UV and IR laser spectroscopy of isolated molecular structural dynamics
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Citation for published version (APA):
Smolarek, S. (2011). UV and IR laser spectroscopy of isolated molecular structural dynamics

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Summary

Electronic and vibrational spectroscopy are powerful magnifying glasses to zoom from the macroscopic world into molecular dimensions. The bands that are observed in UV/Vis and IR spectra are associated with transitions between discrete energy levels that are uniquely associated with the molecule, and directly reflect properties at a submolecular level. They thereby provide distinctive atomic-level fingerprints of aspects like conformational and electronic structure, but also serve as probes for dynamical processes. It is therefore not surprising that these kind of spectroscopies are the primary tools in many scientific areas and technological applications.

As good as the previous may sound, the harsh reality is that under normal experimental conditions spectra contain so many bands that only a very small fraction of the potentially available information can be extracted. One of the big challenges molecular spectroscopy therefore continuously aims to tackle, is to increase the usable information by devising new experimental techniques to reduce spectral complexity. Part of the experimental efforts has been to try to reduce the molecular heterogeneity at the start of a spectroscopic measurement by reducing the internal temperature of molecules. Part of the approach has also been to eliminate perturbing interactions between the molecule of interest and its surroundings by studying isolated molecules. And, of course, the birth of the laser some 50 years ago has made its landmark in molecular spectroscopy as it started an era in which light could be generated in an almost tailor-made fashion with respect to spectral and temporal properties. Over the past decades high-resolution laser spectroscopy has thus become one of the most effective instruments to study the physical and chemical properties of small- to medium-sized neutral molecules. High-resolution laser spectroscopy of larger and charged systems still is a formidable challenge, but one that has been taken up in the present thesis by employing liquid helium nanodroplets as a means to cool down and isolate molecules. Apart from helium nanodroplet spectroscopy, the present thesis also employs traditional molecular beam methods to study the photophysics and photochemistry of molecules of interest from a biological and (nano)technological perspective.

Chapter 1 provides a background on high-resolution spectroscopy. After an introduction on the reasons why high-resolution spectroscopy is so important, a compact overview is given of the methods that are used nowadays to perform high-resolution spectroscopy. Furthermore, a short discussion is given on how scientists currently try and extend the application area of high-resolution spectroscopy to large molecular systems.
In Chapter 2 an extensive description is given of the experimental set-ups that have been used. Particular attention is given to the molecular beam machine at the University of Amsterdam as it has a number of features that generally are not found in other spectrometers. For this reason also the operation and performance of the spectrometer are discussed in more detail. Since a wide variety of multiple-resonant multiphoton ionization techniques have been employed, an important part of this chapter is also formed by an overview and description of these experiments. The chapter ends with a description of the liquid helium nanodroplet setup developed by the group of Dr. Marcel Drabbels at the Ecole Polytechnique Fédérale de Lausanne (EPFL), the setup that actually has been used in the studies described in Chapters 4-6, and in Chapter 9.

Energy and charge transport lie at the basis of many primary processes in nature as well as in technological applications. Linear $\pi$-conjugated polymers have led to the development of a large number of new materials with attractive electronic and electro-optical properties. Branched $\pi$-systems, on the other hand, have attracted considerably less attention despite the large variety of exciting applications one could envision. Chapter 3 describes spectroscopic studies on the ground, excited and ionic states of a prototypical cross-conjugated $\pi$-system, 1,1'-diphenylethylene. Excitation spectra display extensive vibrational progressions, and show that the molecule loses its ground state symmetry upon excitation. As a result, the two phenyl chromophores become nonequivalent. Quantum chemical calculations enable us to quantify these conformational changes. Ionization of 1,1'-diphenylethylene also leads to conformational changes, but without loss of symmetry. One of the striking aspects of the excitation spectrum of 1,1'-diphenylethylene is the plethora of intense vibronic bands ~1000 cm$^{-1}$ above the 0-0 transition to $S_1$, which are reasoned to find their origin in a conical intersection between $S_1$ and $S_2$.

In Chapter 4 an experimental study is reported on the conformational landscape of a succinamide-based molecular thread that is frequently employed in mechanically interlocked molecular assemblies. The latter structures are nowadays starting points for the construction of molecular machinery. Efforts to study the conformational heterogeneity of these kind of systems at a level that individual conformations can be observed have so far not been successful, primarily because of their huge conformational flexibility. Here, we demonstrate that resolution down to the individual conformation level can be obtained by dissolving them at a single-molecule level into helium nanodroplets. This is quite a remarkable accomplishment, even more in the light of the general experience so far that conformational flexibility in helium droplet spectroscopy gives mainly rise to broad phonon wings, and impedes spectral resolution.

From a photochemical point of view, the photostability of DNA bases is quite amazing. Experiments show that the excess energy that is deposited in them by absorption of light is rapidly and efficiently converted into vibrational energy, but there is
still considerable debate on the non-radiative relaxation pathways. These pathways are studied in Chapter 5 by high-resolution spectroscopy on adenine and its 9-methyladenine and 2-aminopurine derivatives seeded into helium nanodroplets. The results reported in this chapter provide novel information on the conical intersections between the lower electronically excited states, which are key to the ultrafast conversion of electronic energy. Interestingly, Chapter 5 also enables us to put the influence of the liquid helium nanodroplet environment in another perspective. As yet, it is generally assumed that this environment is quasi-nonperturbing, but Chapter 5 shows that this assumption may not be appropriate for parts of the electronic potential energy surface further away from the potential minima.

Chapters 6-8 describe high-resolution spectroscopic studies of the chromophore of the Photosactive Yellow Protein (PYP), para-coumaric acid, and derivatives of this chromophore. Since the photocycle of PYP initiates with photoinduced trans-cis isomerisation of the para-coumaric acid chromophore, many studies have pursued - unsuccessfully - the characterization of its electronically excited-state manifold under isolated-molecule conditions. Using a multi-color resonance enhanced multiphoton ionization approach and studies under liquid helium nanodroplet conditions, Chapter 6 shows that para-coumaric acid becomes accessible to high-resolution studies of its conformational and electronically excited states dynamics. The results show that upon excitation the molecule adopts a non-planar geometry. Remarkably, we obtain for the first time direct evidence for the presence and influence of an nπ* state that has been predicted by ab initio calculations, but so far had remained unobserved.

One of the reasons that para-coumaric acid has remained elusive for such a long time is that heating of the molecule appears to lead to thermal decomposition. Mass-resolved ion detection as employed in the studies reported in Chapter 6 is therefore essential to ensure that the observed spectra derive from the target molecule. In Chapter 7 it becomes clear that even under such mass-resolved conditions one still needs to be rather cautious. This chapter reports on the study of another band system detected at the mass of para-coumaric acid. Application of advanced UV and IR depletion methods show, however, that this band system finds its origin in the cluster of 4-hydroxystyrene with CO₂, thereby directly confirming the previously suggested thermal decomposition route. In the rest of this chapter the photophysical properties of the 4-hydroxystyrene-CO₂ cluster and of the mixed cluster of 4-hydroxystyrene with CO₂ and H₂O are investigated. Comparison of the UV and IR spectra of isolated 4-hydroxystyrene with those of microsolvated 4-hydroxystyrene in combination with the results of quantumchemical calculations show how environmental perturbations influence the properties of this chromophore.

In PYP para-coumaric acid is present as a thioester. The oxyster of para-coumaric acid (methyl-4-hydroxycinnamate) is therefore a first step towards a more
realistic representative of the PYP chromophore as it is employed in the protein. Chapter 8 discusses spectroscopic studies of methyl-4-hydroxycinnamate with a special emphasis on the relaxation pathways from electronically excited states by studies of regular methyl-4-OHcinnamate, the deuterated analogue methyl-4-ODcinnamate, and complexes of these two molecules with water. The results provide conclusive evidence that the dominant relaxation pathway involves the lower-lying nπ* state, and not the πσ* state that is frequently invoked for phenol-containing molecules. Apart from electronic excitation studies, Chapter 8 also reports on IR absorption studies. The vibrational markers derived from these studies are important as they enable us to assign the various conformations that are present in the experiments, and offer a probe for determining the influence of hydrogen bonding.

IR spectroscopy furnishes a detailed view on the geometrical structure of molecules, and thereby on their function. The amount of detail that can be derived from such spectra is strongly dependent on the temperature of the molecules and their environment. Superfluid helium nanodroplets have proven to form an ideal matrix for spectroscopic investigations, but until now it has not been possible to use them for the study of ionic species. This is highly unfortunate, since under real-life, aqueous, conditions most molecular systems exist in a charged form. In Chapter 9 a novel technique is presented that finds its origin in the cooling dynamics of molecular ions embedded in helium nanodroplets. We show that following vibrational excitation of the ions, highly non-thermal processes - in many ways not unlike a microexplosion within the droplet - occur that eventually lead to their ejection from the helium droplets. This allows for the detection of IR absorptions with sensitivities that are at least two orders of magnitude better than what has been possible up to now. Analyses of the IR spectra lead to the conclusion that we can also sensitively probe the charge distribution in ions using the widths of the resonances.