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Probing potential energy surfaces with high-resolution spectroscopy

From the Universe's carbon locker to molecular machines

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CHAPTER 1

Introduction

1.1 High-resolution spectroscopy

The interaction of light with matter that occurs in a selective manner—determined by the characteristics of the incident light as well as the intrinsic properties of the studied material—is a powerful tool to study and control its building blocks. Absorption of light, on the one hand, increases the energy content of these building blocks (“powers them up”), changing the ground state to a non-stationary state at elevated energy. When such an absorption occurs in the UV/Vis part of the spectrum, photon energy is used to access electronically excited states. As a result of the change in electronic distribution, changes in the spatial structure of the molecule or, even more drastic, photochemical reactions occur. These processes are essential in nature, enabling photosynthesis,¹ vision² and the synthesis of vitamin D,³ to name a few. They are, however, also employed in technological applications to develop light-controlled materials.^{4–6} One such a field which currently is receiving considerable attention is the one of light-driven molecular machines, molecular constructs that convert photon energy into targeted mechanical motion.^{7–11}

On the other hand, the uniqueness of the molecular architecture, which is directly imprinted onto their energetic structure, makes their absorption spectra act as exclusive structural fingerprints. Light is in this case a probe that is employed to detect these levels and—once the molecular spectral fingerprint is known—to identify the species by its spectrum. Light is thus a powerful tool that allows for the remote detection of compounds, making it widely used in sensor industry,¹² analytical chemistry,¹³ atmospheric science,¹⁴ and astronomy.¹⁵ Since the level structure is directly related to the molecular structure, light also provides an instrument to explore molecular geometry by translating the level structure into the topology of the potential energy surface (PES) by means of quantum chemical calculations.

Clearly, the highest level of detail that can be obtained is strongly related to the characteristics of the employed light source. The discovery and development of lasers have in this respect in many ways revolutionized the field of spectroscopy. They are able to provide tunable monochromatic and coherent radiation with narrow linewidths, but also in the form of ultrashort pulses. As a result, many novel spectroscopic techniques have been developed over the years that have pushed the boundaries in terms of sensitivity, spectral and time resolution, accessing electronic,¹⁶ vibrational,¹⁷ and rotational transitions,¹⁸ and nowadays entering the THz regime in which intermolecular interactions can be brought to light.¹⁹

With the increase in instrumental resolving power has also come the recognition that an effective use of this increase is very much dependent on the state of the sample. In frequency-resolved spectroscopic experiments performed on solutions and solids molecules experience intermolecular interactions with solvent molecules and other nearby sample molecules, leading to a broadening of absorption bands and undesired spectral shifts. Gas-phase spectroscopy does in principle not suffer from these drawbacks but here Doppler (thermal) and collisional (pressure) effects easily broaden bands, thereby hiding natural linewidths and leading to overlapping bands.

Over the years scientific interest has shifted from simple molecules that serve as model systems to complex molecular systems as they are actually employed by nature and technology. This increased complexity is accompanied by a tremendous increase in the density of rovibronic states that can no longer be resolved with conventional spectroscopic methods. In order to minimize the previously mentioned effects molecules need to be (i) free of intermolecular perturbations (which is not possible in liquids and solids, but can be achieved in rarefied gases), (ii) cooled down to have a smaller velocity dis-

tribution (to reduce the Doppler broadening), and (iii) be internally cold (to make sure that only a few rovibrational levels are occupied before photon absorption and thereby reducing the number of observed transitions). Jet-cooled molecular beams allow one to satisfy these conditions and to prepare cold and isolated molecules. The technique uses a supersonic expansion of sample molecules that are seeded in a relatively high-pressure inert gas into a vacuum through an orifice with a diameter that is much larger than the mean free path.²⁰ The subsequent adiabatic expansion of the gas occurs with multiple collisions, resulting in cooling of the translational, rotational and vibrational degrees of freedom of the sample molecules. The combination of cold molecular beams with laser spectroscopy has led to a wealth of experimental studies on inorganic and organic molecules, shining light on their molecular structure,^{21,22} dynamics,^{23–25} and conformational heterogeneity.²⁶ Such experimental studies come hand in hand with quantum chemical calculations which allow for interpretation of the experimental data but, from the other side, can be benchmarked by a gold standard—spectroscopic data obtained for molecules that are free of perturbations and temperature effects.

1.2 High-resolution spectroscopy of photoactive materials

Light does not only have the power to unravel molecular structure but also to change it. Molecules that are prone to light-induced transformations are called photoactive. Light absorption of these molecules initiates a wealth of structural transformations that include bond dissociation,²⁷ cis-trans isomerization,^{28,29} hydrogen transfer³⁰ and electron transfer,³¹ and results in products that have quite different properties from the starting materials. Photoactive molecules are widely used by nature, being inevitably part of photoreceptors that provide vision for animals and humans,³² set circadian rhythms for plants, bacteria and fungi^{33–35} and convert energy of the incident light into chemical energy.³⁶

Inspired by nature, synthetic chemists have succeeded in synthesizing a wide range of photoactive materials for technological applications such as memory storage,³⁷ photolithography,³⁸ and solar energy harvesting.³⁹ With the growing demands for technology at the nanoscale, photoactive compounds have attracted particular interest because they allow for a noninvasive, highly selective and spatially precise control over molecular nanodevices. From the perspective of molecular nanotechnology light-driven molecular machines—photoactive molecules that can repetitively convert energy of light into controlled mechanical motion—are of fundamental importance, ultimately being an essential part of a molecular assembler and soft-robotics. By analogy with industrial machines these molecular machines are represented by molecular motors,⁷ propellers,⁴⁰ switches,⁴¹ brakes,⁴² gears,⁴³ etc., mimicking the functions of their macroscopic counterparts.

One of the first light-driven molecular rotors, suggested by Feringa and co-workers in 1999, was based on symmetric biphenanthrylidenes.⁴⁴ A repetitive unidirectional rotation of the top “rotor” part with respect to the bottom “stator” part of the rotor involves photoexcitation causing cis-trans isomerization of the “axle” ethylenic bond and subsequent thermal helix inversion. A number of modifications in the chemical structure of the rotor have been introduced since 1999 in order to accelerate the rotation from one rotation per hour to more than ten million per second for the latest generation of molecular rotors based on chiral overcrowded alkenes.^{45,46} Further modifications have allowed

mounting the stator part of the motor on top of a gold surface⁴⁷ and the construction of the first four-wheeled molecular “car” that converts the unidirectional rotation of four chiral molecular rotors into a linear translational motion of the “car”.⁴⁸ In the near future molecular nanotechnology is expected to find wide applications in nanorobotics,⁴⁹ photopharmacology,⁵⁰ responsive and self-healing materials,⁵¹ adaptive catalysis⁵² and is thereby now a subject of extensive experimental and theoretical studies.

Rotaxanes form another prominent example of a molecular architecture that holds great promise for nanotechnological applications. They consist of one or more macrocycles that are threaded onto a molecular “thread” containing bulky end groups as “stoppers” to prevent the macrocycle(s) to slip from the “thread”.⁵³ In the standard notion of molecules which revolves around covalently bound atoms, rotaxanes thus feature a novel aspect in that they contain mechanically interlocked parts that are not covalently bound. Normally, the macrocycle occupies specific favorable positions on the thread which are designated as “stations”. By applying an external stimulus in the form of light, electricity, change in pH, environment, etc. the macrocycle can be moved between these stations and thus act as a shuttle.⁵⁴ This externally addressable bi-stability is attractive in the context of technological applications such as molecular-electronics-based computing systems. Rotaxanes have, for example, been successfully used as data storage elements in a 160-kilobit molecular electronic memory circuit⁵⁵ and molecular-based logic gates.^{56,57}

For the fabrication of nanodevices photochemical activation of a rotaxane is of a special interest. Light-triggered shuttling of the macrocycle has been achieved by embedding photoactive units into the rotaxane.^{11,58–60} One of the most impressive examples of photoactive rotaxanes that demonstrates an outstanding performance in terms of speed and mechanical work is based on an hydrogen-bond assembled architecture.¹¹ For this rotaxane shuttling is the result of an interplay between the hydrogen-bond affinity of two stations incorporated into the thread, a succinamide (succ) and a naphthalimide (ni) site. In the neutral form the macrocycle is almost exclusively bound to the succ site. As a result of a photoreduction of the ni site by an external electron donor the hydrogen-bonding affinity of the ni site is modified, and an effective movement of the macrocycle from the succ to the ni station takes place.

Energizing these photoactive molecular machines occurs by electronic photoexcitation and subsequent deactivation of the accessed excited state. Photoexcitation brings the molecule to the Franck-Condon region of the potential energy surface of the excited state. The further fate of this excited state depends on the shape and properties of this potential energy surface, deactivation being possible by various routes that encompass radiative decay, internal conversion to the ground or lower excited states, or intersystem crossing to a state with different multiplicity. In general, it is only one of these energy transformation channels that leads to the desired response of the molecule. For example, in the previously mentioned succ-ni rotaxane the useful deactivation route of the initially excited ni singlet state occurs via intersystem crossing, but this route is in competition with internal conversion to the ground state. Similarly, energizing overcrowded alkene-based molecular rotors involves a cis-trans isomerization of the “axle” via a conical intersection with the ground state, but how this conical intersection is reached exactly is still a matter of debate.⁶¹

Although the structure of these molecules and the evolution of this structure have been relatively well studied^{61–65}—in particular in the time-domain—less attention has been paid to the photochemical step, even though this step governs the energy conversion efficiency of the entire operational cycle. Understanding this step heavily relies on knowledge of the potential energy surface of the involved excited states and is key for a further im-

provement of their functionality and efficiency. In this thesis high-resolution spectroscopy of jet-cooled molecules is used to study the relevant excited state's potential energy surfaces as this approach has proved its unique advantages in elucidating the photodynamics of various photoactive biological and synthetic molecules.⁶⁶⁻⁶⁸

1.3 A comprehensive look at CH-stretches of polycyclic aromatic hydrocarbons

Carbon is one of the most abundant elements in the universe and a key element for known life forms. The lifecycle of carbon begins in stars where carbon is produced by a nuclear fusion reaction from helium nuclei. When those stars run out of fuel, they die, ejecting carbon and other elements into the interstellar medium (ISM) and forming clouds, which give further birth to a new generation of stars. In the ISM various interstellar chemical processes involving reactions on surfaces, ions, UV and gas-phase chemistry take place, resulting in the formation of molecules amongst which polycyclic aromatic hydrocarbons (PAHs).⁶⁹ PAHs are molecules that consists of carbon and hydrogen atoms combined in fused aromatic rings. This aromatic structure provides PAHs with an additional photostability that allows them to lock up to 20% of cosmic carbon⁷⁰ and survive in a wide variety of astrophysical environments.⁷¹ It also makes them the most abundant polyatomic species in space. PAHs are directly involved in the evolution of cosmic carbon as well as in the thermodynamics, dynamics and chemistry of the ISM.

If a gaseous PAH is electronically excited by UV light from the nearest stars, it quickly redistributes the absorbed energy via internal conversion to the vibrational manifold of the ground state where radiative cooling occurs by the emission of IR photons. This IR emission is detected^{72,73} as a series of so-called aromatic infrared (AIR) bands at 3.3, 6.2, 7.7, 8.6, 11.2, 12.7, and 16.4 μm that correspond to different types of vibrations in PAHs.^{74,75} Although much desired, no precise identification of the exact carriers of this emission has been possible yet. PAHs are a powerful probe for the environmental conditions of the universe. Nowadays PAHs are generally accepted to trace the evolution of stars and galaxies.⁷⁶ The precise identification of the carriers of the UIR bands is thus extremely helpful as the local history and physical conditions can be traced back and monitored by the local population of PAHs.

Over the years vibrational spectroscopy of PAHs has been a subject of extensive experimental studies.⁷⁷⁻⁸⁶ With limited exceptions⁸⁷⁻⁸⁹ they concerned studies of PAHs that were either in a hot gaseous form, making these data not matching the astrophysical environment, or embedded in a cold rare gas matrix in which they are affected by the environment.⁸² Appropriate laboratory studies of PAHs that can be used for a direct interpretation of the UIR bands are challenging because, first of all, the number of possible PAHs is extremely large, and, secondly, because gas-phase studies of PAHs that are more likely to dominate the emission processes in the ISM contain more than 20 carbon atoms and are thus complicated to study due to their low volatility.

It is therefore not surprising that a further interpretation of astronomical observations has relied heavily on computational studies. Such studies have covered a large number of PAHs of various sizes, charge states, substitutions and modifications of molecular structure, at this moment yielding extensive IR databases containing up to 700 species (the NASA Ames and Cagliary databases).⁹⁰⁻⁹⁴ However, also these studies have their drawbacks since they are typically performed at a level that is a compromise between

computational time and accuracy. They therefore generally do not take effects of anharmonicity into account even though anharmonicity has been shown to dominate important regions of the IR spectrum. Nowadays significant efforts are put into the development and implementation of anharmonicity in calculations that can compute vibrational spectra at a relatively low computational cost⁹⁵⁻⁹⁸ in order to build solid emission models that allow for a more accurate interpretation of astronomical observations.

The 3 μm region, which is accessible for observations from the earth, is one of the most well-studied regions by astronomers. It is represented by a major feature at 3.29 μm and is accompanied by a series of minor bands at 3.41, 3.46, 3.51 and 3.56 μm as well as a plateau spanning the 3150-2700 cm^{-1} region. Within the framework of the PAHs hypothesis, the 3.29 μm band has been confidently assigned to the fundamental $v=0 \leftarrow v=1$ transition of CH-stretch vibrations,⁷⁴ although fluctuations in the 3.29 μm band observed for different sources of the UIR emission and classified by band position and shape [A_{3.3}, B_{13.3}, and B_{23.3}] still remain matter of discussion.^{99,100} Several hypotheses have been put forward in order to account for the observed variety of the 3.29 μm band. These hypotheses range from the influence of the charge state (the position of CH-stretch bands of cations and anions tend to undergo blue and red shift with respect to the neutral species^{92,93}), the size of molecule¹⁰¹ (but recent computational studies did not find support for this⁹³) molecular heterogeneity (not supported by recent experimental studies on N-substituted PAHs¹⁰²) to differences in molecular structures. The latter seems to be an attractive alternative as it finds further support from both experimental and computational studies.^{93,103}

The precise identification of the carriers of not only the 3.29 μm band but also the 3 μm plateau and the 3.41, 3.46, 3.51, and 3.56 μm bands is of increasing interest as the variation of the 3 μm region, from regular sources with a dominating 3.29 μm band^{100,104-107} to abnormal profiles with prevailing 3 μm plateau,¹⁰⁸⁻¹¹⁰ seems to follow the environmental conditions. They are thus an ideal means to examine the conditions of the emitting region in terms of UV radiation flux, density of ISM, etc.¹¹¹ Many experimental efforts have been put into the assignment of the 3 μm plateau and the minor 3 μm bands, and these have led to assignments that range from hot $v=2 \leftarrow v=1$, $v=3 \leftarrow v=2$ vibrational bands,¹¹² overtones and combination bands of CC-stretch and CH in-plane bending vibrations,⁷⁴ to CH-stretch vibrations carried by side methyl ($-\text{CH}_3$)^{113,114} and methylene ($=\text{CH}_2$)^{111,115,116} groups. Nowadays the 3.4 and 3.51 μm bands are generally accepted as being associated with the asymmetric and symmetric CH-stretch vibrations in methylene groups, but no such a consensus exists for the interpretation of the 3.46 and 3.56 μm bands and the 3 μm plateau.

In order to assign the observed 3 μm features a detailed understanding of the 3 μm region is required. However, experimental and theoretical studies of this region indicate that it is strongly affected by anharmonicity,^{77,78,84,117} impeding a reliable theoretical characterization. In order to develop anharmonic approaches that do allow for accurate vibrational assignments calculations need to be benchmarked by experimental high-resolution IR absorption spectra of cold PAHs that are free of external perturbations.

1.4 Outline of the thesis

In this thesis high-resolution electronic and vibrational absorption spectroscopy is applied on a number of molecules that are either important in the context of the life cycle of cosmic carbon or as functional building blocks in molecular nanotechnology. In the former case the potential energy surface of the ground state is explored, in the latter case we unravel complicated photoresponses of photoactive molecular systems in terms of the characteristics of potential energy surfaces of electronically excited states. A combination of supersonically-cooled molecular beams with laser spectroscopy and mass spectrometry allows us to record vibrationally-resolved, conformationally- and mass-selective absorption spectra of internally cold and isolated molecules in the IR or UV/Vis regions. These experimental studies are accompanied by theoretical predictions of such spectra that serve to provide a solid basis for interpreting the experiments and further our understanding of the studied molecular system, but also to determine in which aspects such theoretical calculations still can- or must-be improved.

Chapters 2, 3 and 4 present comprehensive studies of the 3 μm region of PAHs that aim to (i) obtain 3 μm absorption spectra of PAHs under astrophysically relevant conditions; (ii) identify the 3 μm emission features observed in ISM and account for their variations; and (iii) benchmark quantum chemical calculations that are nowadays widely used for interpretation of the astronomical observations. In order to accomplish this IR-UV double-resonance spectroscopic techniques are used to record CH-stretch absorption spectra of fifteen PAHs that differ in size, shape and modifications of their periphery.

Chapter 2 is dedicated to the “devastating” effects of anharmonicity on the aromatic CH-stretch region of linear PAHs. In this chapter experimental and computational absorption spectra of three linear acenes (naphthalene, anthracene, and tetracene) are presented. The observed deviations from standard harmonic calculations are discussed in terms of resonances and anharmonicity of their potential energy surfaces along CH-stretch coordinates. Importantly, it is shown how a novel computational approach is able to reproduce the experimental spectra, and what the consequences of these newly acquired insights into the role of anharmonicity are for astronomical observations.

Chapter 3 expands the conclusions from Chapter 2 by studies on six non-linear PAHs with regular and irregular shapes—phenanthrene, benz[a]anthracene, chrysene, triphenylene, pyrene, and perylene—comparing their experimental spectra with harmonic and anharmonic calculations as introduced in Chapter 2. The focus of this chapter is on the correlation between the molecular structure of PAHs and the shape of their CH-stretch band. To this purpose we compare the absorption spectra of molecules with the same chemical formula but with a different molecular periphery. This correlation and the anharmonicity of the CH-stretch modes is discussed in the context of astrophysical efforts to interpret the variation of the 3.29 μm emission band and the 3 μm emission plateau.

Chapters 2 and 3 concern studies on unsubstituted PAHs, but there are strong indications that hydrogen- and alkyl-substituted PAHs are equally relevant to properly interpret the AIBs. **Chapter 4** therefore reports on experimental and computational studies on the CH-stretch region of partly hydrogenated and methylated, so-called “decorated” PAHs (1,2,3,4-tetrahydronaphthalene, 9,10-dihydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,6,7,8-hexahdropyrene, 9-methylanthracene, and 9,10-dimethylanthracene). In this chapter we discuss the consequences of anharmonicity for such compounds and the spectral features that arise due to the additional hydrogen atoms and methyl groups on the edges of PAHs. With the extensive knowledge base that has been acquired in Chapters 2, 3, and 4 the origin of the 3 μm emission plateau and of the minor 3 μm

emission bands are discussed. Using our experimental data on hydrogenated PAHs we also provide an estimate of the fraction of aliphatic hydrogens in PAHs for different types of interstellar environments.

In **Chapters 5** and **6** the potential energy surfaces of electronically excited states of jet-cooled photoactive molecules have been studied using various multi-color Resonance Enhanced MultiPhoton Ionization techniques. Together with quantum chemical calculations these studies allow us to disentangle electronically excited state manifolds and determine how the absorbed photon energy is dissipated.

In **Chapter 5** two naphthalene-based compounds are studied that are employed as chromophores in a wide range of technological applications including molecular nanotechnology. High-resolution electronic excitation spectra of these molecules together with quantum chemical calculations are presented as well as studies of the excited-state dynamics. These studies show unambiguously that the current interpretation of the spectroscopic properties of these compounds is far from complete. Instead, three strongly coupled singlet and triplet states need to be taken into account to rationalize and assign excitation spectra and to understand the dynamic following electronic excitation.

Chapter 6 presents molecular beam spectroscopic studies on a prototypical light-driven rotor based on overcrowded alkenes. These studies show that well-resolved excitation spectra can be recorded when this compound is seeded into supersonic expansions. However, further consideration of these spectra and taking into account the spectroscopic knowledge that has been acquired previously in solution leads to the conclusion that the observed excitation spectra do not originate from the isomer that was originally aimed for to be studied. Instead, and supported by computational studies, it is concluded that prior to the expansion a structural isomerization occurs that leads to a rotor with a single bond as “axle” instead of a double bond.

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