1

Introduction

All that is currently known about matter in space, the origin and evolution of stars, or the dynamics of galaxies, has been derived from astronomical observations of absorption or emission of electromagnetic radiation. From these observations, we know that matter is not distributed homogeneously across the sky but occurs rather concentrated in distinct areas. Astronomers distinguish between extended, cloud-like and smaller, point-like structures. So-called molecular clouds belong to the first category. The more point-like structures are directly linked to stars, like hot cores, circumstellar envelopes or planetary nebulae.

Molecular clouds are characterised by typical temperatures in the range of 10 to 120 K and densities between 10^1 and 10^4 cm^{-3}. Within these scales, clouds with low densities but rather high temperatures are denoted ‘diffuse clouds‘, while the ‘dense clouds‘ are quite cold. The temperatures found in hot cores or circumstellar shells are significantly higher and of the order of hundreds of K [50].

The question arises how such detailed information, especially on physical parameters, can be gained by means of remote sensing with telescopes. Matter in space, primarily gaseous molecules, interact with electromagnetic radiation via rotational or vibrational motions or electronic transitions within the molecules. In general, radiation of low energy is sufficient to excite rotations of molecules, while vibrations and electronic transitions require higher energies. Roughly spoken, rotational transitions correspond to the microwave range of the electromagnetic spectrum ($\sim$ 0.3 - 300 GHz), vibrations to the infrared domain ($\sim$ 10 - 13000 cm^{-1}), and electronic transitions to the optical regime ($\sim$ 380 - 780 nm). In most cases, theses interactions occur in combination: if the absorbed energy is high enough to excite a vibrational mode of a molecule, the energy is by far sufficient to put it into rotation simultaneously. The absorbed or emitted frequencies are typical for a specific molecule, representing a kind of fingerprint, since all processes of interaction are quantised. Knowing the transition frequencies of molecules, astronomers are able to gain information on the composition of interstellar clouds or circumstellar shells. Furthermore, temperatures or densities can be derived from observations, because different transitions require different environmental conditions in astronomical sources.

Molecular spectroscopy has an important influence on the field of astronomy and astrophysics, because the knowledge of a molecule's accurate transition frequencies is crucial for its detection in interstellar or stellar sources. Thus, investigations on molecules in the laboratory support astronomers to detect these species in space. Models describing the astrophysics (the formation of stars and the cycle of matter) and the astrochemistry (the reaction pathways of molecules) are evolved with respect to the observations. To improve such models, a close cooperation between astronomers and spectroscopists is indispensable. In the laboratory, much effort is spent on the synthesis of new molecules with prospect of a possible interstellar detection. Further, more transitions of molecules already detected in the interstellar medium may also contribute to perfecting the model. Rotational transitions in different vibrational modes for example can be used to study excitation temperatures in miscellaneous sources.

After hydrogen, helium, and oxygen, carbon was found to be the fourth most abundant element in space, but a look at the list of interstellar detected molecules reveals that more than 70 % of all species identified in space so far are carbon-bearing molecules [15]. The reason might be the extreme versatility of the carbon bond allowing for the building of chains, rings, and even cage-like structures. Thus, carbon-containing molecules are commonly believed to play a dominant role in interstellar chemistry.

Even some pure carbon molecules have been identified in space. The sources are quite diverse ranging from comets and stellar objects to diffuse interstellar clouds. Up to now, only linear species have been found. Since bare carbon chains are non-polar and thereby showing no permanent electronic dipole moment, they display no pure rotational spectrum. Room for their detection in space is therefore restrained to rovibrational (mid- to far-infrared) or rovibronic (optical) transitions.

The first evidence for C_3 in stars was found in 1953, when P. Swings *et al.* noticed a band similar to the well-known λ 4050 band in the spectra of three stars [84]. In 1975 both C_2 and C_3 have been detected in the circumstellar shell of post-carbon star CRL 2688 via their optical spectra [16]. More than ten years later, the first infrared detection of pure carbon chains was achieved in the circumstellar envelope of another carbon star, IRC+10216. P.F. Bernath *et al.* identified the two clusters C_3 and C_5 through two of their antisymmetric stretching modes in 1988 and 1989 [4, 42]. C_3 was also found in the optical spectrum of diffuse interstellar clouds [58]. The interstellar abundance of C_3 was confirmed by the optical detection in translucent clouds [81] and towards 'ζ type' reddened stars [23]. The interstellar abundance of C_3 is quite important since carbon clusters are possible carriers of the 'diffuse interstellar bands' (DIBs) [17]. For the sake of completeness, the tentative astrophysical detections of C_4 and C_6 in ISO spectra are to be mentioned here [14, 28], although they are still not confirmed and appear to be arguable.

The above mentioned sources exhibit rather high temperatures, otherwise the detection of carbon chains by means of their infrared and optical spectra would have been impossible. Nevertheless, some models predict pure carbon chains to occur in significant amounts also in colder regions (e.g. [7]). To probe cold sources, astronomers rely on the bending vibrational modes of the pure carbon chains occuring in the far-infrared (FIR) or THz-domain. C_3 was found through its bending vibration in the FIR towards Sgr B2 and IRC+10216 [13, 27]. So far, no other detection of a bare carbon chain in the FIR has been reported.

Apart from the mere astrophysical interest, carbon chains have drawn the attention of many spectroscopists regarding their part in the formation of larger carbon molecules. With the advent of new production methods in the early 80's, mass spectroscopic studies of vaporised carbon skyrocketed, particularly after significant amounts of molecules in the size range of 40 up to 120 atoms have been revealed (e.g. [80]). The molecule consisting of 60 carbon atoms soon turned out to be exceptional. Two stable modifications of carbon, graphite and diamond, were known, when in 1985, H.W. Kroto, R.F. Curl, R.E. Smalley *et al.* suggested a kind of spheroidal geometry for the C_{60} molecule to explain its remarkable stability [54]. Due to its unusual structure resembling a football, the molecule was thus termed 'Buckminster fullerene'[1]. This discovery triggered many experimental and theoretical investigations on the so-called carbon clusters. The enormous variety of cluster structures as well as the possible formation mechanisms disclosed a whole new field of research. Calculated structures range from linear chains to cyclic and three dimensional configurations depending on the number of carbon atoms (e.g. [75, 79]). Besides the theoretical approach, efforts have been and are still made to determine the structure and properties of carbon clusters by means of spectroscopy [91, 98]. Information on the actual structure can be derived from the following experiments:

- anion photoelectron spectroscopy (e.g. [2, 33, 99, 102])
- electron-spin-resonance (ESR) studies (e.g. [31, 92])
- ion mobility measurements (e.g. [30, 94])
- Coulomb explosion imaging (CEI) method (e.g. [38, 86])
- spectroscopy of cold rare gas matrices (e.g. [19, 87, 95, 96])
- rotationally resolved gas phase spectroscopy of infrared active vibrational modes (e.g. [25, 60, 64])

The first two techniques aim for the electronic properties of the different isomers resulting in indirect evidence for linear or cyclic structures. All methods are described briefly in the following.

In anion photodetachment experiments, the kinetic energies of detached electrons are measured for mass selected anions permitting conclusions on internal energies and electron affinities. The lower the kinetic energy of an electron, the higher is the internal energy of the corresponding electronic state of the neutral.

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[1] Named after the engineer Richard Buckminster Fuller, whose Geodesic Domes bear a high resemblance to the fullerene structure.

Sharp peaks in the photoelectron spectra are associated with linear isomers while broad features are interpreted as tracks of cyclic structures [2].

Electron-spin-resonance is based on the Zeeman effect. Exposed to a magnetic field the degeneracy of states is lifted within a molecule with a magnetic moment. The energy difference between the splitted levels depends on the strength of the magnetic field and corresponds to radiation in the microwave region. Upon irradiation with suited frequencies, resonant absorptions between the levels occur. However, this technique is applicable only for clusters with a resulting spin, like small even-numbered carbon clusters appearing as linear chains in a triplet electronic ground state (e.g. [93]).

In ion mobility measurements, cluster ions are led through a cell filled with helium before mass selected by a quadrupole mass filter. It is easily accepted that the transit time of each ion through the drift cell depends on its mobility and thus on the average cross section. Thus, ions of the same mass have different transit times if they do not possess the same structure. Thereby, both the relative amount of the different isomers and their mobilities can be derived from the arrival time distribution after the mass selection [94].

Coulomb explosions emerge, when fast clusters impinge on a thin foil thereby stripping off the electrons. The remaining positively charged bodies are disrupted due to Coulomb repulsion. The exploding carbon ions can be detected depending on their arrival time and their position. The derived two-dimensional, macroscopic pattern of the ions mirrors the microscopic distribution of the original carbon atoms in the cluster [86], provided that the cluster structure is conserved during the electron stripping in the foil.

For studying clusters in matrices, carbon cluster gas diluted in pure rare gases like Ne or Ar is freezed out on a very cold substrate (10 - 20 K). In contrast to the gas phase methods introduced previously, the cluster molecules are trapped in a solid ‘grid‘ formed by the rare gas atoms. The clusters are further investigated by means of infrared, optical or UV spectroscopy since the matrix structure does not prohibit vibrational or electronical transitions. Careful annealing of the probe allows for the growth of larger clusters as well as the identificaton of correlated absorption peaks. The identification of species is mainly based on the comparison between calculated and measured spectra. Adding significant impurities of ^{13}C to the orignal carbon (mostly ^{12}C) results in an increased number of absorption peaks due to the number of new molecules consisting of both carbon species (so-called isotopomers). The resulting isotopomeric shifts in vibrational spectra provide qualitative information on the cluster structure since a specific number of isotopomeric peaks is expected for a given geometry (e.g. [87]). It is further possible to combine matrix techniques with mass spectroscopy to record mass selected spectra which simplifies the cluster identification [19].

Infrared absorption spectroscopy has proven to be the most powerful tool for structure determination. In principle, measurements are performed by probing carbon cluster gas with an infrared laser and detecting the transmitted radiation. The transmitted signal shows absorption features at frequencies which excite rovibrational transitions of the molecule. The resulting spectrum provides a fingerprint of the investigated molecule. Since the rotational energy of a molecule depends directly on the moment of inertia, the rotationally resolved spectra carry not only qualitative but also quantitative information on a molecule's geometry. It is neither necessary to ionise nor to destroy the clusters in order to determine their structure.

Up to date, only the linear isomers have been detected via their rovibrational spectra. The odd-numbered carbon clusters are fairly better known than the even-numbered ones, in the series of C_n with odd n up to 13 only C_{11} has not yet been detected [91]. The linear chains C_4 and C_6 were already known for several years [34, 46] when C_{10} was identified through the detection of the rotationally resolved ν_6 asymmetrical stretching mode in 2001 [26]. One year later, linear C_8 was detected for the first time in the gas phase [67]. Unfortunately, the signal-to-noise ratio appeared to be not sufficient to allow more than a tentative assignment of the transitions. Thus, further measurements of this transition were strongly recommended, particularly regarding the effects caused by the resulting spin.

As indicated before, the electronic ground state of carbon chains with an even number of atoms is a triplet state. As a result, all transitions in infrared spectra occur as triplets, that is every single absorption feature is splitted into three lines. The analysis of such spectra poses a challenge. In fact, from what is currently known, C_8 appears to be a kind of transition molecule, since the kin molecules, C_4 and C_6 on the one hand and C_{10} on the other hand, have to be described in two different models.

The astrophysical relevance of the bending vibrations of carbon chains was already adressed. *Ab initio* calculations on various levels predict the lowest bendings for the C_n chains with $n = 3$–10 to occur between 0.5 and 4 THz (e.g. [79, 91]). So far, C_3 is the only bare carbon chain for which direct measurements on a bending mode were performed in the laboratory [82]. However, information on the pure bending motions can be derived from infrared measurements of so-called 'hot bands'. This was done for C_3 [51], C_4 [63], C_5 [62], C_7 [36], and C_9 [88], providing the first estimations of their lowest bending frequency based on experimental work rather than calculations.

For C_3, it is evidenced by both experimental and theoretical investigations that the chain executes a large amplitude bending motion (e.g. [48, 60, 68]), thus, C_3 is termed a 'floppy' molecule. This conclusion led to some investigations concerning the floppiness of longer carbon chains. However, there is little doubt about the chains C_4, C_5, and C_9 to be quite rigid (e.g. [91]). But a controversal debate concerns the nature of the C_7 chain. Unlike the interpretation of existing experimental results (e.g. [36]), recent high-level *ab initio* calculations point at a fairly rigid chain [9]. To settle this question, further measurements on transitions involving the lowest bending mode were needed.

It comes clear, that even for the seemingly simple linear chains important aspects are still not well understood.

The main task of this thesis was to enlarge the currently available data set on the linear carbon chains with respect to two challenging aspects: the bending dynamics of carbon chains and the spin-spin interaction in triplet states. Details concerning carbon clusters and the interpretation of their infrared absorption spectra are given in Chapter 2. In particular, properties of the bending modes as well as consequences of the triplet ground state of even-numbered chains are explained.

The measurements carried out in the course of this work were performed with the Cologne Carbon Cluster experiment. Given the experiences with the original setup of this infrared absorption spectrometer, it was a major part of this work to redesign the experiment with a significant increase of the signal-to-noise ratio in mind, especially with regard to rather weak hot band transitions. The revised setup is described in Chapter 3. Both the production of clusters and their detection are illustrated with emphasis on the necessary rearrangements.

In Chapter 4, new measurements and their subsequent analysis of the ν_5 antisymmetric stretching mode of C_8 are described. Finally, the spectra of the ν_4 fundamental and associated hot bands of C_7 are presented in Chapter 5. The results are discussed in context of the dispute concerning the floppiness.

2

On Carbon Clusters

Most of the early investigations concerning carbon clusters have been triggered by astrophysical interest or the interest in the composition of carbon vapour (e.g. [31, 75]). With the discovery of the C_{60} fullerene [54], the interest has conspicuously intensified.

Excellent reviews on carbon clusters have been given by W. Weltner Jr. and R.J. Van Zee [98] and by A. Van Orden and R.J. Saykally [91] summarising both theoretical and experimental work on carbon clusters up to 1989 and 1998, respectively. Additionally to the results outlined in the review articles, the gas phase detections of the two even-numbered linear chains C_{10} and C_8 have to be mentioned here [6, 26, 67].

The following chapter is divided into two parts. In the first section, a brief overview is given on the most likely structures of small carbon clusters as derived by *ab initio* calculations and various experimental studies. Due to the orientation of this work, the section mainly focusses on linear carbon chains and their properties with emphasis on bending dynamics. The second part provides tools necessary to analyse infrared spectra of linear carbon chains.

2.1 Structures of Carbon Clusters

The versatility of the carbon bond leads to an enormous variety of cluster structures. The more atoms included in the clusters, the more structures are imaginable. For a cluster as large as C_{20} not only linear or planar structures are conceivable but also bowls of different shapes and even a variety of cage-like, that is fullerene, structures have been predicted (e.g. [49]). Apart from the mere structure determination against the number of carbon atoms, the growth process of the fullerenes is object of many speculations. Time-of-flight (TOF) mass spectrometry of supersonic carbon cluster beams revealed a bimodal mass distribution [80] providing evidence for different production mechanisms for small and large clusters, respectively.

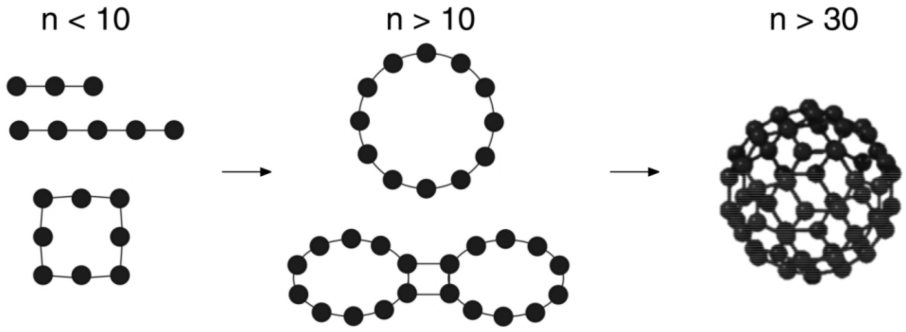

Figure 2.1: Possible configurations for carbon clusters of different sizes after [59]. With increasing size the structures become more complex leading to geometries like the displayed Buckminster fullerene C_{60}.

However, the study of the smaller members of the cluster family is a necessary step on the road of understanding the formation and properties of larger clusters.

Accurate *ab initio* calculations are beyond doubt a high-performance support to study the possible geometries of pure carbon molecules. Though differing in detail, all calculations agree upon different equilibrium geometries depending on the cluster size. Small clusters are predicted to exist rather as linear chains or potentially as cyclic structures in case of the even-numbered clusters. With increasing chain length the energy of the linear structure becomes larger than the energy of the corresponding cyclic geometry [44, 49]. For larger clusters, three-dimensional cage-like structures become energetically favourable. Figure 2.1 gives an impression of the possible geometries.

A number of ten atoms appears to be the magical quantity for the transition between linear and cyclic geometries in theoretical studies [56, 79]. This assumption is supported by photodetachment studies where a fourfold periodicity is found for more than ten atoms pointing at ring structures for this size range [102].

In the following, more details are given on possible structures for small clusters C_n with $n < 10$.

2.1.1 Small Carbon Clusters

In principle, there is not much doubt about the linear character for odd-numbered clusters with few atoms. There have been only minor deviations between calculated values for bond lengths, and, in case of C_3, discussions about a possible small bond angle. The structures of small even-numbered clusters have been found to be more tricky. Depending on the level of calculation, either a linear or a planar cyclic geometry have been predicted to be of lower energy.

Figure 2.2 shows the calculated equilibrium geometries for clusters up to ten atoms. In all cases, those structures were considered which were derived from the highest level of calculation. For the even-numbered ones, both chain and