

Spin-dependent Reaction Through Coupled Nuclear-Spin Dynamics

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Nonadiabatic dynamics plays a crucial role in various chemical relaxation phenomena, including photochemistry and electron transfer processes. In a nonadiabatic system with a complex-valued Hamiltonian (e.g., with spin-orbit coupling (SOC) or external magnetic field), the nuclei experience a Lorentz-like force (Berry force) in a direction perpendicular to their velocity. Since the sign of the Berry force depends on the electronic spin direction, the nuclei associated with opposite electronic spins may undergo different reaction pathways. In particular, such effects could be very strong near an avoided conical intersection (CI) with SOC, where the Berry force becomes huge and will dramatically alter the motion of the nuclei.

We investigate a two-state model Hamiltonian with two nuclear degrees of freedom, one incoming channel and two outgoing channels of nuclei. The model has an ‘avoided’ CI: a CI from diabatic couplings eliminated by a small electronic SOC. By using two-dimensional scattering calculations, we find that the nuclei have a huge spin-dependent selectivity on the outgoing reaction channel. For certain incoming energies (0.63 eV) and SOC (5.4 meV), the selectivity can approach unity. Considering the small magnitude of SOC and the richness of avoided conical intersections, such spin polarization should not be uncommon in molecules. Our discovery may help understanding many important spin-related reactions, such as chiral induced spin selectivity (CISS) or magnetochemical reactions.