

FTIR investigation of the fluorocyclohexane ring inversion in liquid Kr

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Abstract

Midinfrared spectra of solutions of fluorocyclohexane, C₆H₁₁F, in liquid Kr (LKr) have been investigated at temperatures between 120 and 188 K. Three temperature intervals are distinguished for the equatorial (e) ⇌ axial (a) conformational relaxation. At temperatures below 141 K the rate of conformational equilibration is negligible and the population ratio of the conformers is "frozen", while at temperatures above 151 K the equilibrium is established nearly instantaneously. In the intermediate temperature interval, the relaxation times are such that the equilibration can be followed using FTIR spectroscopy. From spectra recorded between 151 and 188 K the standard enthalpy difference ΔH° in LKr was determined to be 1.3 (4) kJ mol⁻¹. Between 141 and 151 K, and starting from solutions with nonequilibrium conformer populations, the conformational relaxation was studied as a function of time. From these data, the enthalpy ΔH^\ddagger and entropy ΔS^\ddagger of activation for the a- to e-conformer interconversion were found to be 37.8 (12) kJ mol⁻¹ and -30 (9) J mol⁻¹ K⁻¹, respectively. From the kinetic data, the extinction coefficients ratio ϵ_e/ϵ_a for the ν_{21} conformational doublet was determined to be 0.38 (4). The standard entropy difference ΔS° was determined using this extinction coefficient ratio, yielding a value of 1.14 (11) J mol⁻¹ K⁻¹, and was also determined from the temperature dependence of the infrared band areas, yielding a value of 1.0 (6) J mol⁻¹ K⁻¹. The results are discussed in light of literature data and in light of Monte Carlo free energy perturbation calculations, which yield information on the difference in solvation enthalpy and difference in solvation entropy of this species studied.

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