

Chapter 1

Introduction

My interest in science is to simply find out about the world, and the more I find out the better it is. I like to find out.

Richard Feynman

A large part of chemistry deals with how atoms bind and how to build any desired, but yet physically possible molecule. This addresses mainly the connectivity of chemically bound atoms, the constitution, which largely determines how a particular molecule reacts, as well as the configuration, which describes the rigid arrangement of atoms in space and might be just as important for the molecular functionality. Still, constitution and configuration do not fully answer the question how a flexible molecule actually “looks like”, that is, how the atoms are arranged around single bonds. The exact arrangement is covered by the conformation, which takes rotations about single bonds into account. Small and simple molecules may have just one or a few stable conformers, but the conformational flexibility increases quickly with the number of single bonds. For large and complex chain molecules, such as those making up living organisms, there exist vast numbers of stable conformations, and yet the occupation of the correct conformation is crucial to their functionality. A popular example are proteins [1], which can only function correctly if they are properly ‘folded’, that is, if they occupy the appropriate conformation. Misfolding leads to improper functioning or may even lead to disease [2]. Therefore, understanding why a particular conformation is preferred and what factors influence conformational preferences is vital when working with complex chemical systems. Among the interactions [3, 4] which determine the stability of molecular conformations are the ubiquitous attractive dispersion forces (London forces), caused by instantaneous dipole (and higher order) moments due to fluctuation in electron density, as well as steric repulsion of electron pairs at short atom distances. The main goal of this thesis is to quantify the interplay between dispersion stabilization and short-range repulsion by studying preferred conformations of unbranched n -alkanes by means of vibrational spectroscopy.

Alkanes are an obvious choice for such a study, because they lack substantially polar groups which would superimpose permanent electrostatic interactions or functional groups which would allow the formation of hydrogen bonds. Rotation

about single carbon-carbon bonds in alkane chains involves relatively low energy barriers and conformers can be converted quickly into one another [5]. Alkanes with not too long chain lengths prefer a fully stretched conformation where all carbon-carbon torsional angles assume a value of 180° . In this *all-trans* conformation, the steric repulsion of adjacent chain segments is minimal. Another stable conformation exists at a torsional angle of about $\pm 65^\circ$, which is termed *synclinal* or *gauche* conformation. Twisting a single carbon-carbon bond of an *all-trans* alkane from the *trans* to the *gauche* conformation raises the energy of the molecule (by about $2\text{--}3\text{ kJ mol}^{-1}$ per *gauche* [6–9]), but several of such twists allow to align two segments of the chain in a way that profits from stabilizing dispersion interaction. The dispersion stabilization increases with the length of aligned chain segments, while the energy cost to fold the molecule stays about the same, such that after a certain *critical chain length* dispersion stabilization wins and the folded conformer is more stable than the *all-trans* conformer. Thus, the appropriate question to ask in this context is: “What is the longest unbranched alkane with a linear global minimum conformation?” [10]. This is the central question which will be addressed here.

Why is this interesting? The general importance of intra- (and inter-) molecular interactions was indicated above, but more specifically, the folding or “self-solvation” of alkanes is an excellent and sensitive benchmark for computational chemistry [10–13]. The importance of computational chemistry was acknowledged by the 2013 Noble Prize in Chemistry, awarded to M. Karplus, M. Levitt, and A. Warshel for their contribution to the field of molecular modeling.¹ Testing such models by rigorous experimental benchmarks is necessary to establish their validity and promote their development. To predict the correct critical chain length, a computational method needs to correctly describe the torsion potentials which determine how much energy the folding of an alkane chain costs, as well as the dispersion forces which stabilize a folded conformer.

A tightly folded conformer results from the conformational sequence *gauche-gauche-trans-gauche-gauche* (ggtgg) where all *gauche* conformations have the same sense of rotation. Since the uniform helicity is absolutely necessary to align two chain segments by this sequence, this may be termed an intramolecular case of chirality synchronization [14, 15]. One of the resulting enantiomeric ‘hairpin’ conformers is depicted in Fig. 1.1, together with a qualitative plot which illustrates how the hairpin conformer becomes more stable with increasing chain length and finally surpasses the stability of the *all-trans* conformer beyond the critical chain length (n_c). This hairpin/*all-trans* competition depends critically on the molecular environment. Alkanes in water, for example, minimize their surface area exposed to the solvent by folding [16, 17], such that the critical chain length in this environment decreases [10]. On the other hand, more favorable dispersion interactions with an unpolar solvent or neighboring alkanes in pure solids withdraw the driving force behind self-solvation, postponing its occurrence to much larger chain lengths [10, 18, 19]. In order to find

¹ http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2013/advanced-chemistryprize2013.pdf (15 October 2013).

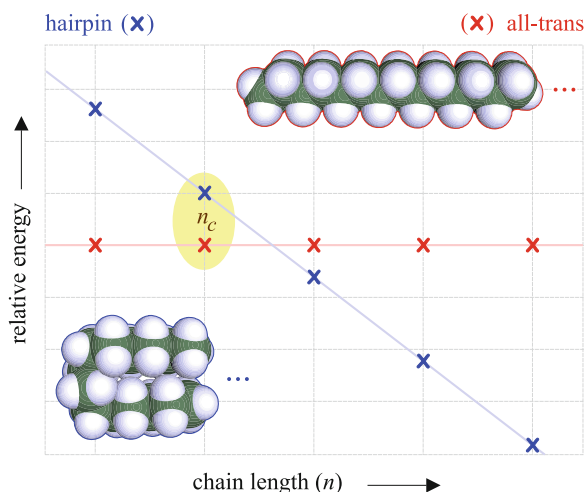


Fig. 1.1 Qualitative plot of the energy of a folded hairpin conformer relative to the energy of the all-trans conformer. n_c marks the critical chain length beyond that the all-trans conformer is not the global minimum structure anymore. Reference II—Reproduced by permission of The Royal Society of Chemistry.

the “true” critical chain length of alkanes free of intermolecular interactions, one has to employ studies in the gas phase.

Current calculations of interaction-free alkanes find a critical chain length in the range $n_c = 15\text{--}21$ [11–13]. The vapor pressure of alkanes in this size range is very low at room temperature [20]. A gas phase study would thus imply substantial heating, but hot alkanes are ordered rather randomly and low-energy conformations such as the all-trans or hairpin conformer are not sufficiently populated to be analyzed. In this work, alkanes were thus cooled in supersonic jet expansions [21, 22] to shift the conformational population from random gauche conformers to all-trans and hairpin conformers. By first heating and subsequent expansion it was possible to investigate cold and isolated alkanes in the relevant size range up to a chain length of 21 carbon atoms for the first time. To determine the critical chain length, jet-cooled alkanes were investigated by vibrational Raman spectroscopy—a routine tool to investigate structural preferences of alkanes and alkyl-systems [23–25]. Although one can resort to numerous spectroscopic investigations of liquid and solid alkanes, especially from T. Shimanouchi, R.G. Snyder and G. Zerbi, Raman spectroscopic studies of alkanes in the gas phase are rare and rather restricted to short chains [9, 26, 27], not least because the preparation of cold gaseous alkanes is technically challenging.

Especially useful to analyze Raman spectra are low-frequency frame vibrations, like the strongly Raman active “accordion” or longitudinal acoustic modes (LAMs) of all-trans segments [28], which have wavenumbers related to the length of the vibrating segment [29]. They will be of particular interest to this work. Observation of accordion vibrations allows furthermore to derive a value for the ultimate

elastic modulus of polyethylene [27, 30, 31], the polymer counterpart of n -alkanes. With the same aim, perfluorinated alkanes were investigated. They are an interesting comparative case to n -alkanes which relates to the technically useful polymer polytetrafluoroethylene (PTFE or Teflon®). The determination of the elastic modulus links this work to polymer physics, but spectroscopy of small oligomers in general [32], and conformational preferences like sharp folding in particular [33–35] are also of interest to deduce the microscopic structure of polymers [36, 37].

The outline of this thesis is as follows. In Chap. 2, Raman spectroscopy will be introduced briefly, focusing on how Raman intensities of vibrational transitions are calculated. The supersonic expansion technique will be discussed there as well. In Chap. 3, the experimental setup used to measure Raman jet-spectra will be outlined, the so-called curry-jet.² This includes a discussion of upgrades which were necessary to allow stable heating of alkanes prior to the expansion and how different measurement conditions influence n -alkane jet-spectra. Chapter 4 addresses n -alkanes and provides information on stable conformations, characteristic vibrations, how spectra are simulated and assigned, and ultimately how the critical chain length is derived from the experimental observations. Chapter 5 deals with perfluorinated alkanes, including Raman jet-spectra of low-frequency vibrations and a discussion regarding self-solvation. Chapter 6 closes the discussion part with the determination of elastic moduli of polyethylene and polytetrafluoroethylene. A summary of the findings of this dissertation is provided in Chap. 7.

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² The name of the setup is a culinary homage to the Indian discoverer of the Raman-effect, Chandrasekhara Venkata Raman, and stands for classical unrestricted Raman spectroscopy in a jet.

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Raman Spectroscopy of Conformational

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