MAR07-2006-000198

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

Rydberg electrons spy conformational dynamics of hot molecules

PETER M. WEBER, Department of Chemistry, Brown University

The observation of structural dynamics of flexible molecules at high temperatures is arguably one of the most challenging problems of molecular dynamics. We succeeded in observing conformational dynamics by using electrons in Rydberg orbits as spies of the molecular structure. The time-resolved photoionization from the Rydberg states, providing a purely electronic spectrum that serves to characterize the molecular structure, allows us to follow the molecular motions in real time. The internal rotation about carbon-carbon bonds affords the unsaturated hydrocarbon chain molecules N,N-dimethyl-2-butanamine (DM2BA) and N,N-dimethyl-3-hexanamine (DM3HA) an opportunity to assume multiple conformeric structures. We explore the equilibrium compositions and the dynamics of transitions between such structures. An ultrashort laser pulse rapidly increases the molecule's internal energy and changes the potential energy landscape. The molecules respond by adjusting their shape, i.e. by converting between conformeric molecular structures. For DM2BA at a total internal energy of 1.79 eV, the time constants for interconversion between conformers are 19 ps and 66 ps, respectively. In DM3HA, the respective time constants are 23 and 41 ps. Comparison with a calculated conformational energy landscape reveals the conformeric forms of DM2BA involved in the molecular shape transformation. Thus, for the first time a time-resolved and quantitative view of the conformational dynamics of a flexible hydrocarbon chain at high temperature is revealed.