The HCS/HSC and HCS^+/HSC^+ systems: molecular properties, isomerization, and energetics

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The thioformyl HCS and isothioformyl HSC radicals and their related cations HCS^+ and HSC^+ contain the CS functional group which is a moiety of great importance in the chemistry of sulfur-containing organic compounds.

The structural and energetic properties of these species have been accurately studied by means of a highly accurate level of theory. For all the species investigated the near-equilibrium potential energy surface (PES) has been calculated using the coupled cluster method in conjunction with correlation consistent basis sets ranging in size from quadruple to sextuple zeta. After extrapolation to the complete basis set limit, additional corrections due to core-valence correlation and scalar relativistic effects have also been included. Consequently, the molecular and spectroscopic properties as well as the ionization potentials and dissociation energies have been predicted to high accuracy. Isomerization path and energy for both radical and cationic species have also been investigated.

The anharmonic vibrational frequencies have been employed in order to obtain zero-point corrections to ionization potentials, dissociation energies, and isomerization barriers: IP_0(HCS) = 7.57(4) eV and IP_0(HSC) = 9.00(5) eV; D_0(C-H) = 49.29(55) kcal/mol and D_0(S-H) = 9.99(37) kcal/mol; ΔE_0(HCS/HSC) = 39.29(49) kcal/mol and ΔE_0(HCS^+/HSC^+) = 72.24(75) kcal/mol. The CCSD(T) ionization potentials, and dissociation and isomerization energies presented in this work are estimated to be accurate to within about 0.04-0.05 eV and 0.4-0.8 kcal/mol, respectively, which reflect the high level of accuracy of the investigation carried out and of the approach followed.
