LASER SPECTROSCOPIES OF BIOMOLECULES IN THE GAS PHASE

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Biomolecules, especially proteins and peptides, are characterized by complicated potential energy landscapes, exhibiting a huge number of minima. Understanding how these different regions of the PES landscape are explored by the system is an important issue for simulations because this motion controls the molecular flexibility, a key property for folding and functionality in the living cell. The characterization of the PES includes the investigation of the most prominent minima and of the barriers which connect them.

Ab initio calculations are a traditional approach to these issues and the development of computers enables nowadays to get reasonable accuracies for molecules as large as peptides having a few (1-5) aminoacids. Conversely, gas phase experiments also provide complementary information on these systems. The development of laser desorption techniques to vaporize molecules without damage as well as their coupling with a molecular jet enables chemical physicists to prepare cooled and isolated molecules in the gas phase. The cooling enables spectroscopists to record resolved UV and IR spectroscopic features using lasers (electronic and vibrational transitions respectively).
Basically, UV spectroscopy is sensitive to conformation whereas double resonance IR/UV spectroscopy reveals the H-bonding network of each conformation identified by its UV signature. The resolution achieved for the spectra are comparable to the best ab initio calculations carried out, and a real synergy exists in this field between experiment and theory.
Although experimentalists have gained enough data to be able to provide rough assignments of the conformations observed, a precise assignment requires a comparison with ab initio spectra, essentially in the vibrational domain. Conversely, once the assignment is carried out, the experimental data, in terms of relative energies between conformers, for instance, enables an assessment of the theoretical methods used.

After a description of the experiments carried out recently on isolated peptides, their principle and their outcome, I will focus my presentation on open issues for a deep understanding of the physics of a short peptide chain, e.g.:
- The need for reliable calculations of the relative energy of conformers, that take into account interactions like dispersion, which are ubiquitous in these systems and unfortunately difficult to account for with current ab initio techniques.
- The need for accurate calculated vibrational spectra, taking into account fine effects, like vibrational anharmonicity.
- The need for theoretical free energy surfaces to understand the conformational relaxation taking place into a molecular jet or more generally temperature effects.