RYDBERG STATES: STEALTHY SPIES OF MOLECULAR STRUCTURE

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Electrons in Rydberg orbits are sensitive spies of molecular structure. Typically, the motions of flexible hydrocarbon chains are famously difficult to observe. Large amplitude vibrations born from high internal temperatures where the molecules vibrate in soft potentials blur the conformeric snapshot. We explore the equilibrium composition and dynamics between conformeric structures of N,N-dimethyl-2-butanamine (DM2BA) and N,N-dimethyl-3-hexanamine (DM3HA) using the Rydberg Fingerprint method. Initial excitation prepares the molecule in the $3p$ state and subsequent relaxation to $3s$ deposits 1.8 eV of vibrational energy, elevating the internal temperature to some 900 K. The time-dependent Rydberg spectrum reveals the conformational dynamics of the hot hydrocarbon chains, enabling us to measure time constants for both the forward and backward reactions.