THEORETICAL INVESTIGATION OF SPIN-ORBIT VIBRONIC COUPLING EFFECTS IN THE ELECTRONIC GROUND STATE OF CrCN

ILIAS SIOUTIS and WOLFGANG DOMCKE, *Department of Chemistry, Technical University of Munich, D-85747 Garching, Germany*.

The spin-orbit-induced vibronic coupling interactions in the $^6\Sigma^+$ electronic ground state of the linear CrCN molecule are investigated, employing the microscopic (Breit-Pauli) spin-orbit (SO) coupling operator. The 6×6 Hamiltonian matrix is derived in a diabatic spin-orbital electronic basis set including terms up to second order in the expansion of the molecular Hamiltonian in the bending normal coordinate. *Ab initio* calculations of the potential energies of the $^6\Sigma^+$ state are performed as a function of the bending normal coordinate. The fitting of the spin degeneracy of the $^6\Sigma^+$ state via various SO coupling terms is investigated. The predicted electronic structure of the $\tilde{X}\ ^6\Sigma^+$ electronic state of CrCN shows a good agreement with the experimentally[a] determined Cr-C bond length but less so for the C-N bond length. The nature of the metal-ligand bonding is also discussed.

[a]M. A. Flory, R. W. Field and L. M. Ziurys *Mol. Phys.* **105**, 585 (2007).