CONFORMATIONAL ISOMERIZATION KINETICS OF ALCOHOLS IN GAS AND DILUTE SOLUTION MEASURED BY TRANSIENT ABSORPTION INFRARED SPECTROSCOPY

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The torsional dynamics of the O-H group in alcohols is examined in the gas and solution phase to understand the role that solvent plays in the conformational isomerization reactions of vibrationally excited molecules. Two-color transient absorption infrared spectroscopy is used to selectively excite the O-H stretch v=1 excited state of a single conformation. This selective excitation is possible due to the strong frequency dependence of the O-H stretch vibrational frequency on the internal rotation angle. The conformer- dependent frequency shift is maintained in solution. The subsequent isomerization dynamics are monitored using a second, time delayed pulse that can detect the population dynamics of either conformer. These measurements have been performed on hexafluoropropanol, hexafluoroisopropanol, and butynol. For the gas phase molecule, the isomerization reaction can only proceed once the energy is redistributed from the prepared O-H stretch excited state. For the alcohols we have studied, this IVR process is the rate limiting step and determines the isomerization rate following mode-selective excitation. This time scale is preserved when the molecule is solvated. However, in solution isomerization can also occur thermally, induced by interactions between solvent and the internal rotation coordinate. The thermal isomerization rate is observed through the time-dependent spectrum of the O-H stretch excited state. The thermal rate determination for hexafluoropropanol will be compared to predictions using RRKM theory.