



A theoretical exploration on the $^1[\text{H}, \text{Se}, \text{I}]$ potential energy surface: energetics, structures, IR spectra, and heats of formation

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Abstract: There has been considerable interest in the spectroscopy and photochemistry of HOX (X = Cl, Br, and I) species since their important role played in the stratospheric ozone balance in polar regions was described [1,2]. It is believed that HOCl, in particular, participates in heterogeneous chemical reactions in polar stratospheric clouds in the conversion of relatively chlorine stable molecules to more reactive species that participate in the catalytic depletion mechanism of the stratospheric ozone [3]. These studies motivated a recent investigation in our group of similar potential energy surfaces for the sulfur series $^1[\text{H}, \text{S}, \text{X}]$, X = Cl, Br and I [4 – 6]. In the case of the HSCl species, for example, it has been shown that in conditions of high concentrations of hydrogen sulfide, as in the vicinity of active volcanic regions, there is a high possibility of formation of the HSCl molecule [7, 8].

As an extension of the previous studies, the group has also recently characterized, at a high level of electronic structure theory, the species contained on the potential energy surface of the selenium series $^1[\text{H}, \text{Se}, \text{X}]$, X = F, Cl, and Br [9 – 11]. Concerning the surface $^1[\text{H}, \text{Se}, \text{I}]$, theoretical/experimental data for the most stable species are still unknown in the literature, although a couple of theoretical calculations on the SeI_2 [12] molecule and an experimental value for the distance SeI in the SeI_3^+ [13] were reported. In this direction, calculations were performed with the highly correlated CCSD(T) [14] method, along with a series of correlation consistent basis set followed by extrapolations to the complete basis set limit. Corrections that arise due to spin-orbit coupling and scalar relativistic effects were also considered in the atomization energy evaluation. Accounting for core-valence correlation into the wave function, and of anharmonic effects on the vibrational frequencies were also explored, making the present results a very reliable source of data. Our results for the structural parameters, IR spectra, as well as the isomerization barrier and determination of the heat of formation of the species involved are the first ones to be reported in the literature. The HSeI species can be seen as normally covalently bonded and more stable by 42.04 kcal



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mol^{-1} than the HSe isomer. These two species are separated by a barrier (ΔG^\ddagger) of 52.35 kcal mol^{-1} . For the diatomic molecule SeI, we estimated enthalpies of formation of 36.87 kcal mol^{-1} and 35.16 kcal mol^{-1} at 0 K and 298.15 K; for the most stable isomer, we obtained 18.25 kcal mol^{-1} and 16.72 kcal mol^{-1} , respectively.

With the results of this study, we can now have an overview of the energy, structural properties, and infrared spectrum of the complete triatomic series (HSeX) containing selenium and halogens. We hope that this study can contribute to the understanding of the potential reactions between halogens and chalcogens in different chemical environments and also further motivate the experimental search and characterization of this new molecular species.

Key-words: Chalcogens-halogens, HSeI and HSe, atomization energy, heats of formation, harmonic and fundamental frequencies, CCSD(T), CBS limit.

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