

ROAMING AND SPECTROSCOPY

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Accurate ab initio theoretical/computational work on dynamics and spectroscopy begins with a potential energy surface (PES). My talk therefore begins with a brief review of progress we have made in developing accurate ab initio global PESs for reaction dynamics. "Roaming" is an unusual alternate pathway to reaction products that was found in the unimolecular dissociation of H₂CO by running roughly 100 000 trajectories on such a PES. The signatures of roaming were seen in the spectroscopic detection of the rotational states of CO correlated with translational energy distribution of the H₂.

I will discuss roaming in NO₃ photodissociation to NO+O₂ and give a short history of the topic. In particular I will recount how poor Franck-Condon factors in pioneering LIF detection experiments in 1997 of the low-lying vibrational states of O₂ plus the assumption of a "prior" vibrational distribution led to the wrong conclusions about the O₂ vibrational-state distribution. Later more sophisticated experiments obtained the correct vibrational distribution, which led to the (correct) speculation about roaming in this system.

I conclude with some comments about roaming wavefunctions and will wonder aloud about ways to detect wavefunctions spectroscopically. (Roaming wavefunctions have been reported by Hua Guo and co-workers for the MgH₂.)