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Gas-phase structures of some hypofluorites: $FOSF_5$, $FOSO_2F$, $FOClO_3$ and $FONO_2$

Bernd Casper, Hans-Georg Mack, Heinz Oberhammer *

Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

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The geometric structures of the four title compounds were determined by gas electron diffraction. These four hypofluorites were synthesized for the first time by Professor G.H. Cady. The most interesting structural parameter in these compounds is the X–O (X=S, Cl or N) bond distance. In pentafluorosulfur hypofluorite, F_5S-OF, the S–O bond [167.1(7) pm] is slightly longer than those in F_5S-OCN [165.3(6) pm] and $F_5S-OO-SF_5$ [166.0(6) pm] and considerably longer than that in $F_5S-O-SF_5$ [158.6(11) pm]. Two conformations can occur in fluorine fluorosulfate, FO_2S-OF, depending on the torsional position of the O–F bond around the S–O bond: synclinal (C_1 symmetry) or antiperiplanar (C_s symmetry) relative to the S–F bond. The synclinal conformer is the prevailing form according to the electron diffraction experiment ($\geqslant 80\%$) and according to ab initio calculations ($\geqslant 95\%$). No second conformer was observed in the matrix infrared spectrum. The S–O bond [160.7(7) pm] is ca. 5 pm longer than that in FO_2S-OCH_3. In fluorine perchlorate, O_3Cl-OF, the Cl–O bond [170.2(5) pm] is longer than that in O_3Cl-OH [163.5(4) pm] and $O_3Cl-OCl$ [167.9(5) pm].

The structure of fluorine nitrate, $FONO_2$, which was synthesized by Professor Cady approximately 60 years ago, has a long and controversial history. In 1937, Pauling and Brockway derived from electron diffraction intensities a non-planar structure with the O–F bond perpendicular to the NO_3 plane. In 1963 and 1966, it was concluded from infrared spectra that this compound is probably planar. Two independent Raman studies in 1974 were interpreted in terms of a non-planar structure. A planar configuration was derived in 1984 from an analysis of infrared band shapes. Several ab initio calculations in the years 1988–93 resulted in planar structures, but the predicted N–O bond distance varied from 138 to 156 pm. Our electron diffraction analysis confirms the planarity of $FONO_2$ and a surprisingly long N–O bond length of 150.7(4) pm is derived. The N–O bond in nitric acid, $HO-NO_2$ [140.6(3) pm] is drastically lengthened if hydrogen is replaced by more electronegative atoms: 145.6(5) pm in $BrO-NO_2$, 149.9(3) pm in $ClO-NO_2$ and 150.7(4) pm in $FO-NO_2$. A large number of ab initio calculations fail to reproduce the experimental N–O and O–F single bond lengths satisfactorily, whereas local density functional theory (LDFT) leads to excellent agreement with experiment.

In the four hypofluorites studied in this work, the X–O bonds (X=S, Cl or N) are longer than in other compounds in which fluorine is replaced by a less electronegative atom or group. The O–F bonds in F_5SOF [140.8(9) pm] and in O_2NOF [140.9(5) pm] are very similar to those in OF_2 [140.5 pm]. The O–F bonds in the other two hypofluorites, FO_2SOF [143(3) pm] and O_3ClOF [144(2) pm], are not well determined by the electron diffraction experiment.

* Corresponding author.

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