CONFORMATIONAL EXPLOSION: UNDERSTANDING THE COMPLEXITY OF THE PARA-DIALKYLBENZENE POTENTIAL ENERGY SURFACES

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This talk focuses on the single-conformation spectroscopy of small-chain para-dialkylbenzenes. This work builds on previous studies from our group on long-chain n-alkylbenzenes that identified the first folded structure in octylbenzene. The dialkylbenzenes are representative of a class of molecules that are common components of coal and aviation fuel and are known to be present in vehicle exhaust. We bring the molecules para-diethylbenzene, para-dipropylbenzene and para-dibutylbenzene into the gas phase and cool the molecules in a supersonic expansion. The jet-cooled molecules are then interrogated using laser-induced fluorescence excitation, fluorescence dip IR spectroscopy (FDIRS) and dispersed fluorescence. The LIF spectra in the S_0-S_1 origin region show dramatic increases in the number of resolved transitions with increasing length of alkyl chains, reflecting an explosion in the number of unique low-energy conformations formed when two independent alkyl chains are present. Since the barriers to isomerization of the alkyl chain are similar in size, this results in an 'egg carton' shape to the potential energy surface. We use a combination of electronic frequency shift and alkyl CH stretch infrared spectra to generate a consistent set of conformational assignments.