MAR07-2006-002575

Abstract for an Invited Paper
for the MAR07 Meeting of
the American Physical Society

Conformation-specific spectroscopy and dynamics in the complexity gap[1]

TIMOTHY ZWIER, Purdue University

Studies of the spectroscopy and conformational isomerization dynamics of flexible molecules typically fall into one of two size regimes: (i) small-molecule studies in which the molecule possesses two minima and a single barrier (e.g., *cis-trans* isomerization about a double bond) or (ii) large macromolecules for which it is impossible to describe the potential energy surface in exhaustive detail (e.g., protein folding). Between them is a 'complexity gap' of considerable proportions. This talk will describe our group's contributions to studies of molecules that are in that complexity gap in the sense that they have potential energy surfaces containing tens to hundreds of minima, and many times that number of transition states. By employing double resonance laser spectroscopy of isolated molecules cooled in a supersonic expansion, it is possible to obtain the ultraviolet and infrared spectral signatures of the individual conformational isomers of these molecules free from interference from others present in the sample. This foundation of spectroscopic data also serves as the basis for conformation-specific studies of the dynamics of conformational isomerization. In these studies, either infrared excitation or stimulated emission pumping (SEP) is used to excite a single conformation with a well-defined internal energy, thereby initiating conformational isomerization. By re-cooling the products prior to interrogation downstream, the energy thresholds for isomerization between individual X$\rightarrow$Y reactant-product pairs can be determined. Several examples from our recent work will be given to illustrate the kinds of insight that can be drawn from these studies regarding the conformational preferences, spectral signatures, barrier heights and relative energies of minima, fractional abundances, isomerization pathways, and internal energy flow accompanying isomerization.

[1] Supported by the National Science Foundation and the Department of Energy Basic Energy Sciences.