DETERMINATION OF THE THERMAL AND VIBRATIONALLY-INDUCED CONFORMATIONAL ISOMERIZATION RATES OF HEXAFLUOROPROPANOL IN GAS AND DILUTE SOLUTION BY INFRARED PICOSECOND SELECTIVE EXCITATION SPECTROSCOPY

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The vibrational and conformational dynamics of 1,1,1,3,3,3-hexafluoropropanol (HFP) in both room-temperature gas and dilute CCl_4 solution (0.05 M) are studied using infrared picosecond pump-probe spectroscopy. HFP has two stable conformational geometries (trans and gauche) where the conformational frequency shift of the O-H stretch normal-mode is about 40 cm^{-1} in both gas and solution. Due to the large conformational frequency splitting, it is possible to selectively excite a single conformer and follow the subsequent dynamics using a picosecond laser system. For gas-phase HFP, the initial event following coherent excitation is intramolecular vibrational energy redistribution (IVR). For the first excited state of the O-H stretch of the trans conformer, the measured IVR lifetime is 6.9 (1.0) ps. This time scale is about an order-of-magnitude slower than the isomerization relaxation rate predicted by RRKM theory. The initial isomerization reaction rate is limited by IVR under the initial conditions of coherent excitation of the O-H stretch. We are also able to measure the forward (trans-to-gauche) and reverse (gauche-to-trans) thermal rate constants for the low-barrier conformational isomerization reaction in dilute CCl_4 solution using a variation of the tag and probe method. We measure four kinetics parameters experimentally for HFP in dilute solution: $\tau_{IVR(trans)}$ = 6 (1) ps, $\tau_{IVR(gauche)}$ = 6 (1) ps, $\tau_{ISOM(trans-to-gauche)}$ = 13 (2) ps, and $\tau_{ISOM(gauche-to-trans)}$ = 10 (2) ps. The similarity in IVR lifetimes for gas and solution samples indicates that IVR, not solvent assisted processes, is the dominant relaxation mechanism for the first excited state of the O-H stretch. This conclusion is supported by gas and dilute solution (0.05 M in CCl_4) population relaxation measurements of the O-H stretch in perfluorotertbutyl alcohol (PFTBA), where we find identical relaxation dynamics in gas and solution. We find that the thermal rate constants predicted by the RRKM calculations using ab initio values of the vibrational frequencies and barrier height are in good agreement with the experimentally obtained isomerization rate constants.