CONFORMATIONAL ISOMERIZATION KINETICS OF HEXAFLUOROPROPANOL IN GAS AND SOLUTION PHASE

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The rate of conformational isomerization between gauche and trans 1,1,1,3,3,3-hexafluoropropanol (HFP) is measured using two-color ultrafast infrared spectroscopy. The O-H stretch fundamental frequencies of the two conformers of HFP are split by approximately 35 cm^{-1}. This differentiation makes it possible to selectively excite one of the conformers using a picosecond infrared laser. The isomerization kinetics are measured by monitoring the induced absorption at the other conformer using a second picosecond laser. The isomerization dynamics were studied in dilute carbon tetrachloride solution and in the room temperature gas. The isomerization reaction rate is limited by the time scale for intramolecular vibrational energy redistribution from the initially excited O-H stretch. This time scale is about 5 ps and is the same in gas and solution. This time scale for isomerization is about an order-of-magnitude slower than predicted by statistical unimolecular reaction rate theory. In gas, the change in the conformer populations induced by infrared excitation persists for longer than 200 ps, as expected because of the low collision rate. In dilute solution, the conformer populations return to their initial values with a time constant of about 30 ps. This time scale, which has no analog in the gas sample, is assigned to the vibrational cooling rate in solution.