INTERMOLECULAR POTENTIAL AND ROTATIONAL SPECTRA OF H_2-OCS COMPLEXES

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The interaction between molecular hydrogen and carbonyl sulfide was studied through *ab initio* calculations and microwave spectroscopy of pH$_2$-OCS, oH$_2$-OCS, pD$_2$-OCS, oD$_2$-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 $\mathrm{cm}^{-1}$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 $\mathrm{cm}^{-1}$for pH$_2$-OCS and -90.3 $\mathrm{cm}^{-1}$for oH$_2$-OCS relative to j = 0 or 1 H$_2$, respectively. Surprisingly, the ground state for all species, including oH$_2$-OCS and pD$_2$-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 pH$_2$-OCS in the presence of the more strongly bound oH$_2$-OCS species. The observed transition frequencies of each species can be fit using a standard asymmetric rotor Hamiltonian with the exception of oH$_2$-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.

[a] Higgins, Yu, and Klemperer 57th International Symposium on Molecular Spectroscopy (2002)