

Project title: Imaging the electronic structure of vibrationally excited molecules by harmonic spectroscopy

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Current state of the art

The application of molecules in photonic devices, sensors, and switches depends not only on their electronic structure but also on the coupling between the electronic and vibrational degrees of freedom. The same holds for energy conversion processes in natural light harvesting. In spite of five decades of studies, the prediction and design of electronic dynamics in the presence of vibronic coupling is still a challenge [1]. High-harmonic (HH) spectroscopy is a powerful tool to study the electronic structure of molecules and solids and its variation with nuclear motions [2]. In this method, a strong ultrashort laser pulse causes tunnel ionization, and the emission resulting from the subsequent recombination of the released and accelerated electron is analyzed. For molecules, it was demonstrated that changes of the electronic structure, such as by isomerization, as well as of the geometry, e.g. by low-frequency vibrations, leave characteristic finger prints in the harmonic spectra that allow to characterize the molecular dynamics and to disentangle electronic, vibronic, and vibrational effects [3]. In these experiments the changes in the molecular structure and the excitation of vibrations are typically induced by impulsive stimulated Raman scattering caused by a strong ultrashort pump pulse, which at the same time drives the HH generation. In pioneering experiments, two pulses were used, with the first one responsible for the Raman excitation, and the second one as driver for the HHs [4]. However, by impulsive Raman scattering in molecules with several vibrational modes, a superposition of random vibrational coherences is launched, and it is not possible to address the nuclear degrees of freedom separately and selectively. In the present project, we will achieve the selectivity by infrared excitation pulses resonant with specific vibrational frequencies.

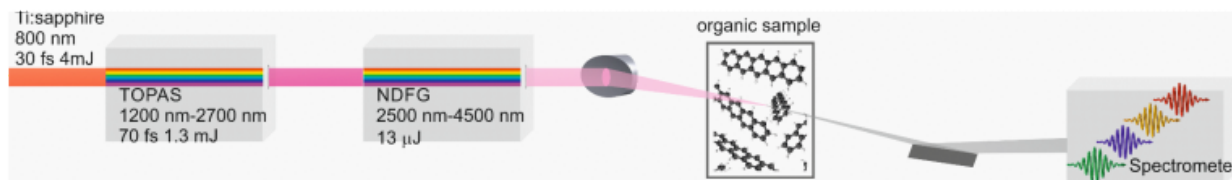


Figure 1: Setup for generation Harmonics from molecular structures using MIR pulses.

Research goals and working program

We combine a broad expertise in high-harmonic generation (HHG) with experience in fast molecular processes. Theoretical support is supplied by experts performing simulations of HH spectra by ab-initio methods and semi-classical modelling.

In the project, HH spectroscopy is combined with the selected excitation of specific vibrational modes of molecular targets to study the impact of vibronic coupling on the electronic structure and the resulting time-dependent changes of this structure. We expect several different processes to influence the harmonic spectra: a lowered ionization potential in the stretched state of a molecule and a corresponding change of the HH cut-off energies as well as a variation of the overlap between the recolliding electron and the nuclear wavefunction changing the efficiency of the generation process. In order to obtain control over the vibrational motion with respect to the harmonic generation process, the vibration is resonantly excited by an ultrashort

MIR pulse, whereas the harmonics are generated by a phase-locked pulse at shorter wavelengths. The MIR pulse is obtained by difference-frequency generation between the signal and the idler of a continuum-seeded optical parametric amplifier, see Fig 1. The carrier-envelope phase of the fundamental pump is transferred to the signal as well as to the MIR pulses. Using the pump also for the HHG in the molecular target, the HH process should occur synchronized with the MIR carrier wave and the vibrational coherences induced by it. As the actual time window of the generation of the harmonics is shorter than a vibrational period, the molecular movement is frozen on the time scale of the HHG. Changing the delay between the pulses allows then to sample the electronic structure during a vibrational oscillation. This experimental approach should be applicable to multiple molecular target classes such as molecules in the gas phase and free-standing polymer films. We will first perform pump-probe studies and investigate how the HH spectrum reacts to the population of vibrational levels. In a second step, control of the MIR carrier phase with respect to the pump pulse will be established, and the impact of vibrational coherences will be studied by varying this phase.

As representatives for large molecules with extended conjugated backbones, polymer films will be used. The MIR pulse induces an anisotropy in the molecular samples as excitation occurs preferentially for molecules with their transition dipole parallel to the MIR polarization. Varying the polarization of the HH pump relative to that of the MIR pulse can be used to filter and enhance the effect of the vibrational excitation and to obtain information about vibronic couplings. In the case of the polymers, stretching the films will induce a prealignment of the molecular constituents, which will be exploited in the analysis.

We are looking for a dedicated PhD candidate that is eager to work on molecular effects in strong field physics such as harmonic generation. Additionally, you accept the challenge to work with ultrashort pulses in the MIR region and state of the art spectroscopic techniques. In our daily lab life, trusting team work and appreciative communication is a mandatory prerequisite for successful work. In this perspective, we would like to offer this research work to a candidate that shares our values and likes to complement our young and motivated team in a fruitful manner.

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