

The Isomers HSI and HIS: A Theoretical Investigation of New Species of Potential Interest in Atmospheric Chemistry

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Introduction

In this work, we investigate theoretically, at a high level of electron correlation treatment, two new molecular species, HSI and HIS, following similar studies in our group of the isomers pairs HSB_r/HBr_S and HSCI/HCIS.^{1,2} It is motivated by the role played by the hypohalous acids in generating halogen radical carriers in the Earth atmosphere that participate in catalytic cycles of ozone depletion. Being this study the first systematic investigation of these new species, our main goal here is to report a set of accurate geometric parameters, relative energies, and vibrational frequencies of both isomers that can unambiguously characterize them and the associated transition state. It is our hope that it can encourage and guide experimentalists in the search of these yet experimentally unknown molecules.

Results and Discussion

All stationary states geometries were optimized at the frozen core, coupled cluster singles and doubles with perturbative contributions of connected triples, CCSD(T). For basis sets, the correlation consistent basis aug-cc-pVQZ for H, the set aug-cc-pV(Q+d)Z for S, and the set aug-cc-pVQZ-PP for I were used. Optimized structural parameters, and relative energies for the three stationary states investigated are illustrated in Figure 1.

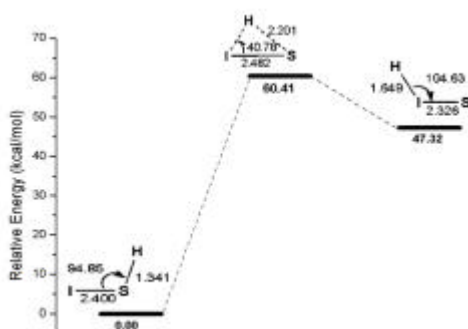


Figure 1. Optimized geometries (Å, degrees) and relative energies (kcal/mol).

Clearly, HSI is more stable than HIS by about 47 kcal/mol, and its bond angle is about 10° smaller than

that found for the species HIS. We note that there is a near invariance of these two angles when compared with those in the pairs HSB_r/HBr_S and HSCI/HCIS. Using a simple orbital picture, we can say that in the three molecules in which sulfur is the central atom, it reflects the participation of two 3p-type orbitals of S with their orientation slightly altered from the ideal 90° angle. In the case of the HXS isomers, in which the central atom octet is complete, a dative-type bond having the halogen as the electron pair donor is formed; the larger angle arises from electron-pairs repulsions that lead to a structure similar to that of the water. We also estimate a high energy barrier of 60 kcal/mol for the direct isomerization process. The harmonic frequencies listed in Table 1 also allow for a distinctive identification of both isomers

Table 1. Harmonic frequencies (cm⁻¹).

Molecule	Frequencies		
	ω_{e1}	ω_{e2}	ω_{e3}
HSI	369,0	809,4	2705,5
HIS	371,6	614,7	2094,0
TS	947,2i	308,6	2119,4

For HSI, the band at 2705.5 cm⁻¹ can be associated with the H-S stretching. In the case of HIS, the ω_{e3} mode corresponds to the H-I stretching. The ω_{e1} frequencies are basically associated with the S-I stretching, and ω_{e2} with the bending.

Conclusions

Accurate and reliable geometric parameters, energies, and vibrational frequencies are reported for the as yet experimentally unknown species, HSI and HIS. It can act as a source of I radicals if present in the atmosphere and photodissociated by sun light.

Agradecimentos

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¹F.R. Ornellas, *Theor. Chem. Acc.* **2000**, *103*, 469.

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