Final Technical Report 4/2010 to 4/2015

Project: Ultrafast Electron Diffraction from Aligned Molecules

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Program Scope or Definition

The aim of this project was to record time-resolved electron diffraction patterns of aligned molecules and to reconstruct the 3D molecular structure. The molecules are aligned non-adiabatically using a femtosecond laser pulse. A femtosecond electron pulse then records a diffraction pattern while the molecules are aligned. The diffraction patterns are then be processed to obtain the molecular structure.

Introduction

A new experimental setup was designed, constructed and tested during the first two years of the project. The experiment consisted of three main components: the electron gun, the laser system and the experimental chamber. A seeded supersonic gas jet was used to introduce the target molecules into the experiment with a low rotational temperate. A femtosecond laser pulse intersects the molecules and aligns them along the direction of the laser polarization. The alignment survives only for a short time (a few ps) after the laser traverses the gas jet. A short electron pulse was used to probe the molecules. The electron pulse was generated using an electron gun that is synchronized with the laser pulses. A small fraction of the laser energy is used to trigger electron emission from a photocathode, and the electrons are accelerated in a static field and collimated before reaching the target. The diffraction pattern from the aligned molecules was captured in a custom-made detector, and the image was stored on the computer for analysis. The detector consists of a phosphor screen, image intensifier and CCD which are all fiber coupled to maximize the transmission through each element. The phosphor screen converts each incident electron into photons which are transmitted to the image intensifier and multiplied before reaching the CCD.

Progress Report

In this project, we have shown, for the first time, the retrieval of the three-dimensional structure of isolated molecules from diffraction patterns, reaching atomic resolution [1]. We have used CF_3I, a symmetric top molecule, for the first demonstration. This molecule has a simple three-dimensional structure and a high polarizability for alignment. It required two major breakthroughs to achieve the image reconstruction, first a very high temporal resolution in the experiment and second a new data analysis algorithm that works for partially aligned molecules.

In order to ensure that a field-free molecular structure is measured, we have used impulsive alignment. A femtosecond laser pulse interacts with the molecules and creates a rotational wavepacket. This wavepacket then evolves and peak alignment is reached 2 ps after the laser interaction. The alignment, however, lasts only for about 1 ps. This required an overall resolution of the experiment of 1 ps or better. We were able to achieve a resolution of 850 fs by careful design of the electron source and experimental geometry, and control of the size of electron, laser and gas beams in the interaction region. This is the first gas phase electron diffraction experiment with sub-ps resolution.

We have also developed a new algorithm to retrieve the structure from diffraction patterns. Several algorithms exist to retrieve structure from diffraction patterns of aligned molecules, but they require perfect (or near perfect) alignment, which is very challenging to achieve in the conditions of a diffraction experiment. We have developed a genetic algorithm that can combine several diffraction patterns with partial alignment to recreate the diffraction pattern corresponding to perfect alignment. For molecules with rotational symmetry, a single diffraction pattern is sufficient to retrieve the structure if the alignment axis is perpendicular to the electron beam. We took diffraction patterns corresponding to different angles between the alignment axis and the electron beam, and then used a genetic algorithm to recreate the pattern for perfect alignment. Once this pattern is available, one can use existing phase retrieval algorithms to recover the structure. An important advantage of laser alignment is that the alignment axis can easily be varied by rotating the linear polarization vector of the laser. Figure 1 shows the retrieved structure. The molecule is aligned only along one axis (in the C-I direction) and is free to rotate about this axis. In this case, the retrieved structure was rotationally averaged, and the off-axis F atoms appear as a continuous band.

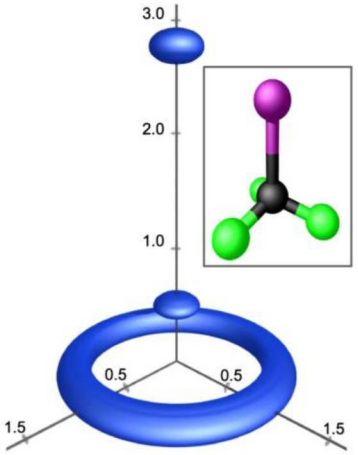

Figure 1. *Experimental reconstruction of the CF_3I molecule [1]. The molecules rotate freely about the C-I axis, which results in a cylindrically symmetric structure. The units are in angstroms. The inset shows a theoretical model of the CF_3I molecule for comparison. The fluorine atoms are colored light green, carbon is black, and the iodine atom is purple.*

Given that our experimental setup already has high temporal resolution, it will only be natural to extend the experiments to image time-varying molecular reactions in real time. Some molecular reactions, however, can take place in just a few femtoseconds, beyond the resolution of our current setup. One possible path to few-femtosecond resolution is to reduce the charge per pulse to a single electron, thus eliminating space charge effects. However, one must still consider the dispersion of single-electron wavepackets. We have recently demonstrated theoretically that the dispersion can be controlled using only static electric and fields, and that an attosecond electron pulse can in principle be delivered on a target [2].

After the first experiments, we have now extended the retrieval algorithm to work also for asymmetric molecules [3]. The alignment process is different for symmetric-top and asymmetric molecules. For symmetric top molecules, a linearly polarized laser will affect the angular distribution of the most polarizable axis, while the angular distribution of the perpendicular axis remains random. We had used this fact in our retrieval algorithm. For asymmetric molecules, two molecular axes are affected by the laser pulse. We found that by probing the molecules at the right time, one can still generate a distribution

where one axis is aligned and the other is quasi-random. In addition, we improved on an existing phase retrieval algorithm to retrieve a true 3D structure, i.e. the x, y and z coordinates of the atoms. We did this by using a two-step retrieval process. In the first step, two diffraction patterns are combined using a genetic algorithm to recreate a diffraction pattern corresponding to perfect 1D alignment. In the second step, we use an iterative phase retrieval algorithm that works with multiple cylindrical harmonics to retrieve the position of the atoms in cylindrical coordinates. Figure 2 shows the results of the algorithm for a simulated diffraction pattern of the of trifluorotoluene ($C_6H_5CF_3$) molecule. The figure shows that the retrieval works in identifying the position of the individual atoms with sub-Angstrom resolution. This is very significant because it allows us to work with a larger class of molecules.

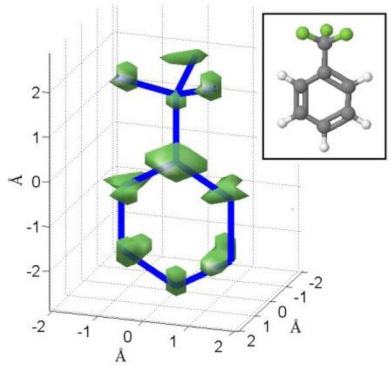

Figure 2. *Isosurface rendering of the reconstructed 3D molecular structure of trifluorotoluene ($C_6H_5CF_3$). The overlapped blue sticks show the frame of the molecule with non-hydrogen atoms in both ends of each stick. The ball-and-stick model of the molecule is shown in the inset. The simulation of the diffraction patterns used realistic experimental parameters.*

Experimentally, we have further explored the effect of a laser field on molecular alignment and structure. More specifically, we have investigated the effects of femtosecond laser pulses that are strong enough to align the molecules but still below the ionization threshold. We have used a linear molecule, carbon disulfide (CS_2), for first experiments. The degree of alignment typically increases with laser intensity, however, we have observed that the degree of alignment saturates well before the intensity reaches a level where ionization becomes significant. In addition, we have seen evidence of structural changes after the laser interaction. We are investigating these issues by probing the molecules with ultrafast electron diffraction. The molecules are probed at the peak of the alignment, and the diffraction pattern provides information on both the structure and angular distribution of the molecule. This research is ongoing at the end of the grant period. Figure 3 shows the angular distribution retrieved from diffraction patterns of CS_2 at three different intensity levels. The angular distribution first becomes narrower with increasing intensity, but little change is observed when the intensity is further increased.

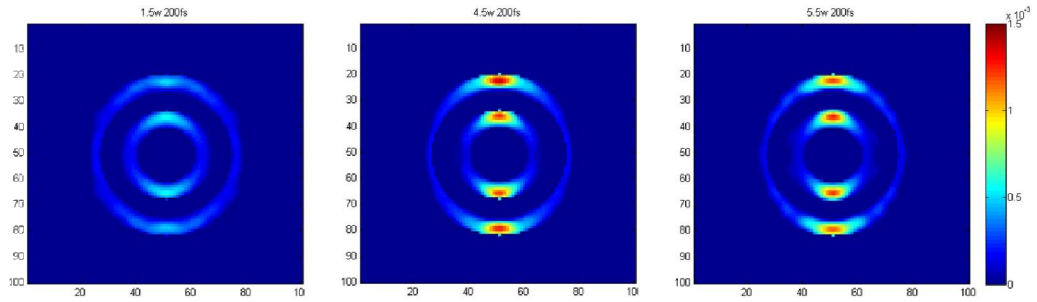

Figure 3. Angular distribution extracted from diffraction patterns of CS_2 at the peak of the laser induced aligment. The inner ring corresponds to the C-S distance, while the outer ring corresponds to the S-S distance. A laser pulse duration of 200 fs was used, and the pulse energy was, from left to right, 0.3 mJ, 0.7 mJ and 0.9 mJ, repectively.

We have also started constructing an oven that will allow us to study molecules with a low vapor pressure. The oven will be used to create a molecular beam that can be made supersonic by adding a flow of helium. The oven is currently being tested.

Publications

1. Christopher J. Hensley, Jie Yang, and Martin Centurion, "Imaging of Isolated Molecules with Ultrafast Electron Pulses" Physical Review Letters **109**, 133202 (2012) (*This publication was featured in APS Physical Review Focus on 9/28/2012 and also appeared as a story on UNL Today on 10/04/2012)*

2. Peter Hansen, Cory Baumgarten, Herman Batelaan, Martin Centurion, "Dispersion Compensation for Attosecond Electron Pulses" Applied Physics Letters **101**, 083501 (2012)

3. Jie Yang, Varun Makhija, Vinod Kumarappan and Martin Centurion, "Reconstruction of three-dimensional molecular structure from diffraction of laser-aligned molecules" Structural Dynamics 1, 044101 (2014).