DAMOP14-2014-000187

Abstract for an Invited Paper
for the DAMOP14 Meeting of
the American Physical Society

Ab initio quantum dynamics on conically intersecting potential energy surfaces: general considerations and application to SO2

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Conical intersections of potential energy surfaces are the typical signatures of strong nonadiabatic coupling effects, whereby the systems undergoes nonradiative transitions on the femtosecond time scale with far-reaching consequences on the spectral intensity distribution, photoreactivity etc. In the talk, after a brief introduction into the field, our specific quantum dynamical approach to describe such phenomena theoretically is outlined. Some emphasis is given on a suitable construction scheme for quasidiabatic electronic states. The general considerations are applied to and exemplified for low-energy singlet and triplet excited states of SO2. These feature several conical intersections and are also mutually coupled through spin-orbit couplings. The relevant electronic structure data are obtained from extensive ab initio MRCI calculations, while the treatment of the nuclear motion relies on wavepacket propagation techniques. The experimental UV spectrum of SO2 in the 290 nm wavelength range is well reproduced. A novel coupling mechanism is proposed which provides for the spectral intensities in the long wavelength (380 nm) regime, and an experimental setup for its verification is suggested. We also demonstrate how these interactions affect the conventional HeI photoelectron spectrum as well as the time-resolved photoelectron-photoion coincidence spectrum measured recently.