The Non-Ergodic Nature of Internal Conversion - DTU Orbit (15/03/2019)

The Non-Ergodic Nature of Internal Conversion
The absorption of light by molecules can induce ultrafast dynamics of coupled electronic and nuclear vibrational motion. The ultrafast nature in many cases rests on the importance of several potential energy surfaces in guiding the nuclear dynamics – a concept of central importance in many aspects of chemical reaction dynamics. In this thesis, we focus on the non-ergodic nature of internal conversion, i.e. the concept that the nuclear dynamics only sample a reduced phase space potentially resulting in localization of the dynamics in real space. In essence, this is a consequence of vibrational energy redistribution simply not being able to compete with the rate of internal conversion.

The work employ the experimental methods of time-resolved mass spectrometry and photoelectron spectroscopy supplemented by electronic structure calculations and quantum dynamics simulations on seven cycloketones, three cyclopentadienes and dithiane. In the case of the cycloketones, the rate of internal conversion varies by more than an order of magnitude between the molecules. This non-ergodic process was found to primarily involve ring-puckering motion, and the different timescales observed could be rationalized on the basis of primarily two parameters: the vibrational frequency and the energy difference between the Franck-Condon and equilibrium geometries of the upper electronic state.

In the cyclopentadienes, the twisting of a single double bond is essential in reaching the conical intersection seam connecting the lowest excited state with the ground state. By methyl substitution, this out-of-plane motion is significantly slowed down resulting in a slower rate of internal conversion.

In dithiane, the coupling of stretching in the disulfide bond with torsion in the carbon backbone allows the molecule to repeatedly access the region near a conical intersection whereby internal conversion to the ground state proceeds before unfolding of the chain to form a diradical.

A common trait of the three types of molecules investigated is the involvement of very few degrees of freedom in the process that leads to internal conversion. By selectively modifying these modes, the rate of internal conversion can be significantly affected and the dynamics possibly tuned from non-ergodic to partially ergodic.

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