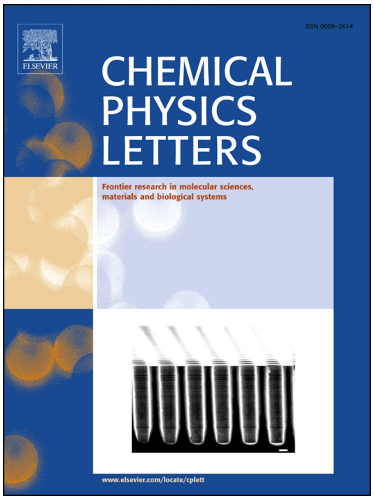

Theoretical study of the thermochemistry of chlorine oxyfluorides

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Theoretical study of the thermochemistry of chlorine oxyfluorides

H. R. Sánchez[1,*], J. Del Pla[1]

Abstract

There is a lack of experimental thermochemical values for most chlorine oxyfluorides. Previous high level theoretical, CCSD(T), results showed uncommonly large errors in the standard heats of formation calculated through the atomization method. We propose that the differences are due to unusually large contributions to energy from higher excitations within the coupled cluster framework, and we tackle the problem by using a calculation scheme based on isodesmic reactions. Our suspicions are supported by results of static correlation diagnostics. Our final recommended values are in better agreement with the experimental data available. Other thermodynamic properties are also calculated.

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1. Introduction

Halogen oxyfluorides (ClF_mO_n) are an interesting field of study because they exhibit a large range of oxidation states, from -I to +VII [26], and coordination numbers. These overvalent species are very reactive and they are mainly used as fluorinating agents and strong oxidizers[1, 27]. A consequence of this is the lack of experimental values for their thermodynamic properties. A common approach to solve this is to estimate these values computationally.

Previous attempts to calculate standard Heats of Formation (HOF) for ClO_mF_n series[26] by the total atomization energy (TAE) method[17] at the CCSD(T)[19] level of theory, resulted in abnormally inaccurate values, compared to CCSD(T) mean error[12]. This is also the case for composite methods[5].

In this work the compounds of the ClF_mO_n family were analyzed. They were suspected to have a similar behavior to those belonging to the Cl_mF_n family, not only due to their similar composition and chemical reactivity, but also due to the previous results by Dixon[26] which show errors of 4.0 kcal·mol^{-1} for ClF_3O and 2.8 kcal·mol^{-1} for $ClFO_3$ when compared to experimental values. These errors are substantially higher than the mean error for the method used, approximately 0.4 kcal·mol^{-1} for CCSD(T)/CBS[12], for well behaved medium sized molecules. The available tests suggest that the contribution due to the superior excitations to the TAE must be large for these compounds. For example Karton estimated[9] that when the value of %TAE[(T)] diagnostic is greater than 10%, the post-CCSD(T) contribution to the total atomization energy

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