

INTERMOLECULAR POTENTIAL AND ROTATIONAL SPECTRA OF H₂-OCS COMPLEXES

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The interaction between molecular hydrogen and carbonyl sulfide was studied through *ab initio* calculations and microwave spectroscopy of *p*H₂-OCS, *o*H₂-OCS, *p*D₂-OCS, *o*D₂-OCS, and HD-OCS. The intermolecular potential surface (IPS) encompasses all four intermolecular degrees of freedom and is an extensive refinement of the IPS previously presented.^a The IPS was calculated at the MP4/aug-cc-pVTZ + bond functions level of theory at a total of 1836 unique geometries. The global minimum is -210.3 cm⁻¹ and places the hydrogen on the side of the OCS in a near parallel arrangement. The interaction is dominated by dispersion with little contribution from the electrostatic dipole-quadrupole term. Four dimensional bound state calculations using this IPS yield binding energies of -76.7 cm⁻¹ for *p*H₂-OCS and -90.3 cm⁻¹ for *o*H₂-OCS relative to *j* = 0 or 1 H₂, respectively. Surprisingly, the ground state for all species, including *o*H₂-OCS and *p*D₂-OCS with hydrogen angular momentum *j* = 1, have total angular momentum *J* = 0.

Eleven to fifteen *a*- and *b*-type pure rotational transitions were measured for each of the five species using a Fourier transform microwave spectrometer. Careful control of the gas mixture was required to observe *p*H₂-OCS in the presence of the more strongly bound *o*H₂-OCS species. The observed transition frequencies of each species can be fit using a standard asymmetric rotor Hamiltonian with the exception of *o*H₂-OCS, for which the effects of internal rotation require a more complicated treatment. Comparison will be made between the *ab initio* calculated and the observed transition frequencies and fitted spectroscopic constants.

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