In the ATTO-DYNAMICS project, we studied the process of high harmonic generation (HHG) from different molecules in order to probe electronic and nuclear rearrangements on an attosecond timescale (1 attosecond=10^{-18} second). In high harmonic generation, a strong laser pulse with a wavelength in the near infrared, typically 800 nm, interacts with a gas medium and a small amount of the light is up-converted into a series of odd multiples (called harmonics) of the laser frequency. These harmonics correspond in the time domain to a train of attosecond bursts of extreme ultraviolet (XUV) light. In this harmonic emission are imprinted: i) the structure of the emitting electronic state(s), which allows a tomographic reconstruction of the radiating orbital(s), and ii) the dynamics occurring in the system. In this project, we proposed to progress towards the acquisition of time-resolved images of molecular orbitals in the most comprehensive and general way, using a 3 step approach: (1) Perform an advanced characterization of the harmonic radiation; (2) Image a changing orbital resulting from nuclear/electronic dynamics; (3) Generalize the scope of molecular tomography to asymmetric and/or low-ionization potential molecules to make the technique ubiquitous.

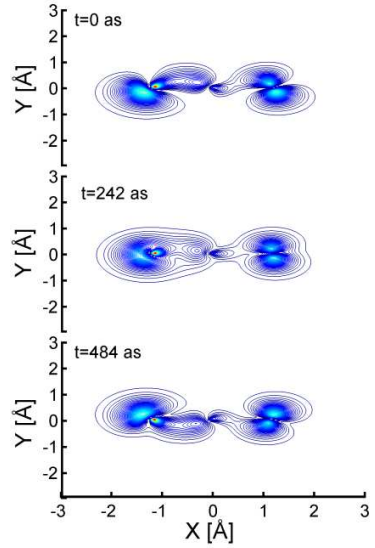

Figure 1: Simulation of the hole movement in the N_2O molecular ion after tunnel ionization. Relative amplitude and phase for the two contributing electronic states are extracted from the experimental data.

First, we have developed a new experimental setup in order to characterize completely the amplitude and phase of the harmonic emission from small linear molecules that are aligned with respect to the polarization of the driving laser. The full mapping of the phase as a function of both photon energy and alignment angle required combining two very complex techniques (RABBIT and 2-source interferometry), which had never been done before. We succeeded to take data from N_2, CO_2 and N_2O aligned molecules. Using another experimental setup, we could combine RABBIT measurements with polarization characterization: this allowed us to perform vectorial orbital tomography of N_2 orbitals.

Second, during the experiments with N_2O, we discovered new effects in the high harmonic generation which could not be explained by the structure of the highest occupied molecular orbital (HOMO). Instead we found that during the interaction with the laser field, two electronic states are coherently excited and form a hole wave packet moving on an attosecond timescale in the molecule after tunnel ionization. The population of each state depends on the angle between the molecular axis and the laser polarization. We focused on exploring this coherent electronic motion inside the molecule, and compared it to the one existing in CO_2, that had already been reported. The striking difference in the harmonic phase behavior led us to the development of a multi-channel model allowing the extraction of the relative weight and phase of the two channels involved in the emission. This allowed in turn reconstructing the image of the “hole” wavepacket evolving in the molecule on an attosecond timescale (Figure 1).

Very spectacular results were obtained in a study of the high harmonic generation from SF_6 molecules, which showed a very complex harmonic spectrum superimposing contributions from several valence states close to the ionization threshold and the presence of two shape resonances within the measured spectral range. Preliminary analysis reveals that from the six valence states (shown in Figure 2.), three are strongly contributing: the two highest states (X and A) and a lower one (E). The contribution from the E state is uncommon, as in general the contribution to the HHG process from lower valence states is exponentially reduced. In SF_6 the structure of the E orbital seems to be so favorable that it compensates

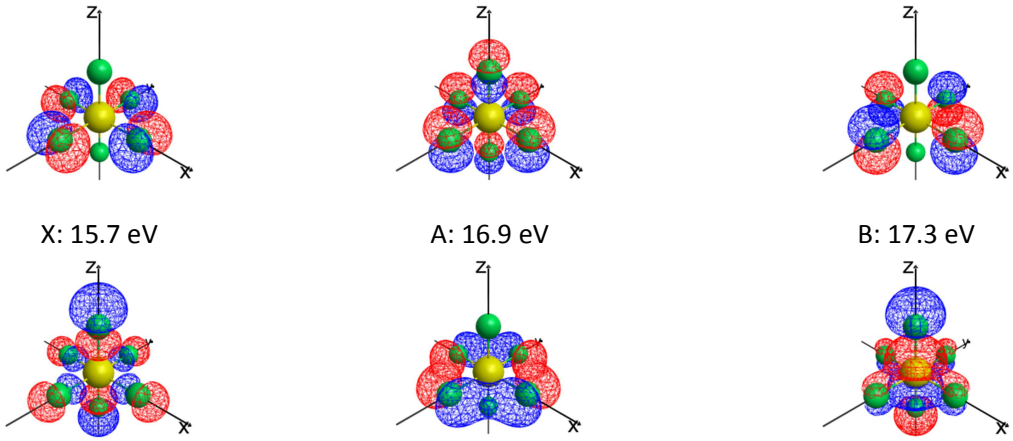

Figure 2: Hartree-Fock calculations of the orbital structure for the six highest valence states of SF_6
The binding energies are taken from high precision synchrotron measurements.

for this reduction. Our results in SF_6 support the assumption that a superposition of several electronic states is a general feature for molecules, if multiple states are close to the ionization threshold with strongly different orbital structures. Our work on N_2O and SF_6 was strongly supported by calculations done by the group of Alfred Maquet and Richard Taieb from the LCPMR in Paris.

Third, our studies of the harmonic emission from different small hydrocarbons, including acetylene, revealed that their low ionization potential strongly limits the extent of the harmonic spectrum and thus the possibility of observing structural/dynamical effects. We thus decided to move the driving wavelength to the mid-IR to extend significantly the harmonic spectrum. An optical parametric amplifier (OPA) has recently been installed on the kHz PLFA laser system. The combination of this mid-IR tunable laser with the full mapping technique developed in Task 1 will allow a significant extension of the scope of molecular tomography, which was the general objective of Task 3.

In conclusion, the advanced experimental tools that we have developed have uncovered new interesting physics occurring in a variety of small molecules. The observation of coherent excitation of molecular states in the ionization process and the ability to model it within some approximations opens ways to a deeper understanding of the interaction of molecules with strong light fields. As we are able to characterize the contribution from multiple states in amplitude and phase, we can visualize the movement of the valence hole in the ion after ionization; the extension of this approach to more complex molecules might allow to follow ultrafast charge migration inside the system. From a fundamental point of view we might have the chance now to extract a very interesting but unknown variable from the data, the phase difference of the different states at the instant of tunnel ionization of the molecule. Our current modeling of the experimental results indicates that there is no such tunnel ionization phase but the theoretical analysis has to be improved further to give a definite answer. A phase difference might indicate a nonzero time delay for the tunnel ionization of the different states, an open topic in the fundamentals of quantum mechanics since many years.