Research paper

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Relating transition-state spectroscopy to standard chemical spectroscopic processes

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Abstract: Transition-state spectra are mapped out using generalized adiabatic electron-transfer theory. This simple model depicts diverse chemical properties, from aromaticity, through bound reactions such as isomerizations and atom-transfer processes with classic transition states, to processes often described as being "non-adiabatic", to those in the "inverted" region that become slower as they are made more exothermic. Predictably, the Born-Oppenheimer approximation is found inadequate for modelling transition-state spectra in the weak-coupling limit. In this limit, the adiabatic Born-Huang approximation is found to perform much better than non-adiabatic surface-hopping approaches. Transition-state spectroscopy is shown to involve significant quantum entanglement between electronic and nuclear motion.

Highlights

- transition-state spectra are calculated over a wide parameter region
- spectral and temporal responses may be simple or quite complex
- surface hopping methods fail to describe spectra usually classified as "non-adiabatic"
- transition-state spectroscopy embodies quantum entanglement