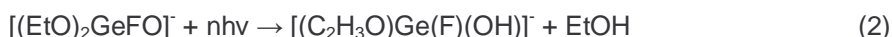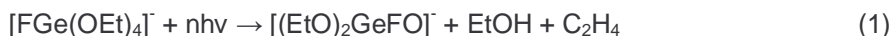# Theorectical Study of Germanium Alkoxides

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Abstract – The gas-phase ion/molecule reaction of F- with $Ge(OEt)_4$ yields readily the pentacoordinated complexes ions. These hypervalent species undergo a series of sequential fragmentations induced by infrared multiphoton excitation (IRMPD) that lead to a large variety of oxygen-containing Ge anion. The photon ionization process is characterized by following reactions: $[FGe(OEt)_4]^-$ + nhv → $[(EtO)_2GeFO]^-$ + EtOH + C_2H_4 and $[(EtO)_2GeFO]^-$ + nhv → $[(C_2H_3O)Ge(F)(OH)]$- + EtOH. Ab initio calculations have been carried out to characterize the primary fragmentation paths induced by IRMPD and the most favorable structure of the resulting anions. The PA (in $kJ.mol^{-1}$) obtained for isomeric structures of $[(C_2H_3O)Ge(F)(OH)]^-$ are c-$FGe(OCH_2)_2^-$ 1373.43; p-$FGe(OH)(OCH=CH_2)^-$ 1358.80; and t-$FGe(H)(O)(OCHCH_2)^-$ 1423.44.

Germanium alkoxides, $Ge(OR)_n$, are recognized as being excellent and versatile precursors for deposition of metal oxides by chemical vapor deposition (CVD) processes, for synthesis of advanced materials and ceramics, in sol-gel processes for preparing Ge-containing glasses[1], and etc. The gas-phase ion/molecule reaction of F^- with $Ge(OEt)_4$ yields readily the pentacoordinated complexes ions. These hypervalent species undergo a series of sequential fragmentations induced by infrared multiphoton excitation (IRMPD) that lead to a large variety of oxygen-containing Ge anion. The photon ionization process is characterized by following reactions:

$$[FGe(OEt)_4]^- + nhv \rightarrow [(EtO)_2GeFO]^- + EtOH + C_2H_4 \qquad (1)$$

$$[(EtO)_2GeFO]^- + nhv \rightarrow [(C_2H_3O)Ge(F)(OH)]^- + EtOH \qquad (2)$$

Ab initio calculations have been carried out to characterize the primary fragmentation paths induced by IRMPD and the most favorable structure of the resulting anions. Bracketing experiments were also carried out to determine the gas-phase acidity of a number of theses geramanium substrates. The computational procedure follows the methodology that has been previously described in our studies regarding the gas-phase acidity (PA) of organogermanes, the electron affinity of simple germyl radicals, and anionic hypervalent complexes of Si and Ge[2]. The PA (in kJ.mol-1) obtained for isomeric structures of $[(C_2H_3O)Ge(F)(OH)]^-$ are c-$FGe(OCH_2)_2^-$ 1373.43; p-$FGe(OH)(OCH=CH_2)^-$ 1358.80; and t-$FGe(H)(O)(OCHCH_2)^-$ 1423.44. All calculations in this work performed with the Gaussian computer program[3].

References

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