AB INITIO STRUCTURES, VIBRATIONS, AND THERMOCHEMISTRY OF IO, IO^-, AND IO^+

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Ab initio internuclear distances and anharmonic constants for IO, IO^-, and IO^+ were calculated at the CCSD(T) level using 6-311+G(3df,2p) basis sets. The reliability of the calculations was tested against the available experimental values for IO and IO^-.

Electronic energies were also calculated at the CCSD(T) level using the 6-311+G(3df,2p) basis sets, Sadlej's polarized basis sets (PBS), and Wadt and Hay's effective core potential (ECP) basis sets at the experimental geometries and corrected by the experimental zero-point vibrational energies. The enthalpy of formation of the hypoiodite anion IO^- ($^1\Sigma^+$) ($\Delta_f H_0^o$ -109 $\pm$ 5 kJ/mol, uncertainties are 2σ) was obtained from *ab initio* energetics for the metathesis reactions $IO^- + Cl^- \rightarrow ClO^- + I^-$ and $IO^- + Cl_2 \rightarrow ClO^- + ICl$. The reliability of the computational procedure was tested by performing analogous calculations for BrO^- and comparing the results with the accepted value for the enthalpy of formation of BrO^-.

The enthalpy of formation for IO ($X^2\Pi_{3/2}$ ($\Delta_f H_0^o$ = 120 $\pm$ 5 kJ/mol) was deduced from the calculated $\Delta_f H_0^o(IO^-)$ and the experimental electron affinity of IO (EA = 229.43 $\pm$ 0.06 kJ/mol) measured by Gilles et al.. The enthalpy of formation of $IO^+(^3\Sigma^-)$ ($\Delta_f H_0^o$ = - 1060 $\pm$ 5 kJ/mol) was also derived from the present enthalpy of formation of IO and the experimental adiabatic ionization energy of IO (IE = 939.4 $\pm$ 1.7 kJ/mol) measured by Zhang et al. The corresponding bond dissociation energies are $D_0^o(IO)$= 167 $\pm$ 5 kJ/mol, $D_0^o(IO)$ = 234 $\pm$ 5 kJ/mol, and $D_0^o(IO^+)$= 303 $\pm$ 5 kJ/mol.

JANAF-style thermodynamic functions for IO, IO^-, and IO^+ from 0 to 1000 K are also tabulated.

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