Raman Spectroscopy of Conformational Rearrangements at Low Temperatures: Folding and Stretching of Alkanes in Supersonic Jets (Springer Theses)

Nils Olaf Bernd Lüttschwager

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This thesis identifies the turning point in chain length, after which alkanes self-solvate into a folded structure instead of an extended stretched conformation. After this turning point, London dispersion forces rearrange isolated *n*-alkanes into a particular hairpin-structure, while for shorter chain lengths, a simple stretched conformation is energetically preferred. This thesis can locate the experimental turning point for the first time in an interaction-free manner from measurements of unbranched alkanes at low temperatures in supersonic jet expansions. It contains a detailed analysis of the vibrational Raman spectra of the chain molecules, which is supported by comprehensive quantum chemical simulations. In this way, the detailed balance between inter-chain attraction and conformational flexibility can be quantified. The investigations are complemented by measurements of perfluoroalkanes and similarities and differences between the compounds are discussed. Furthermore, Nils Lüttschwager determines the stiffnesses (elastic moduli) of two of the most common industrial polymers: polyethylene and polytetrafluorethylene. He uses in this thesis a sophisticated extrapolation to calculate this value from quantities of their building blocks, showing that the single polymer molecules can be as stiff as a rod of steel.

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