Geophysical Research Abstracts,
Vol. 10, EGU2008-A-05600, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-05600
EGU General Assembly 2008

A Spectroscopic and ab initio Study of Halogen Oxides and their Molecular Complexes

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Halogen oxides, especially those containing chlorine and bromine, have received considerable attention in the last two decades, since they are involved in atmospheric processes and play a leading role in stratospheric and tropospheric ozone depletion reactions. Chlorine oxides have been investigated extensively for many years, [1] but studies on bromine oxides are much scarcer, because they are less abundant in the atmosphere and are thermodynamically less stable than the chlorine oxides. Nevertheless, during the past decade it has been shown that the bromine species have a higher ozone depletion potential than their chlorine analogues. Enhanced concentrations of bromine species have been associated with arctic tropospheric ozone depletion episodes, probably caused by catalytic cycles mainly involving the radicals Br and BrO. Consequently, the interest in characterizing atmospheric bromine species has been stimulated in the past few years.

Bromine oxides have been generated by passing a mixture of $Br_2/O_2/Ar$ through a microwave discharge. [2] The products were stabilized at 6.5 K in an excess amount of argon. Infrared spectroscopy was used to analyze the species formed; experiments with enriched $^{18}O_2$ and ab initio calculations were carried out to assist in the assignment of the spectra. Besides the known species BrO, OBrO, and BrBrO, spectroscopic evidence for BrOBrO, $BrBrO_2$, and a new isomer of Br_2O_3 is reported for the first time.

The hydrates of halogen monoxides, $XO{\cdot}(H_2O)_n$, n = 1–6, [3, 4] have been studied by means of DFT (B3LYP) method along with aug-ccpVTZ basis set. Ab initio (MP2 and CCSD(T)) methods and extension of the basis sets up to quintuple-ζ have been done for monohydrates in order to test the methodology. Two rather different intermolecular interactions have been found, namely: conventional hydrogen bonds and OX···O associations.

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