STSM scientific report

Purpose of the visit

The objective of the short-term scientific mission (STSM) was to work in collaboration with Professor Sobolewski on the characterization of conical intersections in phenol. The laboratory of Professor Sobolewski is an outstanding address for *ab initio* calculations on excited electronic states of biological molecules. Professor Sobolewski possesses the experience and methodical competence, which is essential for such non-standard calculations.

Background

Previous experimental results and electronic-structure calculations have revealed that the UV photochemistry of phenol essentially involves the three lowest electronic states S_0, $^1\pi\pi^*$ and $^1\pi\sigma^*$. Phenol has 33 internal degrees of freedom. 10 of them transforming according to the A'' irreducible representation of the C_s point group are able in principle to couple the $^1\pi\pi^*$ and $^1\pi\sigma^*$, and the $^1\pi\sigma^*$ and S_0 states at two conical intersections previously identified.

Results

After localizing precisely along the OH-stretching coordinate (tuning mode) the two conical intersections of interest, calculations of potential energy surfaces were performed for all of the 10 vibrational modes of the right symmetry. The potential energy was computed at the CASSCF level of theory as a function of dimensionless normal coordinates for all the relevant modes so as to enable a direct comparison of the vibronic interaction between the electronic states. A least-squares fitting procedure was used to quantify this interaction expressed in the form of interstate vibronic coupling constants within the linear vibronic coupling theory.

From these fittings, the torsion of the OH group was found to be by far the dominant coupling mode at both conical intersections. These results appear to contradict the interpretation of recent experimental results by Ashfold and coworkers who suggested other vibrational modes to promote the nonadiabatic coupling. These same modes included in our procedure were found to couple only very weakly in comparison with the CCOH dihedral angle.

The grantee still works in collaboration with the host of the STSM to provide an alternative interpretation for the experimental results. Cooperation with the host and his group is also projected for future related projects. The results obtained during the STSM will be finalized in the near-future in a published communication or short article.