A theoretical study of HArF, a newly observed neutral argon compound

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Computational results up to the CCSD(T)/aug-cc-pV5Z level are presented as support for the newly observed argon containing compound, hydrido argonfluoride (HArF). The molecule is calculated to be linear with $R(H-Ar)=132.9$ pm and $R(Ar-F)=196.9$ pm. The calculated vibrational frequencies, corrected for anharmonicity and matrix effects, are 462 (Ar–F stretch), 686 (bend) and 1916 cm^{-1} (Ar–H stretch). These are in good agreement with the corresponding experimentally observed frequencies of 435.7, 687.0, and 1969.5 cm^{-1} for the matrix isolated species [Nature **406**, 874 (2000)]. Including corrections for the finite basis set as well as for the zero-point energy, the new molecule is stable by 0.15 eV compared to the dissociated atoms. HArF is further stabilized by an additional barrier of 0.18 eV, arising from the avoided crossing between the states corresponding to the ionic $(HAr^{\delta+})(F^{\delta-})$ equilibrium structure and the covalent $(HAr^{\cdot})(F^{\cdot})$ dissociation limit. The dissociation of HArF via bending into the thermodynamic ground-state system, consisting of Ar and HF, is protected by a 1.0 eV barrier. © *2001 American Institute of Physics.*
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I. INTRODUCTION

The experimental chemistry of the noble gases (Ng) began less than 40 years ago with Neil Bartlett's success to chemically activate one of the ''inert gases'' by creating the first Xe–F bond.[1,2] Since then, a multitude of Ng compounds have been synthesized and experimentally characterized. Stable Ng compounds are typically either salts derived from the fluorides or oxofluorides, or species prepared in solid noble-gas matrices. Compounds containing xenon are still the most common, and xenon is known to form chemical bonds with H, F, Cl, Br, I, B, C, N, O, S, and Xe.[3–9] Excluding reactive gas-phase ions and transient excited states, krypton is the only one of the lighter noble gases possessing a well established chemistry. Known krypton compounds involve Kr chemically bonded to H, F, C, N, O, and Cl.[3,10–12] Frenking and Kremer have done an extensive theoretical study on the nature of bonding in noble-gas compounds, and predict possible new molecules containing He, Ne and Ar.[13] Until recently, no neutral ground-state molecule containing chemical bonds to argon was experimentally known. One serious candidate has been the complex between Ar and the strongest known neutral Lewis acid BeO,[14] which was prepared by Thompson and Andrews in low-temperature matrices.[15] However, in theoretical analysis by Veldkamp and Frenking, ArBeO is described as an unusually stable complex between closed-shell fragments Ar···BeO, held together by induced dipole interactions.[16] Strong interactions between closed-shell fragments involving Ar–MX (M=Cu,Ag,Au; X=F,Cl,Br) have also been recently reported.[17–19]

The stability of ArF^{+} is well known,[20] and there has been speculations in the prospects to find a suitable counter-anion to stabilize an ArF^{+} salt. Ignoring questions concerning synthetic strategies and concentrating on thermodynamic features, $ArF^{+}AuF_6^{-}$, $ArF^{+}SbF_6^{-}$ and $ArF^{+}BiF_6^{-}$ have been considered the most promising candidates for stable argon salts.[21–23] Also ArH^{+} is known to be strongly bound and it has been thoroughly characterized in the gas phase.[24,25] In the solid state, for example in a low-temperature Ar matrix, this cation cannot be isolated but instead a centrosymmetric cation $ArHAr^{+}$ is formed.[26]

Another fruitful route for preparing new noble-gas species has been developed by Räsänen's group.[3] They synthesized a whole series of neutral noble-gas molecules of the HNgY-type (Ng=Kr,Xe;Y=H,halogen,pseudohalogen), in solid noble-gas matrices. In short, the synthesis involves homolytic photodissociation of a HY precursor generating isolated H atoms and Y fragments, which are trapped in the matrix. The diffusion of hydrogen in the matrix is effectively controlled by temperature, and a selective mobilization of the hydrogens is achieved by careful annealing. The diffusing hydrogen can then approach a noble-gas atom with an Y fragment as neighbor, upon which the new HNgY molecule is formed. The molecules are characterized by their vibrational spectra, often supported by *ab initio* calculations. In this article we will present theoretical results as support for the latest HNgY compound, HArF, which is the first experimentally known covalent neutral condensed-phase argon compound.[27] The central theoretical results presented here have been obtained before the actual experimental observation of HArF,[28–30] and they had a decisive influence on the experimental work. In fact, the first computational report on HArF was given by Pettersson *et al.*[31] in 1995, using the UCCSD/6-31G** level of theory. They found a protective

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barrier for the H–Ar dissociation, but the calculated overall atomization of HArF was exothermic.

II. METHODS

Most of the calculations have been performed using the MOLPRO program package.[32] For the open-shell MP2 calculations on the fluorine atom and the calculation of IR intensities at the CCSD(T) level, the ACESII package was used.[33] NBO population analysis was done with GAUSSIAN 98.[34,35] The basis sets used are from the augmented correlation-consistent polarized n-tuple zeta (aug-cc-pVnZ) family of Dunning,[36–38] which we denote by AVnZ. The effect of inner-shell correlation was studied by using the completely uncontracted AV5Z basis set, augmented with tight functions. The exponents for the one p, three d, two f and one g tight functions were obtained by successively multiplying the highest exponent in the original basis set by a factor of 3, as suggested by Martin and Taylor.[39,40] This basis is denoted as MTAV5Z. The optimized geometries and vibrational frequencies were obtained by numerical differentiation, without including effects from the inner-shell correlation or the basis-set superposition error (BSSE). The geometry of HArF was fixed to the CCSD(T)/AVnZ optimized values, when the atomization energy (AE) (HArF→H+Ar+F) was estimated at different levels of correlation. At the coupled-cluster level both the spin restricted (RCC) and unrestricted (UCC) coupled-cluster theories, as implemented in MOLPRO, were used for the open-shell fluorine atom. The calculated atomization energy was corrected for inner-shell correlation by correlating all electrons in the MTAV5Z basis. BSSE was estimated by performing the full counterpoise correction (CP).[41]

An estimate for the property Q at the complete basis set (CBS) limit was extrapolated from the exponential functions utilized by van Mourik et al.,[42]

$$Q(n) = Q_{CBS} + \Delta Q(2) e^{-\alpha(n-2)}, \tag{1}$$

$$Q(n) = Q_{CBS} + A e^{-n} + B e^{-n^2}, \tag{2}$$

where n is the highest angular momentum appearing in the basis set (i.e., $n=2$ for AVDZ, $n=3$ for AVTZ, etc.). The three parameters, Q_{CBS}, $\Delta Q(2)$, and α in Eq. (1), as well as Q_{CBS}, A and B in Eq. (2), are determined through least-square minimization.

Various parts of the H–Ar–F hypersurface were analyzed at the internally contracted MR-CISD level,[43,44] with a CAS reference including the 16 valence electrons and 9 molecular orbitals. All MR-CISD energies were Davidson-corrected for quadruple excitations.[45]

The anharmonic vibrational properties of HArF were studied by combining the GAMESS[46] ab initio code with the vibrational self-consistent field (VSCF) and its extension, correlation-corrected VSCF (CC-VSCF) which includes corrections via second-order perturbation theory.[47–50] CC-VSCF is used to calculate the vibrational wave functions and energies, by only including interactions between pairs of normal modes. Each pair of normal modes is pictured with a 16*16 potential surface grid and the normal-mode couplings are

TABLE I. Calculated HArF($C_{\infty v}$) equilibrium geometry (in pm), and (HArF→H+Ar+F) atomization energy, AE (in eV) obtained at RCCSD(T) level of theory.

Basis set	R(H–Ar)	R(Ar–F)	AE[a]	AE(CP)[b]
AVDZ	136.72	202.84	−0.09(−0.09)	−0.22
AVTZ	133.80	199.26	0.24(0.23)	0.14
AVQZ	133.38	197.96	0.33(0.32)	0.29
AV5Z	132.88	196.90	0.40(0.39)	0.37
AV∞Z[c]	132.90	196.33	0.41	0.41
AV∞Z[d]	132.86	196.74	0.41	0.40

[a]Values in parentheses are obtained by using UCCSD(T) energy for the open-shell fluorine atom.
[b]Counterpoise corrected energy.
[c]Extrapolated using Eq. (1).
[d]Extrapolated using Eq. (2).

then evaluated by ab initio calculations over this grid. Full details of CC-VSCF combined with an ab initio electronic structure code are given in Refs. 49 and 50.

The effect of the surrounding argon matrix on HArF was studied by optimizing the structure of HArF in an octahedral argon cavity at the local MP2 (LMP2) level.[51–55] The LMP2 approach is particularly suited for this kind of study since it provides significant computational savings and reduction of BSSE.[56,57]

III. RESULTS AND DISCUSSION

The optimized bond lengths and the corresponding atomization energies (AE) obtained at the valence-correlated CCSD(T) level using different basis sets are given in Table I. The AVDZ basis set is inferior in all respects, since it gives both significantly longer bonds and weaker interactions than the larger basis sets. For the AVDZ basis set the system is, in fact, thermodynamically unstable toward dissociation into atoms. Starting from AVTZ the bond lengths appear to converge smoothly with rather small corrections. On the other hand the difference between AE obtained with the AVQZ and AV5Z basis set is still substantial. The difference between the RCCSD(T) and UCCSD(T) energies is negligible. BSSE is monotonically decreasing with increasing size of the basis set, and it is less than 8% for the AE using the largest basis set. The dipole moment at the CCSD(T)/AV5Z level is 2.56 a.u. or 6.51 Debye. The rather high value of the dipole moment, as well as the results of the population analysis given in Table II, reflects the substantial ionic $(HAr)^{+}(F)^{-}$ character at the equilibrium geometry. The corrections obtained from the CBS extrapolation to the AV5Z results are cosmetic, and the extrapolation of both the counterpoise-corrected and the uncorrected results converge toward the same value for AE (see Fig. 1).

The effects of the level of correlation on the atomization energy are summarized in Table III. At the SCF level all basis sets give atomization energies which are strongly negative. The BSSE at SCF level is already negligible for the smallest basis set. The smallest basis set also gives slightly negative AE at the MP2 level. When the basis set is enlarged to AVTZ, AE becomes positive, but further extensions to AVQZ and AV5Z basis sets increase the destabilization. At the CCSD and CCSD(T) levels the basis-set enlargement

TABLE II. Calculated Mulliken (M) and Natural Bond Orbital (NBO) charges at the extrapolated CCSD(T) geometry.

Method	Basis set	M(H)	NBO(H)	M(Ar)	NBO(Ar)	M(F)	NBO(F)
MP2	AVDZ	0.200	0.252	0.511	0.507	−0.711	−0.760
	AVTZ	0.116	0.221	0.578	0.536	−0.694	−0.757
	AVQZ	0.302	—	0.355	—	−0.657	—
MP4(SDQ)	AVDZ	0.183	0.235	0.524	0.517	−0.707	−0.752
	AVTZ	0.129	0.207	0.567	0.546	−0.696	−0.753
QCISD	AVDZ	0.184	0.235	0.524	0.517	−0.708	−0.752
	AVTZ	0.110	0.209	0.591	0.547	−0.701	−0.756

monotonically increases AE. The contribution from the triply excited clusters to AE is large, and starting from the AVTZ basis set their contribution is steadily about 0.3 eV. The effect of inner-shell correlation on AE is negligible. At the CCSD(T)/MTAV5Z level the calculated AE is increased by 0.0002 eV due to inner-shell correlation.

The calculated harmonic and anharmonic vibrational frequencies are given in Tables IV and V, respectively. In general, the harmonic approximation overestimates all vibrational frequeicies of HArF compared with the experimentally observed values.[27] In the anharmonic CC-VSCF calculations, the diagonal values correspond to a situation where no couplings between vibrational modes are taken into account. Clearly the ν(Ar–H) mode is strongly anharmonic, similar to the corresponding modes for the HKrY and HXeY molecules reported previously.[58,59] Both MP2/AVD2 and MP2/AVT2 calculations predict a 200 cm^{-1} lowering of the Ar–H stretch, due to anharmonicity. The other vibrational modes appear less anharmonic and the H–Ar–F bending mode is lowered by ca. 35 cm^{-1} from its harmonic value in both calculations. The ν(Ar–F) mode is quite harmonic with only a few wave numbers shift upon introducing the anharmonicity.

In the experiment[27] HArF is trapped in low concentration in a solid argon matrix. We therefore assume that its interaction with the matrix is dominated by the presence of the nearest argon atoms. To estimate the matrix effects on

the frequencies, we optimized the structure of HArF in an octahedral argon cavity, at the local MP2 (LMP2) level (Fig. 2). The calculated LMP2/AVDZ results for HArF, with the nearest neighbors consisting of six octahedrally cordinated argon atoms, are compared with corresponding results for the isolated molecule in Table VI. In the argon cage the calculated Ar–H stretch is shifted 38 cm^{-1} upward. This is in agreement with the experimental shifts of about 40–50 cm^{-1} found for HXeCl and HXeBr, when the matrix medium is changed from neon to xenon.[60] Combining the harmonic CCSD(T)/AVQZ frequencies of 480, 729 and 2097 cm^{-1} with the CC-VSCF(MP2/AVTZ) anharmonicities of −8, −36 and −210 cm^{-1}, and with the matrix effects obtained at the LMP2/AVDZ level of −9, −7 and 38 cm^{-1}, our best estimates for the vibrational frequencies therefore become 463, 686 and 1925 cm^{-1}. These frequencies are in good agreement with those observed at 435.7, 687.0 and 1969.5 cm^{-1}.[27] The corresponding estimated zero-point energy (ZPE) is 0.23 eV.

The relative energies corresponding to different fragmentations of HArF are given in Table VII.[61,62] The thermodynamic ground-state of the system is Ar+HF, which is almost 6 eV below HArF in energy. This state can be reached via the HArF bending coordinate. The interaction energy for the minimum-energy path for bending at the full-valence MR-CISD/AVTZ level (which corresponds to a CAS reference with 16 electrons and 9 orbitals) is shown in Fig. 3. The interaction-energy curve in Fig. 3 indicates that the dissociation of HArF into Ar+HF along the bending coordinate is protected by a barrier which is at least as high as the AE limit. The transition barrier obtained by Wong[30] at the CCSD(T)/cc-pVQZ//CCSD/cc-pVTZ level is 1.16 eV. The
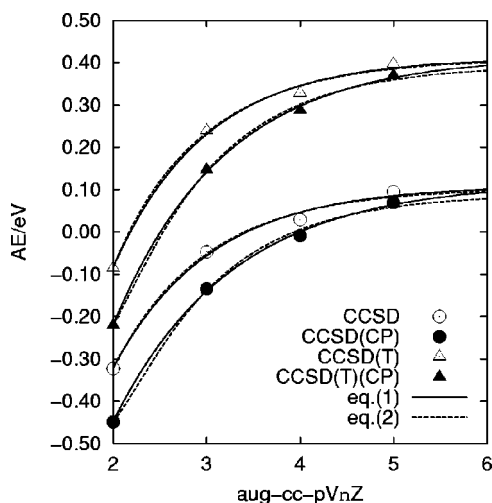

FIG. 1. Extrapolated atomization energy (AE) of HArF corresponding to the complete basis-set limit. Solid symbols denote counterpoise-corrected energies.

TABLE III. Atomization energies (in eV) obtained at different levels of calculation. The geometries are fixed to the RCCSD(T) optimized geometry, corresponding to respective basis set. The values in parentheses are the counterpoise corrected values.

Method	Basis set			
	AVDZ	AVTZ	AVQZ	AV5Z
RHF	−2.65(−2.66)	−2.49(−2.50)	−2.44(−2.44)	−2.39(−2.39)
UHF	−2.75	−2.62	−2.57	−2.52
RMP2	−0.04	0.07	−0.31	−0.42
UMP2	−0.03	0.08	−0.30	−0.40
RCCSD	−0.32(−0.45)	−0.05(−0.13)	0.03(−0.01)	0.09(0.07)
UCCSD	−0.33	−0.05	0.02	0.09
RCCSD(T)	−0.09(−0.22)	0.24(0.14)	0.33(0.29)	0.40(0.37)
UCCSD(T)	−0.09	0.23	0.32	0.39

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TABLE IV. Calculated harmonic vibrational frequencies (in cm^{-1}) for various isotopomers of HArF. The numbers in parentheses are the calculated intensities in km/mol.

Isotopes	Method	Basis set	ν(Ar–F)	δ(H–Ar–F)	ν(Ar–H)
^{1}H^{40}ArF	MP2	AVDZ	458(272)	706(33)	2222(1181)
	LMP2	AVDZ	457(270)	707(33)	2223(1169)
	LMP2	AVQZ	483(262)	755(30)	2305(816)
	CCSD(T)	AVDZ	461	674	1865
		AVTZ	474	725	2053
		AVTZ[a]	478(212)	729(25)	2088(1515)
		AVQZ	480	729	2097
	Expt.[b]		435.7	687.0	1969.5
^{2}H^{40}ArF	LMP2	AVDZ	456(266)	521(10)	1588(631)
	CCSD(T)	AVQZ	479	538	1500
	Expt.[b]		435.3	513.0	1466.3
^{1}H^{36}ArF	LMP2	AVDZ	465(279)	710(32)	2225(1182)
	CCSD(T)	AVQZ	488	731	2100
	Expt.[b]		442.9	689.3	1971.3
^{2}H^{36}ArF	LMP2	AVDZ	464(274)	724(9)	1592(645)
	CCSD(T)	AVQZ	487	542	1503

[a]ACESII results in which all electrons are correlated.
[b]From Ref. 27.

TABLE V. Calculated MP2 anharmonic frequencies (in cm^{-1}) and intensities (in km/mol) for HArF.

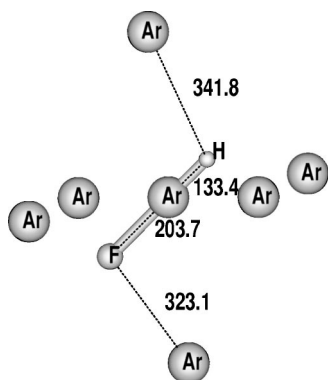| Basis	Mode	Harmonic	Diag	VSCF	CC-VSCF	Intensity
AVDZ[a]	ν(Ar–H)	2249	2011	1966	1957	77
	δ(H–Ar–F)	708	743	686	674	51
	ν(Ar–F)	457	452	455	455	266
AVTZ[b]	ν(Ar–H)	2313	2121	2077	2103	84
	δ(H–Ar–F)	749	782	724	713	44
	ν(Ar–F)	482	476	476	474	279

[a]Calculated equilibrium structure: R(H–Ar)=133.7 pm, R(Ar–F)=202.3 pm.
[b]Calculated equilibrium structure: R(H–Ar)=131.7 pm, R(Ar–F)=197.5 pm.

TABLE VI. Calculated LMP2/AVDZ bond distances (in pm) and vibrational frequencies (in cm^{-1}) for the isolated HArF, compared with those obtained for the molecule in an octahedral argon cavity HArF@Ar$_6$ (see Fig. 2). The values in parentheses are the intensities in km/mol.

	R(H–Ar)	R(Ar–F)	ν(Ar–F)	δ(H–Ar–F)	ν(Ar–H)
HArF	133.8	203.0	457(270)	707(33)	2223(1169)
HArF@Ar$_6$	133.4	203.7	448(259)	700(44)	2261(945)
"matrix effect"	−0.4	+0.7	−9	−7	+38

TABLE VII. Calculated relative energies E_0 (in eV) obtained at the CCSD(T)/AV5Z level. Energies are obtained at the optimized geometry neglecting counterpoise correction or inner-shell correlation. Zero-point corrections are included using CCSD(T)/AVQZ frequencies.

System	E_0
ArF$^+$+H$^-$	18.76
HAr$^+$+F$^-$	12.16
H+Ar+F	5.87
HAr+F[a]	5.87
ArF+H[a]	5.87
HArF	5.72
Ar+HF	0.00

[a]Stabilized only by the van der Waals attractions which are around 0.004–0.007 eV (Refs. 61, 62).

FIG. 2. The LMP2/AVDZ optimized structure of HArF in an octahedral argon cavity.
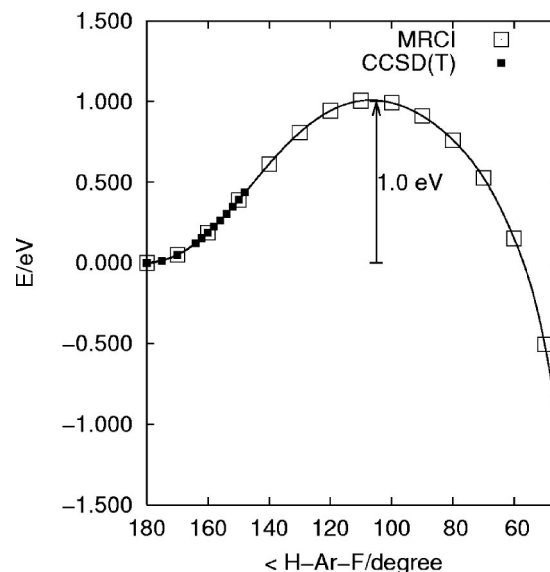
FIG. 3. Calculated MR-CISD/AVTZ minimum-energy path for the H–Ar–F bending.
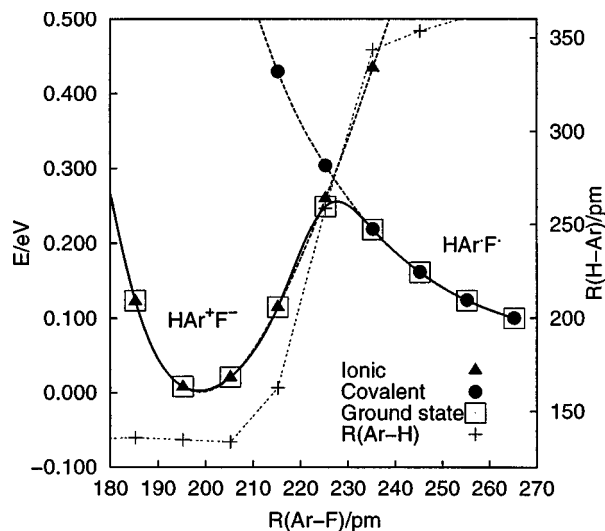
FIG. 4. The calculated MRCI/AVTZ minimum-energy path for hydrogen (or fluorine) abstraction from HArF.

barrier height is calculated to be 1.0 eV at the MR-CISD/ AVTZ level. Due to the absence of a substantial fraction of the triple excitations, the MR-CISD results should be considered only semi-quantitative. The calculated AE at the MR-CISD/AVTZ level is 0.05 eV, which is higher than the CCSD value of -0.05 eV but still significantly lower than 0.24 eV, which is obtained at the CCSD(T) level. At the equilibrium geometry the value for the T1 diagnostic is 0.028, 0.023, 0.021 and 0.021 for basis sets AVDZ, AVTZ, AVQZ and AV5Z, respectively. Attempts were also made to scan the bending coordinate at the CCSD(T)/AVTZ level (see Fig. 3), but the strong multireference character of the wave function, introduced at smaller angles, leads to insurmountable difficulties to converge either the SCF or CCSD calculations, as expected.

Stability of the system along the minimum-energy path corresponding to fluorine (or hydrogen) abstraction is shown in Fig. 4. At shorter distances the system is dominated by the ionic $(HAr)^+F^-$ configuration accompanied with its relatively high dipole moment. The ground-state dissociation limit is, however, reached via a homolytic dissociation into the neutral fragments $H(^2S) + Ar(^1S) + F(^2P)$. Depending on whether it is H or F which is completely removed, the dissociation limit will only be stabilized by the van der Waals (vdW) energy of $H\cdots Ar$ or $Ar\cdots F$, respectively. The crossing between the states corresponding to the ionic equilibrium structure and the covalent dissociation limit gives rise to a barrier which further increases the stability of HArF. The calculated barrier hight at the MRCI/AVTZ level is 0.18 eV. As a result of a delicate interplay between, on the one hand, the strong and short H–Ar bond in HAr^+, and, on the other hand, the strong Pauli repulsion in the neutral vdW complex, $H\cdots Ar$, at the corresponding short distance, the intermediate region around the crossing involves large H–Ar movements.

IV. CONCLUSIONS

Using the extensive computational results presented in this work, we have been able to support the experimental

introduction of neutral ground-state argon chemistry.[27] The structure of the newly synthesized hydrido argonfluoride, HArF, has been predicted to a high accuracy. The strongly ionic equilibrium structure of hydrido argonfluoride, HAr^+F^-, differs essentially from the structures found in the previously predicted ArF^+ salts.[13,22] Including corrections for anharmonicity and matrix effects, the vibrational frequencies agree with those measured for the matrix-isolated molecule. According to our calculations HArF should be stable in gas phase as well.

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