

Very strong chalcogen bonding: Is oxygen in molecules capable of forming it? A First-Principles Perspective

Pradeep Varadwaj¹, Arpita Varadwaj², and Helder Marques³

¹The University of Tokyo

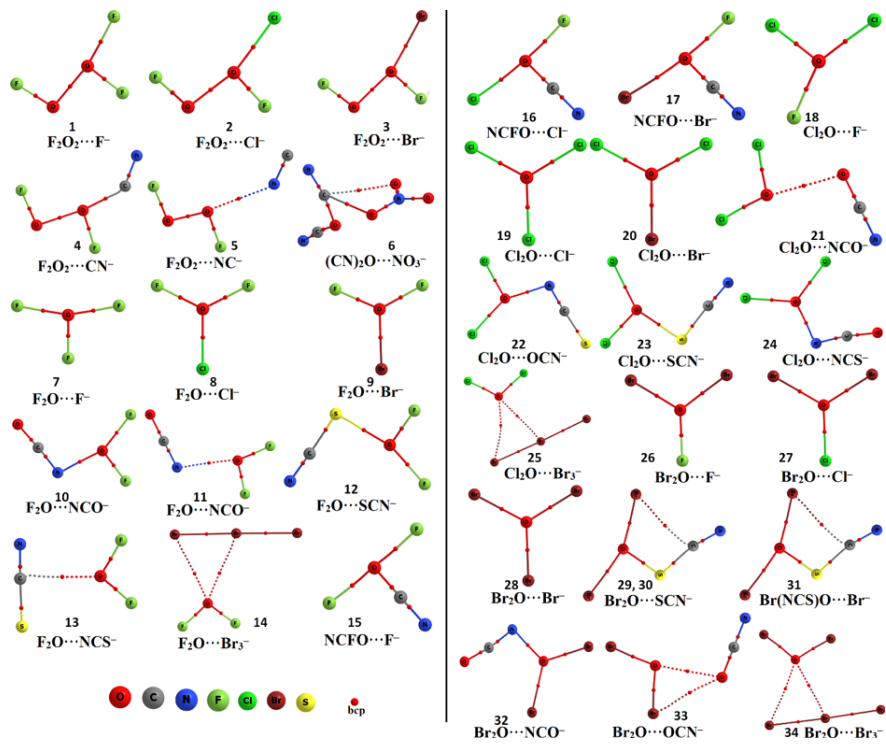
²National Institute of Advanced Industrial Science and Technology Tsukuba Center
Tsukuba Central

³University of the Witwatersrand

June 18, 2020

Abstract

There are views prevalent in the noncovalent chemistry literature that i) the O atom in molecules cannot form a chalcogen bond, and ii) if formed, this bond is very weak. We have shown here that these views are not necessarily true since the attractive energy between the oxygen atom of some molecules and several electron-rich anionic bases examined in a series of 34 ion-molecule complexes varied from the weak (ca -2.30 kcal mol⁻¹) to the ultra-strong (-90.10 kcal mol⁻¹). The [MP2 /aug-cc-pVTZ] binding energies for several of these complexes were found to be comparable to or significantly larger than that of the well-known hydrogen bond complex [FH...F]⁻ (~ 40 kcal mol⁻¹). The nature of the intermolecular interactions was examined using the quantum theory of atoms in molecules, second-order natural bond orbital and symmetric adaptive perturbation theory energy decomposition analyses. It was found that many of these interactions comprise mixed bonding character (ionic and covalent), especially manifest in the moderate to strongly bound complexes. All these can be explained by an n (lone-pair bonding orbital) $\rightarrow \sigma^*$ (anti-bonding orbital) donor-acceptor charge transfer delocalization. This study, therefore, demonstrates that the covalently bound oxygen atom in molecules can have a significant ability to act as an unusually strong chalcogen bond donor.



Hosted file

MS_s.pdf available at <https://authorea.com/users/334543/articles/460514-very-strong-chalcogen-bonding-is-oxygen-in-molecules-capable-of-forming-it-a-first-principles-perspective>

Hosted file

Supplementary_Information.docx available at <https://authorea.com/users/334543/articles/460514-very-strong-chalcogen-bonding-is-oxygen-in-molecules-capable-of-forming-it-a-first-principles-perspective>