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Structure-specific vibrational modes of isolated biomolecules studied with mid- and far-infrared laser spectroscopy

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Akademisk avhandling för filosofie doktorsexamen i fysik, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 8 februari 2019, kl. 10.00 i PJ-salen, Institutionen för fysik, Fysikgården 2, Göteborg.

ISBN: 978-91-7833-296-0, tryckt version
ISBN: 978-91-7833-297-7, pdf nätet
Tillgänglig via http://hdl.handle.net/2077/58138

Structure-specific vibrational modes of isolated biomolecules studied with mid- and far-infrared laser spectroscopy

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Biomolecular structure elucidation is crucial for our detailed understanding of various biological processes, since there is an intimate relationship between the biomolecular function and structure. In this respect, isolated biomolecules, despite being outside of their natural environment, are perfect model systems for in-depth studies of various fundamental interactions that govern the formation of biomolecular structure. This thesis focuses on structure elucidation of isolated molecules of biological importance, with special emphasis on the development of novel infrared (IR) laser spectroscopic tools.

The first part of the thesis applies far-IR spectroscopy, which excites low-frequency molecular vibrations in the IR light wavelength range of $\lambda > 12$ μm. The far-IR range provides valuable structural information complementing the well-established mid-IR (λ = 2.5 - 12 μm) spectroscopic analysis. However, routine application of far-IR spectroscopy to biomolecular structure elucidation is complicated by the limited knowledge of structure-specific far-IR spectral features, as well as poor performance of conventional theoretical approaches for the treatment of delocalized and anharmonic far-IR vibrational modes. In the attempt to fill these knowledge gaps, we applied far-IR spectroscopy to small, aromatic molecules of biological importance, which have a relatively low number of vibrational modes in the far-IR and are amenable to highly-accurate quantum-chemical calculations and detailed vibrational assignment. Isomer- and conformer-specific far-IR features of cold isolated aminophenol and methylacetanilide molecules were obtained with IR-UV ion-dip spectroscopy and assigned with the help of quantum chemical calculations. The observed far-IR transitions associated with deformation of the peptide link, an important structural unit in proteins, were found to be highly sensitive to the peptide link planarity, trans/cis configuration, and hydrogen bonding.

The powerful conformer-selective IR-UV ion-dip spectroscopy technique applied in the first part of the thesis is unfortunately restricted to molecules that possess an aromatic UV-absorption chromophore. The studies presented in the second part of the thesis attempt to circumvent this limitation by introducing a novel approach that combines cooling of molecules in a supersonic jet, IR multiple photon dissociation (IRMPD), vacuum ultraviolet (VUV) ionization, and mass spectrometry. The approach was demonstrated by measuring the vibrational spectrum of the simplest peptide analog, N-methylacetamide, and its oligomers. The possibility to extract structural information from the IRMPD-VUV spectra was investigated for the Gly-Gly and Ala-Ala dipeptides, which are particularly interesting due to possible competition between their extended (β-strand like) and folded structures. The measured spectra for these dipeptides showed that the extended structure with weak hydrogen bonding interactions is strongly favored in the cold molecular beam due to its higher flexibility (larger entropy), as well as due to efficient collisional relaxation processes in the supersonic jet. The results show that even though IRMPD-VUV spectroscopy does not allow recording spectra of individual conformers, it nonetheless provides valuable structural information, especially for molecules that are not suited to conventional spectroscopy techniques.

Keywords: far-infrared gas-phase spectroscopy, conformers, vibrational anharmonicity, infrared multiple photon dissociation, peptide structure, folded and extended peptides, hydrogen bonding