transition state over the minima, resulting in a reduction in the transfer barriers.

Earlier work involving the C=O group of neutral molecules like H_2CO and HCOOH had demonstrated that, as the proton acceptor molecule is moved toward the C=O axis, there is a marked propensity of the bridging proton to shift its equilibrium position away from the C=O and toward the acceptor. The calculations reported here have provided evidence that the anionic $-COO^-$ group is characterized by the same tendency. This similarity is perhaps surprising at first sight, given the very different character of the subunits in the $(HC(OH)O{\cdot}H{\cdot}OH_2)^+$ and $(HCOO{\cdot}H{\cdot}OH)^-$ systems. Nevertheless, analysis of the results reveals that the trends in both systems can be attributed in a straightforward manner to a single principle relating to the ion–dipole interactions within the configurations corresponding to the two minima in the potential.

Proton-transfer potentials were examined for a number of different relative orientations of the $HCOO^-$ and OH^- subunits, i.e. cis or trans. In all cases, it was possible to explain qualitatively the calculated differences in optimized geometries and in the potentials on the basis of interactions between the partial charges on individual atoms at various stages during the proton-transfer process.

A notable distinction between the properties of HCOOH and $HCOO^-$ arises when the proton acceptor is removed from the carboxyl plane. Whereas the nonplanar geometry favors association of the bridging proton with the neutral carboxyl group, either the hydroxide or carboxylate is favored in the anionic system, depending upon their relative orientation. Nonetheless, as above, this behavior is simply explained in either case on the basis of the interaction between the dipole moment of the neutral subunit and the charge of the other. That is, in $(HC(OH)O{\cdot}H{\cdot}OH_2)^+$ association of the bridging proton with either subunit yields a cation, e.g. $HC(OH)_2^+$, leaving the other subunit neutral. In contrast, association of the proton with either subunit in $(HCOO{\cdot}H{\cdot}OH)^-$ yields a *neutral*, e.g. HCOOH while the other subunit is charged.

It is important to consider the proton-transfer properties of the carboxyl group within the context of a larger molecule such as an enzyme. Considering as a first example a H bond between –COOH and water, the former species has a somewhat higher proton affinity, making it a more likely acceptor of a proton, all things being equal. However, other factors may influence this propensity, most notably the interaction of the H-bonded system with the remainder of the protein. In addition, we have illustrated previously[7] that the position of the bridging proton may be shifted toward the water if the latter group is located more nearly along the C–O axis. In the case of higher pH where both the carboxyl and water have been deprotonated and exist as $-COO^-$ and $-OH^-$ ions, the situation is different since the proton affinity of hydroxide is very much larger than that of carboxylate. Nonetheless, the results reported here have suggested that if the basicities of the two ions can be equalized to some extent by the protein environment, the equilibrium proton position can again be shifted from one subunit to the other by adjustments in the angular features of the H bond. Whereas the –COOH and $-COO^-$ species are consistent with regard to in-plane aspects of the geometry, out-of-plane distortions can produce different proton shifts in the two charge states.

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The ArF^+ Cation. Is It Stable Enough To Be Isolated in a Salt?

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Abstract: Ab initio calculations at the MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) level of theory predict that the dissociation energy D_0 of ArF^+ in the $^1\Sigma^+$ ground state is 49 ± 3 kcal/mol. The stabilization energies of ArF^+ salt compounds with suitable counteranions are estimated. The best candidates to form stable argon salts appear to be $ArF^+AuF_6^-$ and $ArF^+SbF_6^-$.

Since the synthesis of the first noble gas salt compound in 1962,[2] numerous molecules of the "inert" elements have become accessible as chemical reagents.[3,4] However, while many neutral and ionic species containing a noble gas element are known in the gas phase, no salt or stable solution containing a noble gas lighter than krypton has ever been prepared. It has generally been concluded that the threshold of true chemical reactivity is reached with Kr.[4] The most promising candidate to break that barrier seems to be ArF^+, salts of which might be preparable. ArF^+ is unique among

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Table I. Optimized Bond Lengths (Å) and Calculated Total Energies E_{tot} (au), Vibrational Frequencies[a] ν (cm^{-1}), Zero-Point Energies ZPE, and Basis-Set Superposition Errors BSSE (kcal/mol)

		MP2/6-31G(d,p)				MP4/6-311G(2df,2pd)	
struct	symm	r_e	E_{tot}	ν	ZPE	E_{tot}	BSSE
HeF^+	$^3\Pi$	2.123	−101.7523	162	0.2	−101.8779	0.3
HeF^+	$^1\Sigma^+$	1.024	−101.7144	1656	2.4	−101.8576	1.1
NeF^+	$^3\Pi$	2.123	−227.5076	266	0.4	−227.7725	1.3
NeF^+	$^1\Sigma^+$	1.456	−227.4593	876	1.3	−227.7375	2.7
ArF^+	$^1\Sigma^+$	1.637	−625.9122	750	1.1	−626.1402	2.8
ArF^+	$^3\Pi$	2.120	−625.8745	391	0.6	−626.0955	1.3
ClF	$^1\Sigma^+$	1.659	−559.1393	748	1.1	−559.3532	1.0
F_2^+	$^2\Pi$	1.410	−198.4948	1338	1.9	−198.7092	
HF	$^1\Sigma^+$	0.921	−100.1967	3909	5.6	−100.3270	
He	^1S		−2.8806			−2.8972	
Ne	^1S		−128.6262			−128.7867	
Ar	^1S		−526.9200			−527.0313	
Ar^+	^2P		−526.3560			−526.4590	
F	^2P		−99.4890			−99.6079	
F^+	^3P		−98.8712			−98.9780	
Cl	^2P		−459.5621			−459.6563	
H	^2S		−0.4982			−0.4998	

[a] The MP2/6-31G(d,p) frequencies and ZPE values are scaled by a factor of 0.93.[23]

the lighter NgX^+ ions (Ng = He, Ne, Ar; X = any other element) in that the ionization energy (IE) of Ar (15.759 eV)[5] is *smaller* than the IE of F (17.422 eV).[5] Thus, the energetically most favorable dissociation limit of ArF^+ corresponds to $Ar^+ + F$ and not to $Ng + X^+$ as for the lighter homologues. Consequently, for ArF^+ the $(^1\Sigma^+)$ $\sigma^2\sigma^2\sigma^2\pi^4\pi^4\sigma^0$ valence electron configuration can correlate with the lowest dissociation limit and thus be the main contributor to the ground-state wave function. This configuration is expected to be the most important one for the Ar–F bond, because the highly antibonding 8σ orbital remains unoccupied. For NeF^+ and HeF^+, the corresponding electron configurations correlate with the second dissociation limit,[6] which makes it very unlikely that the $^1\Sigma^+$ state represents the electronic ground state for these ions. Chupka and Berkowitz[7] detected ArF^+ as a stable gas-phase species by means of the following reaction.

$$F_2^+ + Ng \rightarrow Ng \tag{1}$$

When the noble gas was He or Ne, no stable NgF^+ ions were observed; the bond dissociation energy of ArF^+ was estimated to be >38 kcal/mol.[7]

In order to investigate the possibility of stable salts containing ArF^+, reliable data on the bonding energy of this ion are necessary.[8] To this end we performed high-level ab initio calculations on the lowest singlet and triplet states of ArF^+, NeF^+, and HeF^+. The latter two cations were included to provide quantitative comparisons.[6] The theoretical level used is MP4(SDTQ)/6-311G(2df,2pd)//MP2/6-31G(d,p) + ZPE + BSSE.[9,10] Table I shows the calculated total energies, ZPE and BSSE corrections, and equilibrium distances of all species involved.

The calculated electronic ground state of ArF^+ indeed has $^1\Sigma^+$ symmetry and exhibits a deep potential minimum with an Ar–F equilibrium distance of 1.637 Å. The first excited state, $a^3\Pi$, is more weakly bound with an Ar–F distance of 2.120 Å. Both states correlate with the lowest dissociation limit, $Ar^+(^2P) + F(^2P)$. This is in distinct contrast to HeF^+ and NeF^+, which have weakly bound $^3\Pi$ ground states. We calculate $X^3\Pi$ HeF^+ to be bound by merely 1.2 kcal/mol while the $X^3\Pi$ state of NeF^+ has a D_0 value of 4.0 kcal/mol. In a recent CASSCF study of NeF^+, Hottoka et al.[11] found the $X^3\Pi$ state to be completely repulsive. The excited $a^1\Sigma^+$ states of HeF^+ and NeF^+ are more strongly bound with dissociation energies of 45.1 and 41.2 kcal/mol [with respect to the $Ng(^1S) + F^+(^1D)$ limit], respectively.[12]

$$HeF^+(X^+\Pi) \rightarrow He(^1S) + F^+(^3P) \qquad \Delta E_R = 1.2\ \text{kcal/mol} \tag{2}$$

$$HeF^+(a^1\Sigma^+) \rightarrow He(^1S) + F^+(^1D) \qquad \Delta E_R = 45.1\ \text{kcal/mol} \tag{3}$$

$$NeF^+(X^3\Pi) \rightarrow Ne(^1S) + F^+(^3P) \qquad \Delta E_R = 4.0\ \text{kcal/mol} \tag{4}$$

$$NeF^+(a^1\Sigma^+) \rightarrow Ne(^1S) + F^+(^1D) \qquad \Delta E_R = 41.2\ \text{kcal/mol} \tag{5}$$

Since the dissociation energy of $X^1\Sigma^+$ ArF^+ (reaction 6) represents a homolytic bond cleavage with the transition of a closed-shell species into two open-shell fragments, the D_0 value

$$ArF^+(X^1\Sigma^+) \rightarrow Ar^+(^2P) + F(^2P) \qquad \Delta E_R = 42.1\ \text{kcal/mol} \tag{6}$$

$$ArF^+(X^1\Sigma^+) + H(^2S) \rightarrow Ar^+(^2P) + HF(X^1\Sigma^+) \qquad \Delta E_R = -87.1\ \text{kcal/mol} \tag{7}$$

$$ArF^+(X^1\Sigma^+) + Cl(^2P) \rightarrow Ar^+(^2P) + ClF(X^1\Sigma^+) \qquad \Delta E_R = -9.8\ \text{kcal/mol} \tag{8}$$

computed directly from reaction 6 (42.1 kcal/mol) will suffer from severe electron correlation effects. To circumvent these problems, we made use of the isogyric[13] reactions 7 and 8 to compute the bond dissociation energy of $X^1\Sigma^+$ ArF^+. In these reactions, the number of unpaired electrons remains constant, thus minimizing errors due to insufficient accounting for electron correlation. By use of the experimentally known[14] dissociation energy D_0 of HF

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(135.3 kcal/mol) and ClF (60.3 kcal/mol) and the computed reaction energies ΔE_R of reactions 7 and 8, $D_0(ArF^+)$ is predicted to be 48.2 kcal/mol (reaction 7) and 50.5 kcal/mol (reaction 8). To check the accuracy of the evaluated D_0 data we used the isogyric reaction 9 to calculate the dissociation energy of ClF.

$$ClF^+(X^1\Sigma^+) + H(^2S) \rightarrow Cl(^2P) + HF(X^1\Sigma^+) \qquad \Delta E_R = -77.2 \text{ kcal/mol} \quad (9)$$

Our theoretical D_0 value for ClF is 58.1 kcal/mol, which is in good agreement with the experimental value of D_0 = 60.3 kcal/mol.[14] Using these numbers, we predict the bond dissociation energy D_0 of $X^1\Sigma^+$ ArF^+ to be 49 ± 3 kcal/mol.

The calculation of the dissociation energy is much simpler for the $a^3\Pi$ state because the dissociation reaction 10 is isogyric. Our theoretical D_0 value for the $a^3\Pi$ state of ArF^+ is 16.0 kcal/mol.

$$ArF^+(a^3\Pi) \rightarrow Ar^+(^2P) + F(^2P) \qquad \Delta E_R = 16.0 \text{ kcal/mol} \quad (10)$$

Our calculations provide an explanation for why only ArF^+ was detected in the gas-phase experiments (reaction 1) of Chupka and Berkowitz.[7] Reaction 1 is exothermic only for Ng = Ar (by −5.6 kcal/mol); for Ng = He and Ne, reaction 1 is strongly endothermic by 88.9 kcal/mol (Ng = He) and 106.0 kcal/mol (Ng = Ne).

Since the ArF radical is not bound, $E(ArF^+)$ = IE(Ar) − $D_0(ArF^+)$; for which, therefore, the value of 315 kcal/mol is indicated. Any anion that would stabilize this cation must have an ionization energy that, when combined with the lattice energy of the salt formed, would exceed 315 kcal/mol. Although BF_4^- has been suggested[15] as a suitable counteranion, consideration of available energetics illustrates its unsuitability. The lattice energy for $(ArF)^+(BF_4)^-(c)$ must lie between the lattice energies for the salts KBF_4 and ClO_2BF_4 which, in a comparative study,[16] were found to be respectively 149.9 and 149.4 kcal/mol. But the F^- affinity as assessed[16] in the enthalpy change $\Delta H^\circ_{298}[BF_3(g) + F^-(g) \rightarrow BF_4(g)^-] = -92 \pm 6$ kcal/mol. Since $\Delta H^\circ_{298}[F(g)^- \rightarrow F(g) + e^-] = -81 \pm 1$ kcal/mol, this means that $\Delta H^\circ_{298}[BF_4(g)^- \rightarrow BF_3(g) + F(g) + e^-] = 173 \pm 6$ kcal/mol. This must represent the maximum value for the ionization enthalpy of BF_4^- since there must be appreciable binding of BF_3 and the F atom. Thus, $IE[BF_4(g)^-]$ must be $\ll 173 \pm 6$ kcal/mol, and the combination of this ionization energy and lattice energy lost on transfer of the electron must be $\ll 323 \pm 6$ kcal/mol. Evidently the $ArF^+BF_4^-$ salt is very unlikely to be stable with respect to electron transfer from anion to cation. There are, however, some anions that may be able to stabilize the cation.

The chemical properties of the nearly isodimensional third transition series hexafluorides show[17] that the electron affinity (EA) increases smoothly. Electron affinities have been determined for WF_6 by Beauchamp and George[18] at 81 kcal/mol, and by Nikitin et al.[19] for PtF_6 at 184 kcal/mol. Therefore the increase in EA per atomic number unit must be approximately 25 kcal/mol. Since the AuF_6^- ion[20] has a t_{2g}^6 configuration, it is anticipated that the trend established for the electron affinities of MF_6 will continue to AuF_6 and that accordingly $EA(AuF_6) = 205 \pm 5$ kcal/mol. For $ArF^+AuF_6^-$, the lattice energy on the basis of an estimated formula unit volume of 129 Å^3 is given by the method of Mallouk et al.[16] to be −136 kcal/mol. This combined with the estimated electron affinity yields 341 kcal/mol and exceeds the anticipated electron affinity of the cation, perhaps sufficiently to preserve the salt at low temperatures. The instability[21] of $KrF^+AuF_6^-$ ($\rightarrow Kr + F_2 + AuF_5$), however, indicates that the AuF_6^- anion does at 333 K lose F^- to that cation. Since ArF_2 is unbound, $\Delta H[ArF(g)^+ + F(g)^- \rightarrow Ar(g) + 2F(g)] = -235$ kcal/mol. Therefore, the enthalpy of ionization of the hexafluoroanion $\Delta H^\circ_{298}[MF_6(g)^- \rightarrow MF_5(g) + F(g)^-]$ and the lattice energy of the salt (−136 kcal/mol) must exceed 235 kcal/mol if annihilation by F^- transfer is to be avoided. The F^- ionization enthalpy of AuF_6^- has not been measured, but it appears to be comparable[22] with SbF_6^-. Both AuF_6^- and SbF_6^- are more stable with respect to F^- loss as AsF_6^- for which the enthalpy change has been estimated[16] to be 111 ± 4 kcal/mol.

It is probable that neither AuF_6 nor SbF_6 would oxidize Ar atom; therefore, any synthesis of $ArF^+MF_6^-$ would need to generate ArF^+ or F^+ as precursors to the cation. The synthesis of an ArF^+ salt is therefore attended by formidable obstacles, but the cation would be an oxidizer of unprecedented power and argon is an abundant element.

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