			0.0
$\nu_1 + \nu_5$	ν(OH) + δ_s(HXeOH)		4131.6			1.1
$\nu_1 + \nu_6$	ν(OH) + ν(XeOH)		4024.5			0.6
ν_1	O−H str	3842.1	3639.4	3835.6		8.1
$2\nu_2$	2ν(HXe)		3341.8			11.8
$3\nu_3$	$3\delta_{as}$(HXeOH)		2949.0			0.5
$\nu_2 + \nu_3$	ν(HXe) + δ_{as}(HXeOH)		2478.4			0.9
$\nu_2 + \nu_4$	ν(HXe) + δ(HXeO)		2311.3			1.1
$\nu_2 + \nu_5$	ν(HXe) + δ_s(HXeOH		2258.9			1.1
$\nu_2 + \nu_6$	ν(HXe) + δ(HXeO)		2120.9			3.3
$2\nu_3$	$2\delta_{as}$(HXeOH)		1939.8			2.0
$3\nu_4$	3δ(HXeO)		1843.7			0.0
ν_2	Xe−H str	1823.4	1713.9	1677.9	1577.6	1042.8
$\nu_3 + \nu_5$	δ_{as}(HXeOH) + δ_s(HXeOH)		1441.5			7.8
$\nu_3 + \nu_4$	δ_{as}(HXeOH) + δ(HXeO)		1407.7			0.0
$3\nu_6$	3ν(XeOH)		1263.7			0.0
$2\nu_4$	2δ(HXeO)		1241.9			3.7
$\nu_3 + \nu_6$	δ_{as}(HXeOH) + ν(XeOH)		1208.2			0.5
$\nu_4 + \nu_5$	δ(HXeO) + δ_s(HXeOH)		1180.0			0.0
$3\nu_5$	$3\delta_s$(HXeOH)		1121.8			1.3
$\nu_4 + \nu_6$	δ(HXeO) + ν(XeOH)		1049.2			0.6
$\nu_5 + \nu_6$	δ_s(HXeOH) + ν(XeOH)		983.6			0.8
ν_3	HXeOH asym bend	818.7	908.0	812.1		10.2
$2\nu_5$	$2\delta_s$(HXeOH)		888.0			1.4
$2\nu_6$	ν(XeOH)		846.5			2.7
ν_4	HXeO oop bend	652.8	627.1	629.5		4.6
ν_5	HXeOH sym bend	584.1	510.8	574.5		19.1
ν_6	Xe−OH str	436.5	425.2	419.2		269.1

[a] From ref 10. [b] Calculated using dipole moments obtained from Hartree−Fock wave functions and given in km mol^{-1}.

being. The Xe−H stretch in a Xe matrix appears at 1578 cm^{-1}, the vibrational frequency being between those of HXeCl and HXeBr. The similarity of the three molecules can be noted also in the calculated structural parameters where all Xe−H bonds of HXeOH and the halogen-containing HXeY compounds are of similar length. The harmonic MP2 calculation overestimates the Xe−H stretch of HXeOH value by almost 250 cm^{-1} compared to the experimental data. Being quite an anharmonic vibration, the CC-VSCF reduces the position of this vibrational mode to 1714 cm^{-1}. The harmonic CCSD(T) value is even lower than the CC-VSCF value but it still overestimates the Xe−H stretch by ca. 100 cm^{-1}. This indicates that the electron correlation is also more important in HXeOH than for HXeCl and HXeBr. A crude approximation of the Xe−H stretch can be obtained by combining again both electron correlation effects at the CCSD(T) level and the anharmonicity calculated at the MP2-level. We find the ν(Xe−H) frequency at $1823 - 109 - 145 = 1569$ cm^{-1}, which is quite close to the experimental value of 1578 cm^{-1} in solid Xe.[10]

The CC-VSCF calculation predicts the OH stretch to be at 3639 cm^{-1}, and it should be intense enough to be experimentally searched for. The HXeOH bending modes are predicted to be less anharmonic than the Xe−H and O−H stretching modes, and all bands have calculated relative intensities to warrant experimental detection, being nevertheless much weaker than the strong Xe−H stretch observed experimentally. The heavy atom stretch ν(Xe−OH) is predicted to lie in the far-infrared region at 425 cm^{-1}, and the calculated intensity is about 20% compared to the Xe−H stretch.

Another vibrational band that could be experimentally searched for is the overtone of ν(Xe−H) predicted to lie at 3341 cm^{-1}. If this value is corrected by taking into account the mismatch in the fundamental region, this band should appear around 3070 cm^{-1}. In fact, preliminary tentative results on the photochemistry of HXeOH have revealed that a possible candidate for this band could be at 3046 cm^{-1} in solid Xe.[39] Other experimentally interesting bands would be the two bending overtones in the 800−900 cm^{-1} region, the $2\nu_4$ band at 1242 cm^{-1} and the $\nu_2 + \nu_6$ combination band at 2121 cm^{-1}. In the near-infrared region lie two bands that could be used as additional fingerprints of HXeOH: the $\nu_1 + \nu_2$ combination band at 5289 cm^{-1} and the first overtone of ν(O−H) at 7123 cm^{-1}.

4. Conclusions

In this paper, we report anharmonic vibrational calculations for the rare-gas-containing molecules HXeH, HXeCl, HXeBr, and HXeOH. The computational method applied combines 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 HXeY 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 both harmonic ones and those derived from low-temperature matrix experiments. The comparison of the anharmonic vibrational frequencies of the HXeY molecules with the experimental ones also strengthens the interpretation that the spectroscopy is indeed due to these Xe-containing compounds. However, even with the anharmonic theory, deviations from experiments are sometimes large, and this is mostly due to inaccuracy of the electronic structure theory (MP2). Development of the anharmonic theory to be combined with high-level electron correlation methods like CCSD(T) would give a powerful tool to predict the vibrational modes of the HXeY molecules but this would be a very expensive method for larger molecular species. Instead, we propose another strategy in which the harmonic frequencies calculated at the CCSD(T) level could be "corrected" by anharmonic effects from MP2 calculations. This approach is well suited for the weaker rare gas hydrides like HXeH. For strongly bound HXeCl and HXeBr already the MP2 calculations are able to reproduce their spectral characteristics. Finally, agreement of the anharmonic calculations with experiments is much better compared with the corresponding harmonic calculations, and the anharmonic vibrational calculations can be used to extend the interpretation of other rare-gas-containing molecules as well.

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