

# Reaction of $[\text{Xe-F}]^+$ with HI

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## ABSTRACT

The reaction behavior of  $[\text{XeF}][\text{AsF}_6]$  in solution toward hydrogen iodide, HI, was investigated, and Xe, HF, and  $[\text{I}_4][\text{AsF}_6]_2$  were identified as the final reaction products. The reaction enthalpy of the gas-phase reaction  $[\text{XeF}]^+ + \text{HI} \rightarrow [\text{XeI}]^+ ({}^1\Sigma) + \text{HF}$  was calculated at the optimized MP4(SDQ) geometries at the QCISD(TQ) level to be:  $\Delta H_{298}^{\circ} [\text{QCISD(TQ)/LANL2DZ}/\text{MP4(SDQ)/LANL2DZ}] = -63.3 \text{ kcal mol}^{-1}$ . The  $[\text{XeI}]^+$  cation is bound only in the  ${}^1\Sigma$  singlet state, and the triplet state ( ${}^3\Pi$ ) was shown to be essentially unbound at all levels of theory applied and very close in energy to the singlet state at equilibrium structure. According to the *ab initio* calculations,  $[\text{XeI}]^+$  can react with HI in a thermodynamically and spin-symmetry allowed reaction to yield the  $[\text{XeI}]^+ ({}^1\Sigma)$  cation that may, after interconversion into the unbound triplet state, immediately dissociate into xenon ( ${}^1\text{S}$ ) and  $\text{I}^+$  ( ${}^3\text{P}$ ). © 1997 John Wiley & Sons, Inc. Heteroatom Chem 8:473–478, 1997

## INTRODUCTION

Whereas numerous examples of xenon bonded to fluorine are known [1], much fewer reports have

been published on compounds containing a direct xenon–chlorine or xenon–bromine bond [2]. Although  $[\text{Xe-F}]^+$  is a well-known and stable cation, the isoelectronic counterpart to  $\text{I}_2$ ,  $[\text{Xe-I}]^+$ , is still an unknown species [3a]. The only reports on Xe/I systems are gas-phase studies of atomic xenon lasers and related investigations of ionic recombination reactions (e.g.,  $\text{Xe}_2^+ + \text{I}^- + \text{Xe} \rightarrow \text{XeI}^* + 2\text{Xe}$ ) [4]. The driving force for many substitution reactions in xenon (and krypton) solution chemistry starting from  $\text{NgF}_2$  (Ng = Kr, Xe) is the formation HF [3b,c] that can be attributed to the particularly strong H–F bond ( $\Delta H_{\text{diss}} = 137.3 \text{ kcal mol}^{-1}$ ) [5]. The aim of this study was to investigate the reaction of  $[\text{Xe-F}]^+$  with HI experimentally and theoretically on the basis of *ab initio* calculations.

## EXPERIMENTAL

### General Procedures

The vacuum lines, handling techniques, and spectrometers used in this study have been described elsewhere [3,6]. All solvents were commercial materials and were dried and purified by condensation prior to use (HF, Merck,  $\text{BiF}_5$ ;  $\text{SO}_2$ , BOC,  $\text{CaH}_2$ ;  $\text{SO}_2\text{ClF}$ , Aldrich,  $\text{CaH}_2$ ). Commercial HI (Matheson) was purified by fractional condensation prior to its use.  $[\text{XeF}][\text{AsF}_6]$  was prepared by literature methods from  $\text{XeF}_2$  and  $\text{AsF}_5$  in anhydrous HF (aHF) [7].

### Reaction of $[\text{XeF}][\text{AsF}_6]$ with HI

In a typical reaction,  $[\text{XeF}][\text{AsF}_6]$  (2.31 g, 6.8 mmol) was dissolved in 15 mL of aHF in an FEP reaction vessel, and the solution was cooled to  $-196^\circ\text{C}$ . In the next step, HI (0.87 g, 6.8 mmol) was condensed onto the frozen solution, and the reaction mixture was

Dedicated to my mom, Christa Klapötke, who as a chemist herself recognized the true worth of a scientific education, on the occasion of her Seventieth birthday.

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allowed to slowly warm to 0°C. Reaction occurred already below 20°C with evolution of gaseous products. Volatile materials were removed under dynamic vacuum at room temperature where xenon was identified by its characteristic gas discharge color (violet), leaving a black crystalline solid, which was identified by its solution SO<sub>2</sub> Raman spectrum ( $\Delta\nu$ , SO<sub>2</sub> = 517 cm<sup>-1</sup> to be an essentially [I<sub>4</sub>][AsF<sub>6</sub>]<sub>2</sub> ( $\Delta\nu$  = 237, 672 cm<sup>-1</sup>) [8], which exists in solution as [I<sub>2</sub>][AsF<sub>6</sub>]. Yield: 0.95 g, 79% (see Equation 8). (Note: At low temperature, there was also evidence for the formation of the thermally unstable [IF<sub>4</sub>][AsF<sub>6</sub>].)

A second experiment carried out in a SO<sub>2</sub>/SO<sub>2</sub>ClF mixture (2:1) in a two-bulb glass vessel led qualitatively to the same results. Etching of the inside glass surface of the NMR tube indicated the formation of HF in the reaction.

A third experiment was carried out in HF in an 8-mm FEP NMR tube fixed in a 10-mm glass NMR tube and followed by <sup>129</sup>Xe NMR (shifts rel. to ext. XeOF<sub>4</sub>, cf. Ref. [3a]). After addition of the HI, the sample was allowed to warm to 0°C, and the reaction started with evolution of gaseous products. Cessation of the gas evolution signaled completion of the reaction, and a <sup>129</sup>Xe NMR spectrum was recorded without delay at -40°C. No resonance was found in the range of +1000 to -2000 ppm, indicating that all [XeF][AsF<sub>6</sub>] had reacted yielding exclusively xenon-free reaction products (cf.  $\delta^{129}\text{Xe}[\text{XeF}]^+ = -863$  ppm) [9].

### Computational Methods

The structures, energies, vibrational frequencies, and zero point energies of the species [XeF]<sup>+</sup>, [XeI]<sup>+</sup>, HF, and HI were computed ab initio and fully optimized at the HF and electron-correlated MP2, MP4(SDQ), and QCISD levels of theory with the program package Gaussian 94 [10]. In addition, energies at the MP4 structures were computed at the QCISD(TQ) level of theory. The potential energy curve was also calculated with the CASSCF (complete active space SCF) method by using the program Gaussian 94 [10]. The active space consisted of the two  $\sigma_p$  and four  $\pi_p$  valence orbitals, i.e., 10 electrons in 6 orbitals [notation CASSCF(10,6)]. For H and F, a 6-31G(*d,p*) basis set was used; for I and Xe, a quasi-relativistic pseudopotential (LANL2DZ, Los Alamos potential) [11a-c] was used where the basis functions for the valence *s* and *p* electrons consist of the standard double- $\zeta$  basis set (notation HF/LANL2DZ, MP2/LANL2DZ, etc.).

In order to establish that the rather small basis set that was used in this study is sufficient, we also calculated the heat of Reaction 1 and the bond dis-

sociation energy according to Equation 2 using a 6-311+G(*d,p*) basis set including polarization and diffuse functions for the first and second-row elements (H, F), and for I and Xe, a quasi-relativistic pseudopotential (ECP46MWB, Stuttgart potential) was used where the basis functions for the valence *s* and *p* electrons consist of a split-valence basis set including additional polarization functions and diffuse functions {I, (5s6p1d)/[3s4p1d]; Xe, (6s6p3d)/[4s4p3d]} [11d,e].

## RESULTS AND DISCUSSION

### Computational Results

For the diatomic species for which experimental data are available (HF, HI, [XeF]<sup>+</sup>), the agreement between the computed and experimental structural and vibrational parameters is good [12]. This gives credence to the calculated parameters for the hitherto unknown [XeI]<sup>+</sup> and also to the predicted thermodynamic values for reactions involving the [XeI]<sup>+</sup> cation. We are here referring to the <sup>1</sup>Σ state of [XeI]<sup>+</sup>.

The calculated total energies of [XeF]<sup>+</sup>, [XeI]<sup>+</sup>, Xe, I<sup>+</sup>, HF, and HI (Tables 1 and 2) can be used to predict theoretically the energy of Reaction 1. After correction for zero-point energies [zpe, taken from MP4(SDQ) computation, Table 2; NB:  $p\Delta V$ ,  $\Delta U^{\text{tr}}$ ,  $\Delta U^{\text{rot}} = 0$ ], the reaction enthalpy of the gas-phase reaction according to Equation 1 was calculated at the optimized MP4(SDQ) geometries at the QCISD(TQ) level to be

$$\Delta H_{298}^0(1)[\text{QCISD(TQ)/LANL2DZ//MP4(SDQ)/LANL2DZ}] = -63.3 \text{ kcal mol}^{-1}.$$

The dissociation energy of the spin-symmetry allowed Reaction 2 was calculated (cf. Tables 1 and 2),

**TABLE 1** Ab initio Calculated Energies for Monoatomic Species

		I <sup>+</sup> ( <sup>1</sup> D)	I( <sup>3</sup> P)	Xe( <sup>1</sup> S)
HF <sup>a</sup>	-E/a.u.	10.72292	10.80100	15.22433
	⟨S <sup>2</sup> ⟩	0.000	2.001	0.000
MP2 <sup>a</sup>	-E/a.u.	10.73645	10.80541	15.23496
	⟨S <sup>2</sup> ⟩	0.000	2.001	0.000
QCISD <sup>a</sup>	-E/a.u.	10.75375	10.80672	15.23704
	⟨S <sup>2</sup> ⟩	0.000	2.001	0.000
MP4(SDQ) <sup>a</sup>	E/a.u.	10.74283	10.80661	15.23694
	⟨S <sup>2</sup> ⟩	0.000	2.001	0.000
QCISD(TQ) <sup>a</sup>	-E/a.u.	10.75514	10.80674	15.23709
	⟨S <sup>2</sup> ⟩	0.000	2.001	0.000

<sup>a</sup>For H and F, a 6-31G(*d,p*) basis set was used; for I and Xe, a quasi-relativistic pseudopotential (LANL2DZ) [11a-c] was used, where the basis functions for the valence *s* and *p* electrons consist of the standard double- $\zeta$  basis set (notation HF/LANL2DZ, MP2/LANL2DZ, etc.).

**TABLE 2** Ab initio Calculated Energies, Structural Parameters, and Vibrational Data for Diatomic Species

		HF ( <sup>1</sup> Σ)	HI ( <sup>1</sup> Σ)	[XeF] <sup>+</sup> ( <sup>1</sup> Σ)	[XeI] <sup>+</sup> ( <sup>1</sup> Σ)	[XeI] <sup>+</sup> ( <sup>3</sup> Π)
HF <sup>a</sup>	−E/a.u.	100.01169	11.73214	114.13774	25.98323	26.02688
	d/Å	0.901	1.600	1.850	3.007	3.824
	ν/cm <sup>−1</sup>	4493.1	2367.0	695.7	138.8	
	zpe <sup>b</sup>	6.42	3.38	1.00	0.20	
MP2 <sup>a</sup>	−E/a.u.	100.19464	11.76492	114.34334	26.01833	26.04389
	d/Å	0.921	1.596	1.900	3.005	3.636
	ν/cm <sup>−1</sup>	4195.0	2297.0	613.6	145.7	
	zpe <sup>b</sup>	6.00	3.28	0.88	0.21	
QCISD <sup>a</sup>	−E/a.u.	−100.19938	11.77338	114.34892	26.02865	26.04841
	d/Å	0.9204	1.606	1.914	3.034	3.605
	ν/cm <sup>−1</sup>	4191.6	2201.4	567.9	138.3	
	zpe <sup>b</sup>	5.99	3.15	0.81	0.20	
MP4 (SDQ) <sup>a</sup>	−E/a.u.	100.19912	11.77266	114.34845	26.02685	26.04767
	d/Å	0.9204	1.603	1.912	3.015	3.607
	ν/cm <sup>−1</sup>	4195.9	2226.2	571.7	145.0	
	zpe <sup>b</sup>	6.00	3.18	0.82	0.21	
QCISD (TQ) <sup>a,c</sup>	−E/a.u.	100.20139	11.77367	114.35288	26.02956	26.04851

<sup>a</sup>For H and F, a 6-31G(*d,p*) basis set was used; for I and Xe, a quasi-relativistic pseudopotential (LANL2DZ) [11a–c] was used, where the basis functions for the valence *s* and *p* electrons consist of the standard double-ζ basis set (notation HF/LANL2DZ, MP2/LANL2DZ, etc.).

<sup>b</sup>Zero-point energy in kcal mol<sup>−1</sup>.

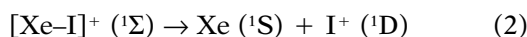
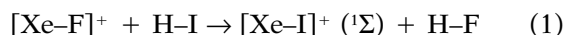
<sup>c</sup>QCISD(TQ) energy at the MP4(SDQ) structure.

which, after correction for zero-point energies (zpe, Table 2), differences in rotational (−RT) and translational (3/2 RT) degrees of freedom, and the work term (RT), was converted into the bond dissociation enthalpy (BDE) at room temperature:

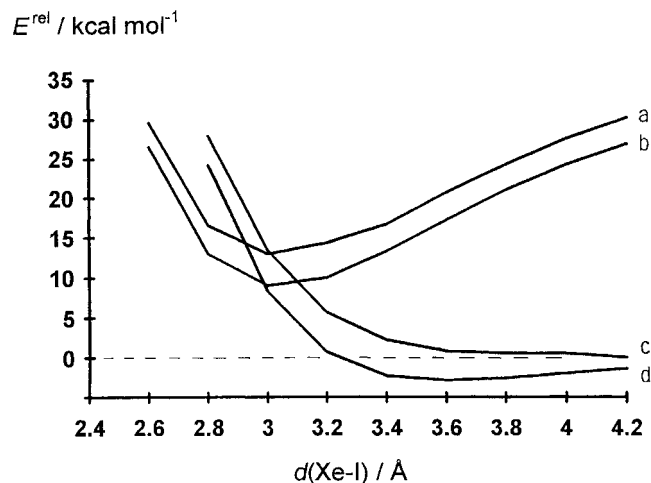
$$\text{BDE}([\text{Xe-I}]^+[\text{QCISD(TQ)/LANL2DZ/MP4(SDQ)/LANL2DZ}]) \\ = +24.1 \text{ kcal mol}^{-1}.$$

These results clearly show that Reaction 1 is thermodynamically favorable and that the [Xe-I]<sup>+</sup> cation is a bound molecule in the singlet state.

The NBO-calculated (MP2 level) charges indicate a slightly polarized Xe–I bond ( $q_{\text{Xe}} = 0.42$ ,  $q_{\text{I}} = 0.58$ ) [14]. The calculated Xe–I bond length in [Xe–I]<sup>+</sup> ( $d^{\text{MP4}} = 3.01 \text{ \AA}$ ) corresponds to a very weak bond that is much longer than the I–I single bond in I<sub>2</sub> ( $d = 2.67 \text{ \AA}$ , gas phase) [13a] and very similar to the quite recently reported value for the Xe–Xe bond in solid [Xe<sub>2</sub>]<sup>+</sup>[Sb<sub>4</sub>F<sub>21</sub>] ( $d = 3.08 \text{ \AA}$ ), which formally has a bond order (BO) of = 0.5 [13b].



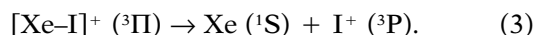
The calculated exothermicity of Reaction 1 and the predicted stability of the [XeI]<sup>+</sup> cation in the singlet state (Equation 2), however, are misleading since the singlet state represents an excited state and the triplet ground state (Table 2) was shown to be essentially unbound at all levels of theory applied (Figure 1). It



**FIGURE 1** Potential energy curves for [XeI]<sup>+</sup> in the singlet and the triplet;  $E^{\text{rel}}$  values with respect to  $E[\text{Xe}(^1\text{S})] + E[\text{I}(^3\text{P})] = 0 \text{ kcal mol}^{-1}$ ; (a) and (c): CASSCF(10,6)MP2/LANL2DZ calculation; (b) and (d): QCISD(TQ)/LANL2DZ calculation; singlet state (<sup>1</sup>Σ): curves (a) and (b); triplet state: curves (c) and (d) [<sup>3</sup>Π for (d)].

is somewhat surprising that the <sup>3</sup>Π state is essentially unbound; perhaps the bond length is so long that ion-induced dipole interaction of I<sup>+</sup> with Xe contributes quite negligibly. At the QCISD(TQ) level, the triplet ground state shows a very shallow and flat minimum at very large distances (3.6–3.8 Å, cf. Figure 1) that did not appear at the CASSCF(10,6)MP2

level (Figure 1). This result shows that for weakly interacting systems, the bonding features are generally not accounted for by nondynamical correlation (e.g., CASSCF) alone and that their accurate determination requires dynamical correlation (e.g., CI) treatments. At the CASSCF(10,6)MP2 level, the energy of the singlet state ( $^1\Sigma$ ) is just less than 1 kcal mol $^{-1}$  below that of the unbound triplet state (Figure 1). As expected, for  $r \rightarrow \infty$ , the energy of the triplet ground state converges against the sum of the energies of the isolated species I $^+$  and Xe. One would therefore expect that [XeI] $^+$  reacts in a thermodynamically and spin-symmetry allowed reaction according to Equation 1, yielding the excited [XeI] $^+$  cation that after quite facile singlet–triplet interconversion dissociates into xenon ( $^1S$ ) and I $^+$  ( $^3P$ ) (Figure 1, Equation 3).



With the large basis set including diffuse and polarization functions that was used in combination with the ECP46MWB Stuttgart pseudopotentials and that was too CPU-time expensive to calculate the potential energy curves (cf. Figure 1), we also calculated the reaction enthalpy of the gas-phase reaction according to Equation 1 at the optimized MP4(SDQ) geometries at the QCISD(TQ) level to be

$$\begin{aligned} \Delta H_{298}^{\circ}(1)[\text{QCISD(TQ)/ECP46MWB//MP4(SDQ)/ECP46MWB}] \\ = -84.1 \text{ kcal mol}^{-1}. \end{aligned}$$

This energy value of  $-84 \text{ kcal mol}^{-1}$  is very similar to that obtained with the much smaller basis set ( $-63 \text{ kcal mol}^{-1}$ ) and gives credence to the energy values obtained and discussed earlier. The equilibrium distance of the [XeI] $^+$  cation in the  $^1\Sigma$  state at the MP4(SDQ)/ECP46MWB level is 2.79 Å and is therefore somewhat shorter than that calculated at the MP4(SDQ)/LANL2DZ level (3.01 Å) but still considerably longer than the I–I distance in the isoelectronic I $_2$  neutral molecule (2.67 Å) [13a].

The dissociation energy of the spin-symmetry allowed Reaction 2 was calculated (cf. Table 3), which, after correction for zero-point energies (zpe, Table 2), differences in rotational ( $-RT$ ) and translational ( $3/2 RT$ ) degrees of freedom, and the work term ( $RT$ ), was converted into the BDE at room temperature:

$$\begin{aligned} \text{BDE}([\text{Xe-I}]^+)[\text{QCISD(TQ)/ECP46MWB//MP4(SDQ)/ECP46MWB}] \\ = +39.2 \text{ kcal mol}^{-1}. \end{aligned}$$

Also, this value compares well with that of  $+24.1 \text{ kcal mol}^{-1}$ , which was calculated with the much smaller basis set (see above).

At the MP4(SDQ)/ECP46MWB level, the triplet ground state also shows only a very shallow and flat minimum at a large distance (3.4 Å). At 2.79 Å, the essentially unbound triplet state lies 13.2 kcal mol $^{-1}$  above the bound singlet state.

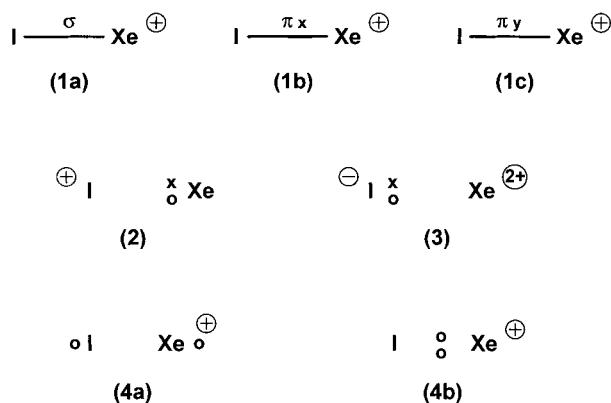
In the qualitative VB picture (Figure 2), the sin-

**TABLE 3** Ab initio Calculated Parameters at the ECP46MWB Level (cf. Computational Methods)<sup>a</sup>

	MP4(SDQ)	QCISD(TQ) <sup>b</sup>
[XeI] $^+$ ( $^1\Sigma$ )	$-E/\text{a.u.}$	26.306460
	$d/\text{Å}$	2.785
	$\nu/\text{cm}^{-1}$	183.0
	$\text{zpe}/\text{kcal mol}^{-1}$	0.26
[XeI] $^+$ ( $^3\Pi$ )	$-E/\text{a.u.}$	26.311643
	$d/\text{Å}$	3.355
	$\nu/\text{cm}^{-1}$	85.7
	$\text{zpe}/\text{kcal mol}^{-1}$	0.1
HI ( $^1\Sigma$ )	$-E/\text{a.u.}$	11.884021
	$d/\text{Å}$	1.614
	$\nu/\text{cm}^{-1}$	2349.1
	$\text{zpe}/\text{kcal mol}^{-1}$	3.4
HF ( $^1\Sigma$ )	$-E/\text{a.u.}$	100.281144
	$d/\text{Å}$	0.915
	$\nu/\text{cm}^{-1}$	4213.4
	$\text{zpe}/\text{kcal mol}^{-1}$	6.0
[XeF] $^+$ ( $^1\Sigma$ )	$-E/\text{a.u.}$	114.56369
	$d/\text{Å}$	1.960
	$\nu/\text{cm}^{-1}$	556.9
	$\text{zpe}/\text{kcal mol}^{-1}$	0.80
Xe ( $^1S$ )	$-E/\text{a.u.}$	15.400001
I $^+$ ( $^3P$ )	$-E/\text{a.u.}$	10.898872
I $^+$ ( $^1D$ )	$-E/\text{a.u.}$	10.8342019
		10.8499936

<sup>a</sup>For H and F, a 6-311 + G( $d,p$ ) basis set was used; for I and Xe, a quasi-relativistic pseudopotential (ECP46MWB) [11d,e] was used, where the basis functions for the valence  $s$  and  $p$  electrons consist of a split-valence basis set including additional polarization functions and diffuse functions (I, (5s6p1d)/[3s4p1d]<sup>+</sup>, (6s6p3d)/[4s4p3d].)

<sup>b</sup>QCISD(TQ) energy at the MP4(SDQ) structure.

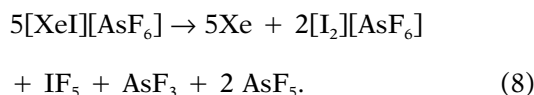
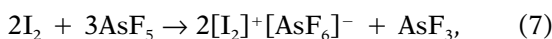
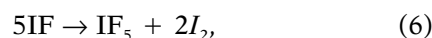
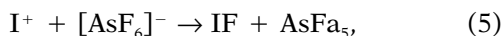
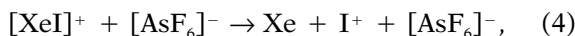


**FIGURE 2** Structures (1a)–(4b) to account for the singlet and triplet state in [XeI] $^+$  when the remaining electrons are omitted, x =  $\uparrow$ , o =  $\downarrow$ .

glet state of the [XeI]<sup>+</sup> cation can be described by structures (1)–(3) where structure (1) is a resonance hybrid of (1a), (1b), and (1c). If structure (1) has a  $\sigma$  bond [i.e., structure (1a)], then a spin flip would give structure (4a) as  $|\sigma\sigma^*\alpha\rangle$ . This corresponds to a  $^3\Sigma$  state, which would dissociate to give Xe<sup>+</sup>( $^2P$ ) + I( $^2P$ ) [if 5p AOs form the sigma bond of structure (1a)]. To obtain [XeI]<sup>+</sup>( $^3\Pi$ ) → Xe( $^1S$ ) +  $^+(^3P)$ , it would be necessary to have a  $|\sigma^{\alpha}\pi^{\alpha}\rangle$  configuration for the two electrons as shown in structure (4b). Structures (1)–(3) account for some net bonding between Xe and I and therefore lead to an energy lowering at equilibrium distance. Structure (4a) is antibonding since when two electrons have parallel spins, i.e., one bonding and one antibonding electron, due to overlap effects, an antibonding situation results [15]. This is in accord with the above-discussed results from the ab initio calculations that show that only the singlet state has a minimum on its potential energy curve.

### Experimental Results

In agreement with the thermodynamic data derived from the quantumchemical calculations, [XeF][AsF<sub>6</sub>]<sup>-</sup> reacted spontaneously with HI, and HF was formed in the reaction (Equation 2). No experimental evidence for the formation of a cationic species of the composition [XeI]<sup>+</sup> was observed. This finding is also consistent with the predicted instability of [XeI]<sup>+</sup> in its triplet ground state and its expected dissociation into I<sup>+</sup> and xenon, the latter of which was identified in the experiment (Equation 4). Salts of the composition [I][AsF<sub>6</sub>]<sup>-</sup> are unstable both in solution and in the solid state, and it has been shown that all attempts to prepare such systems will initially lead to the formation of IF and AsF<sub>5</sub> (Equation 5) [6]. Iodine monofluoride itself is unstable with respect to IF<sub>5</sub> and disproportionates (via IF<sub>3</sub>) at temperatures above -28°C to form iodine and IF<sub>5</sub> (Equation 6) [5,16]. Elemental iodine is readily oxidized to yield [I<sub>2</sub>][AsF<sub>6</sub>]<sup>-</sup> (Equation 7, see Experimental), which dimerizes ( $\pi^*-\pi^*$  interaction) in the solid state to form [I<sub>4</sub>][AsF<sub>6</sub>]<sub>2</sub> [17]. Equations 4–7 can be combined to give for the decomposition of the hypothetical “[XeI][AsF<sub>6</sub>]<sup>-</sup>” the overall Reaction 8 (note: Equations 6 and 7 are multistep themselves).



From this study, the following conclusions can be drawn: (1) The [XeI]<sup>+</sup> cation does not possess a real minimum in the  $^1\Sigma$  state on its potential energy surface. (2) The [XeI]<sup>+</sup> cation is bound only in the  $^1\Sigma$  state, and at its equilibrium geometry, the unbound triplet state is very close in energy. (3) Since the instability of the [XeI]<sup>+</sup> cation and not the basicity of the [AsF<sub>6</sub>]<sup>-</sup> counterion are responsible for its instability, it may not be possible that this species will ever be made and identified in solution (i.e., without crystal-lattice stabilization).

### ACKNOWLEDGMENTS

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