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Theoretical Investigation of Superelectrophilic Fluorooxonium Dications FOH_3^{2+} and $F_2OH_2^{2+}$: Comparison with Parent H_4O^{2+} Dication[1]

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Structures of the superelectrophilic fluorooxonium dications FOH_3^{2+} and $F_2OH_2^{2+}$ were calculated at the QCISD(T)/6-311G** level. Proton affinities of their precursor monocationic species were estimated by using G2 theory. For comparison, the parent oxonium dication H_4O^{2+} was also calculated at the same level. The O,O- and O,F-diprotonated HFO structures **2c** and **2d**, respectively, were found to be energy minima. However, the oxonium dication **2c** is less stable than the oxonium−fluoronium dication **2d** by 14.9 kcal/mol. On the other hand, O,O-diprotonated F_2O **3c** was found to be the only minimum for the analogous system. All of these superelectrophilic, dicationic species have substantial kinetic barriers for deprotonations. The possible existence of these dicationic species in either superacidic media or the gas phase is implicated from these studies. The ^{17}O and ^{19}F NMR chemical shifts of the mono- and dications were also computed by the GIAO-MP2 method.

Introduction

Oxonium dications are of substantial interest. The first and second proton affinities of water to give the oxonium monocation (H_3O^+) and oxonium dication (H_4O^{2+}) have been estimated at the MP2/6-31G*//HF/6-31G* level and later with Gaussian-2 (G2) theories.[1] At the former level, the first and second proton affinities of water are found to be 168.1 and −58.9 kcal/mol, respectively. The corresponding G2 values are closely related (164.6 and −60.4 kcal/mol). The experimentally measured first proton affinity of water (166.5 kcal/mol), using the ion cyclotron resonance method, is in close agreement with these values.[2,3]

Jursic has compared HF, DFT, MP2, and other methods for the calculation of the proton affinities of H_2O, and other related systems.[4] The proton affinity values of H_2O obtained by MP2/6-31G* (176.5 kcal/mol) are comparable with those of B3LYP/6-311G** (175.7 kcal/mol). The G2 level of theory shows that the deprotonation of the oxonium dication to the oxonium monocation is exothermic by 61.9 kcal/mol, although interestingly, it has a kinetic barrier of 38.2 kcal/mol for the deprotonation.[1] Thus under proper conditions, the oxonium dication (H_4O^{2+}) is predicted to be at least a metastable species. Indeed, the H/D exchange of H_3O^+ in superacidic media strongly supports the intermediacy of such dicationic species.[5,6] The GIAO-MP2 derived $\delta^{17}O$ for H_4O^{2+} is 39.2 ppm, which is 29 ppm deshielded as compared to the experimentally determined $\delta^{17}O$ for the H_3O^+ (experimental $\delta^{17}O$ 10.2 ppm; GIAO-MP2 $\delta^{17}O = 24.4$ ppm).[7]

The proton affinities of the fluorinated analogues of H_3O^+ (H_2FO^+ and HF_2O^+) have not been studied in similar detail to date.[8,9] Thus, although the first proton affinity values for HOF and F_2O have been calculated at various levels of theory, their second proton affinities (i.e., proton affinities of the corresponding monoprotonated species) have not been investigated.

Apeloig and co-workers have calculated the structures, vibrational frequencies, and NMR spectra of HOF at high levels.[11] They have shown that the ^{19}F NMR chemical shifts can be reliably calculated using GIAO at the correlated levels. At the GIAO-MP2/QZP//MP2(fu)6-31G* level of calculation, they have obtained a $\delta^{19}F$ of 33.6 ppm for HOF, which is 12 ppm downfield of the experimental value of 21 ppm.

In view of the superelectrophilicity exhibited by oxonium dications,[6] it would be of interest to calculate the relevant data, as such species are expected to be too unstable for characterization by spectral means under experimental conditions. However, they may be observable in the gas phase by using mass spectrometric techniques, if they have sufficiently high barriers for deprotonations.

In light of the theoretical and experimental evidence for the existence of the H_4O^{2+} dication, we now report the high-level ab initio studies of the structures, energies, and proton affinities of the corresponding fluorinated oxonium dications. We have also calculated $\delta^{17}O$ and $\delta^{19}F$ of these mono- and dications using the GIAO-MP2 method.

Calculations

Calculations were performed with the Gaussian 98 program series.[12] The geometry and frequency calculations were initially performed at the MP2/6-31G** level. The vibrational frequencies obtained at this level are scaled by a factor of 0.96 for evaluation of zero-point vibrational energies (ZPE). The calculated frequencies were used to characterize the optimized structures as minima (number of imaginary frequency (NIMAG) = 0 or number of transition structures (NIMAG) = 1).[13] For the MP2/6-31G** optimized structures further geometry opti-

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TABLE 1: Energies (au), ZPE,[a] Relative Energies,[b] and Proton Affinity (PA)[c]

compd	MP2/6-31G**// MP2/6-31G**	ZPE	QCISD(T)/6-311G**// QCISD(T)/6-311G**	G2	rel energy (kcal/mol)	PA (kcal/mol)
H_2O (**1a**)	76.21979	13.2	76.27633	76.33206	163.1	164.6
H_3O^+ (**1b**)	76.50611	21.3	76.56247	76.59193	0.0	−60.4
H_4O^{2+} (**1c**)	76.42164	26.6	76.47719	76.49330	61.9	
H_4O^{2+} (**1cts**)	76.35247	22.5	76.40719	76.43237	100.1	
HOF (**2a**)	175.09948	8.2	175.22106	175.35340	133.8	135.3
H_2OF^+ (**2b**)	175.33425	16.4	175.45524	175.56658	0.0	−75.3
H_3OF^{2+} (**2c**)	175.22289	21.3	175.34556	175.44412	76.8	
H_3OF^{2+} (**2d**)	175.24533	20.6	175.36763	175.46798	61.9	
H_3OF^{2+} (**2cts**)	175.17149	17.0	175.29054	175.39937	104.9	
H_3OF^{2+} (**2dts**)	175.19623	16.5	175.31626	175.42628	88.0	
H_3OF^{2+} (**2ets**)	175.17999	17.6	175.29947	175.40483	101.5	
F_2O (**3a**)	273.99335	3.2	274.17634	274.39108	106.0	107.5
HOF_2^+ (**3b**)	274.17821	11.0	274.36379	274.56005	0.0	−93.5
H_3OF^{2+} (**3c**)	274.03452	16.1	274.22513	274.40872	95.0	
H_3OF^{2+} (**3cts**)	274.00095	11.6	274.18547	274.38066	112.6	

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.96. [b] Based on G2 energies. [c] Gas-phase proton affinities were calculated at 298 K based on G2 energies.[20]

TABLE 2: Calculated and Experimental NMR Chemical Shifts[a]

compd	atom	GIAO-MP2/tzp	expt
H_3O^+ (**1b**)	^{17}O	30.0	10.2[b]
	^1H	7.2	
H_4O^{2+} (**1c**)	^{17}O	50.8	
	^1H	13.6	
FH_2O^+ (**2b**)	^{17}O	195.9	
	^{19}F	403.0	
	^1H	10.8	
FH_3O^{2+} (**2c**)	^{17}O	115.5	
	^{19}F	993.6	
	^1H	14.8	
FH_3O^{2+} (**2d**)	^{17}O	528.7	
	^{19}F	189.6	
	^1H	18.9	
F_2HO^+ (**3b**)	^{17}O	415.7	
	^{19}F	560.4	
	^1H	14.6	
$F_2H_2O^{2+}$ (**3c**)	^{17}O	270.1	
	^{19}F	1071.4	
	^1H	17.4	

[a] Calculated ^{17}O, ^{19}F, and ^1H NMR chemical shifts were referenced to the absolute shifts of H_2O ($\sigma(O) = 354.8$), $CFCl_3$ ($\sigma(F) = 211.3$), and $(CH_3)_4Si$ (calculated using MP2/6-31G* geometry; $\sigma(H) = 31.8$), respectively. [b] Reference 21

mizations were carried out at the QCISD(T)/6-311G** level. The proton affinity values are estimated based on the Gaussian-2 (G2) energies.[14,20] Calculated energies are given in Table 1. QCISD(T)/6-311G** geometrical parameters and G2 calculated energies will be discussed throughout, unless stated otherwise. Atomic charges were obtained by using the natural bond orbital analysis (NBO)[15] method at the QCISD(T)/6-311G**//QCISD-(T)/6-311G** level. NMR chemical shifts were calculated by the GIAO method.[16] GIAO-MP2[17] calculations with the tzp/dz basis set[17,18] have been performed with the ACES II program.[19] The ^{17}O, ^{19}F, and ^1H NMR chemical shifts were referenced to the calculated absolute shifts of H_2O ($\sigma(O) = 354.8$), $CFCl_3$ ($\sigma(F) = 211.3$), and $(CH_3)_4Si$ ($\sigma(H) = 31.8$, using MP2/6-31G* geometry), respectively. Calculated chemical shifts are listed in Table 2.

Results and Discussion

Calculated structures of oxonium dications (**1c**−**3c** and **2d**) and their dissociative transition states (**2cts 2dts**, **2ets**, and **3cts**) are displayed in Figure 1. Calculated proton affinities of the neutral species **1a**−**3a** and oxonium monocations **1b**−**3b** are given in Table 1. The optimized geometrical parameters of neutral species (H_2O, HFO, and F_2O (**1a**−**3a**)) and monocations (H_3O^+, H_2FO^+, and HF_2O^+ (**1b**−**3b**)) are given in Table 3. Pictorial representation of the potential energy surface (PES) involving the formation of dications **2c** and **2d** from **2b** is given in Figure 2.

Whereas in H_3O^+ the oxygen atom is the only protonation site, the oxonium ion **2b** can undergo either O-protonation or F-protonation (Figure 2). Both O-protonated structure **2c** and F-protonated structure **2d** were found to be energy minima. The oxonium dication **2c** has C_{3v} symmetry with a O−F bond distance of 1.473 Å. The Oxonium−fluoronium dication **2d** has C_s symmetry with a relatively longer O−F bond distance of 1.525 Å. These variations are in accordance with the bond activation−reinforcement (BAR) rule (vide infra).[22] The F-protonation to give compound **2d** is favored over O-protonation to give compound **2c** by 14.9 kcal/mol. On the other hand, O-protonated structure **3c** (Figure 1) was found to be the only minimum for the protonation of the oxonium monocation **3b**. The F-protonated structure derived from **3b** did not correspond to a minimum and dissociates into HOF^{2+} and HF upon optimization. Structure **3c** has C_{2v} symmetry with an O−F bond distance of 1.443 Å.

From the computed G2 energies, the proton affinity of **2b** is estimated to be −75.3 kcal/mol for O-protonation (to give **2c**). This value is similar to that of the proton affinity of the oxonium ion (**1b**, −60.4 kcal/mol) implying that the gitonic dication[6] can be an observable species in superacidic media or in the gas phase.

For comparison, we have also computed the proton affinities of the neutral species H_2O, HOF, and F_2O at the same level. The O-protonations as well as the F-protonations in these cases are exothermic, and in accordance with the earlier theoretical calculations, the O-protonations are favored over the F-protonations. The O-protonations for HOF and F_2O to give the oxonium monocations, **2b** and **3b**, respectively, are less exothermic than that for H_2O by 29.3 and 57.1 kcal/mol, respectively, reflecting the lowered electron density on the oxygen atom due to the electron-withdrawing nature of the attached fluorine atom(s).

Of importance to note are the opposing trends in the O- vs F-protonation of the HOF (**2a**) and the oxonium monocation, **2b**. Whereas O-protonation is favored over F-protonation in **2a** (to give **2b**), **2b** undergoes preferentially F-protonation (to give

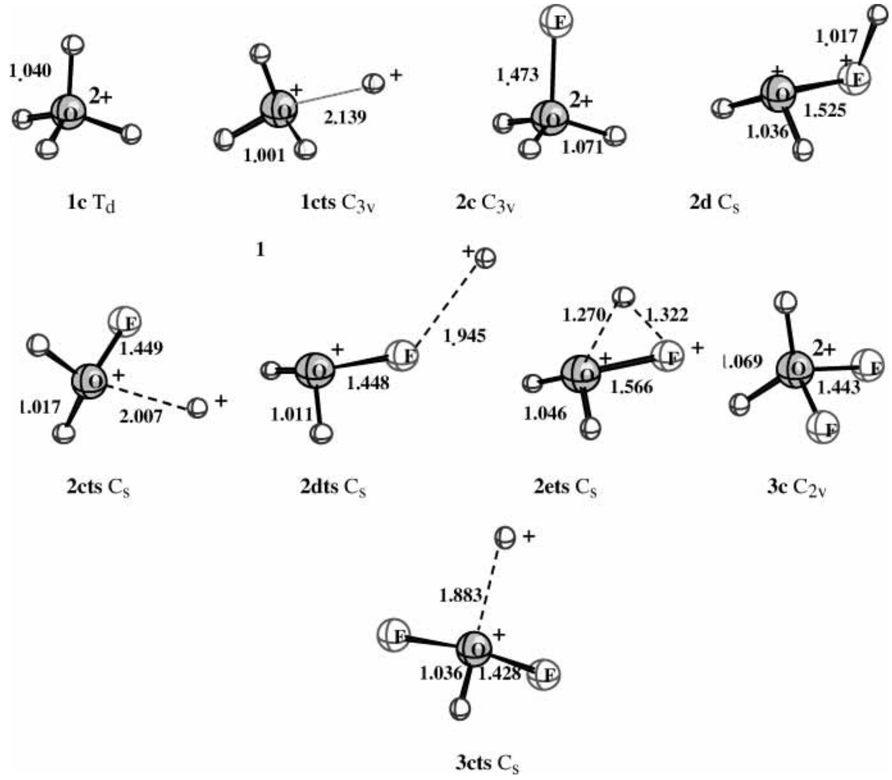


Figure 1. QCISD(T)/6-311G** calculated structures of **1**−**3**.

TABLE 3: QCISD(T)/6-311G Optimized Geometries of 1a(b)−3a(b)**[a]

compd	sym	optimized geometrical parameters
H_2O (**1a**)	C_{2v}	r(OH) = 0.997, a(HOH) = 104.2
H_3O^+ (**1b**)	C_{3v}	r(OH) = 0.977, a(HOH) = 111.9
HOF (**2a**)	C_s	r(OH) = 0.967, r(OF) = 1.445, a(HOF) = 97.5
H_2OF^+ (**2b**)	C_s	r(OH) = 0.993, r(OF) = 1.423, a(HOF) = 103.9; a(HOH) = 110.4; d(HOFH = 115.5)
F_2O (**3a**)	C_{2v}	r(OF) = 1.419, a(FOF) = 103.4
HOF_2^+ (**3b**)	C_s	r(OH) = 1.009, r(OF) = 1.413, a(HOF) = 101.9; a(FOF) = 106.4; d(FOHF = 109.8)

[a] Bond distances and bond angles are given in Å and deg, respectively.

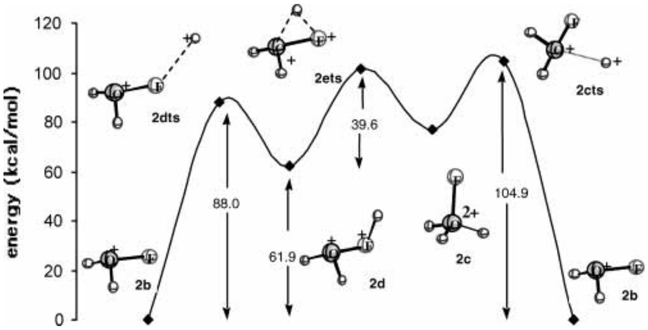
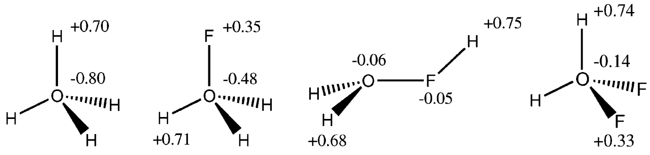


Figure 2. Pictorial representation of the potential energy surface of dications **2c** and **2d**.

2d) (Figure 2 and Table 1). In other words, the charge-dispersed oxonium−fluoronium dication (**2d**) is lower in energy than the charge-localized oxonium dication (**2c**).

Although the formations of the oxonium dications are significantly more endothermic (i.e., more negative proton affinities), they have significantly high barriers for deprotonations to the monocationic species. For example, the dications **2c** and **2d** have activation barriers of 28.1 and 26.1 kcal/mol, respectively, for the deprotonation through transition structures **2cts** and **2dts** (Figure 2). Similarly, dication **3c** has a barrier of 17.67 kcal/mol for the deprotonation through transition structure **3cts** (Figure 1). These values, although smaller than that for H_4O^{2+} (**1c**) (38.2 kcal/mol), are of significant magnitude, preventing the dissociation of the once formed dicationic species (**2c**, **2d**, and **3c**) to the corresponding monocationic species at sufficiently low temperatures.



1c **2c** **2d** **3c**

Figure 3. QCISD(T)/6-311G**//QCISD(T)/6-311G** calculated NBO charges of **1c**, **2c**, **2d**, and **3c**.

We have also calculated the energy barriers involved in the isomerization of the dication **2c** (O-protonated species) to **2d** (F-protonated species) through transition structure **2ets** as 39.6 kcal/mol (Table 1, Figure 2). Thus although kinetically less feasible, once formed, the dication **2c** is unlikely to undergo further rearrangement at sufficiently low temperatures. Thus both **2c** and **2d** are potentially observable species if they can be prepared. It should be emphasized that the gas-phase calculations may not necessarily agree with those of condensed phases. In the latter media, solvation effects may further stabilize the dicationic species so that they may be observable under long-lived stable ion conditions in superacid media.

NBO charge calculations show that in the parent hydronium dication (**1c**) the oxygen carries a negative charge of −0.80 and the four hydrogens carry a positive charge of +2.80 (Figure 3). In the dication **2c** the oxygen carries considerably less negative charge (−0.48) and the fluorine carries a positive charge of +0.35. On the other hand, in **2d** both oxygen and fluorine bear a slight negative charge of −0.06 and −0.05, respectively. This indicates enhanced dissipation of the negative charge of oxygen by the adjacent fluorine atom in the dications **2c** and **2d**. Similar dissipation of the negative charge on oxygen was also observed in the dication **3c**.

We have also calculated the ^{17}O, ^{19}F, and ^{1}H NMR chemical shifts of all of the mono- and dications by the GIAO-MP2 method using QCISD(T)/6-311G** optimized geometries (Table 2). The calculated $\delta^{17}O$ of H_3O^+ (**1b**; $\delta^{17}O = 30.0$ ppm) deviates from the experimental value ($\delta^{17}O = 10.2$ ppm) by 19.8 ppm (referenced with respect to H_2O).[21] The calculated $\delta^{17}O$ of H_4O^{2+} (**1c**, $\delta^{17}O = 50.8$ ppm) is downfield by 20.8 ppm as compared to that of the corresponding value for **1b**, reflecting increased deshielding due to its dicationic nature. Accordingly, the calculated $\delta^{1}H$ of H_4O^{2+} (**1c**, $\delta^{1}H = 13.6$ ppm) is farther downfield as compared to that of H_3O^+ (**1b**, $\delta^{1}H = 7.2$) ppm. The calculated $\delta^{17}O$ values of dications **2c** and **3c** are much more deshielded than **1c**, at 115.5 and 270.1 ppm, respectively, due to the attached fluorine atoms. Interestingly, the calculated $\delta^{17}O$ of the dication **2d** (F-protonated) is 528.7 ppm, which is deshielded by 413.2 ppm as compared to that of the **2c** (O-protonated, $\delta^{17}O = 115.5$ ppm). The corresponding calculated O−F bond lengths for **2d** and **2c** are 1.525 and 1.473 Å, respectively (Figure 1). The variations in these bond lengths and chemical shifts can be explained by using the BAR rule, which was originally proposed by Yanez and co-workers to account for the bond elongation and bond shortening upon protonation of neutral compounds (vide supra).[22] The F-protonation of **2b** results in a dramatic increase in the O−F bond length (1.525 Å; $\Delta r = 0.102$ Å), whereas O-protonation of **2b** results in a relatively smaller increase in the O−F bond length (1.473 Å; $\Delta r = 0.050$ Å), as compared to that of the monocation **2b**. The increased bond lengths in **2d** and **2c** are a result of partial recovering of the positive charge on fluorine (in **2d**) and oxygen (in **2c**) by depopulating the O−F bonding region. Apparently, the electronegativity of the protonated fluorine atom (in **2d**) is much higher than that of the adjacent positively charged oxygen. In case of **2c**, the dipositively charged oxygen has higher electronegativity than that of the adjacent fluorine atom. According to the BAR rule the higher the difference in electronegativity between the base center and the adjacent atom, the higher the bond elongation (or bond shortening if the adjacent atom is more electronegative) is. The difference in the electronegativity is apparently much smaller for **2c** than for **2d**, resulting in a relatively greater O−F bond length for **2d**. The relatively increased polarization of the O−F bond in **2d** toward the fluorine atom thus results in significantly reduced negative charge density on oxygen, which is reflected in its calculated NBO charge of −0.06. The corresponding NBO charge for **2c** is −0.48 (Figure 3). The significantly lowered negative charge density in **2d** relative to that of **2c** readily explains the enormous deshielding of the oxygen in **2d** as compared to that of **2c**. The calculated $\delta^{19}F$ values of dications **2c** and **3c** are highly deshielded ($\delta^{19}F$ 993.6 and 1071.4 ppm for **2c** and **3c**, respectively; with respect to $CFCl_3$), whereas the calculated $\delta^{19}F$ (189.6) of **2d** is relatively much shielded. The relatively more deshielding of fluorine in **2c** over that of **2d** can similarly be explained based on the relatively increased positive charge density on the fluorine atom in **2c** as compared to that in **2d** (NBO charges: +0.35 (**2c**) and −0.05 (**2d**); Figure 3).

Conclusions

High-level ab initio calculations show that the O,O-diprotonated oxonium dications derived from HOF and F_2O (**2c** and **3c**) do exist as stable minima. They have significantly high activation barriers for their deprotonation to give the corresponding monocations, **2b** and **3b**. The isomeric oxonium−fluoronium dication, **2d**, is also a minimum on the PES and is more stable than the O,O-diprotonated species **2c** by 14.9 kcal/mol. The proton affinity of **2b** (to give **2c**) is also similar to that of H_3O^+ (to give **1c**), indicating that under appropriate gas-phase or superacidic conditions, the dicationic species **2c** can be an observable species. The ^{17}O, ^{1}H, and ^{19}F NMR chemical shifts of the mono- and dications were also calculated by the GIAO-MP2 method and substantiated by the BAR rule.

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