ROTATIONAL SPECTRA AND *AB INITIO* POTENTIAL ENERGY SURFACE OF THE H_2-OCS VAN DER WAALS COMPLEX

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The four-dimensional intermolecular potential energy surface for the H_2-OCS complex was obtained at the MP4 level. The potential gives a T-shaped global minimum with a distance of 3.2 Å between H_2 and OCS, in which H_2 is nearly parallel to OCS. Bound state calculations of *para*H_2-OCS give predicted rotational constants of A = 22652, B = 5994, and C = 4611 MHz, in good agreement with the measured results from high-resolution infrared studies.[a] The calculated binding energy of *para*H_2-OCS is 75 cm^{-1}, almost four times greater than that of He-OCS.[b] Preliminary bound state calculations of *ortho*H_2-OCS predict binding energies of 99 $\mathrm{cm}^{-1}$for the Σ state and 64 $\mathrm{cm}^{-1}$for the Π state.

a-type rotational transitions of two isotopomers of the *ortho*H_2-OCS complex were observed between 9 to 31 GHz. The spectral constants of *ortho*H_2-$OC^{32}S$ are (B+C)/2 = 5113.372(23), (B-C)/2 = 580.337(40), and D_J = 2.118(2) MHz. The observed 1_{01}-0_{00} transition is very close to the expectation of *para*H_2-OCS. This shows that the ground state of the complex is a Σ bound state with the T-shaped geometry. The H_2 nuclear spin dipole-dipole coupling constant d_{HH}[c] is 14.4(1) kHz which indicates a zero-point energy averaged angle of 45° of H_2 with respect to the molecular *a* axis. Preliminary spectra of D_2-OCS show the existence of both *ortho*D_2-OCS and *para*D_2-OCS complexes.

[a] Jian Tang and A. R. W. McKellar, J. Chem. Phys. 116, 646 (2002).
[b] Kelly Higgins and William Klemperer, J. Chem. Phys. 103, 1138 (1999).
[c] N. F. Ramsey, Molecular beam (Oxford University, London, 1953).