Laser-controlled Molecular Alignment and Orientation at FLASH and XFEL

Marc Vrakking
FOM Institute AMOLF

XFEL Workshop Hamburg – October 8-10, 2008
Acknowledgements

FOM-AMOLF, NL
Per Johnsson (FLASH)
Arnaud Rouzee (FLASH, NO)
Omair Ghafur (NO)
Wing Kiu Siu (FLASH, NO)
Ymkje Huismans (FLASH)
Arjan Gijsbertsen (NO)

University of Lyon
Franck Lépine

Garching, D
Matthias Kling

LOA, Paris
Tatiana Martchenko

+ technical support
Rob Kemper
Hinco Schoenmaker
Ad de Snaijer

Funding:
NWO-VICI, NWO-ECHO, FOM-PR
EU (MC-RTN „XTRA“)

FLASH, Hamburg
Stefan Duesterer
Artem Azima
Franz Tavella
Nikola Stojanovic
Contents

- What is molecular alignment resp. orientation, and why is it an interesting property?
- Laser-controlled molecular alignment (adiabatic vs. impulsive, 2D vs. 3D)
- Laser-controlled molecular orientation
- Laser-controlled molecular alignment at FLASH
What is molecular alignment resp. orientation, and why is it an interesting property?

Alignment: \( \langle \cos^2 \theta \rangle \)

Orientation: \( \langle \cos \theta \rangle \)

\[ \langle \cos^2 \theta \rangle = 1/3 \]
\[ \langle \cos \theta \rangle = 0 \]

“Isotropic”

\[ \langle \cos^2 \theta \rangle > 1/3 \]
\[ \langle \cos \theta \rangle = 0 \]

“Aligned”

\[ \langle \cos^2 \theta \rangle > 1/3 \]
\[ \langle \cos \theta \rangle > 0 \]

“Oriented”
What is molecular alignment resp. orientation, and why is it an interesting property?

- Molecular alignment and orientation are suitable observables that allow us to assess our ability to exert strong-field control over molecular properties.

- Molecular alignment and orientation provide the connection between laboratory-frame measurements and measurements in the molecular-frame.

Example: Photoionization of H₂ at XUV wavelengths

Laboratory frame Photoionisation $\leftrightarrow$ Molecular Frame Photoionisation

$P(\cos\theta) = 1 + \beta P_2(\cos\theta)$

$P(\cos\theta) \sim$ electron scattering in the molecular frame
Photoionization of H$_2$ at XUV wavelengths

**Laboratory frame Photofragmentation** ↔ **Molecular Frame Photofragmentation**

Raw velocity map image, recorded at FLASH, February 2007

Inverted velocity map image

**46 eV photoionization of H$_2$ VMI**
Johnsson et al., J. Mod. Optics 55, 2693 (2008)

**240 eV photoionization of H$_2$ COLTRIMS**
Velocity Map Imaging - 1

Experimental setup

Characterization of an attosecond pulse train using RABBITT

Velocity Map Imaging - 2

Raw image for 2-photon ionisation of Ar by 532 nm light

Slice through the 3D velocity distribution, obtained by Abel inversion of the image $\Delta v/v = 1\%$ (N.B. also use iterative technique)
COLTRIMS (Reaction Microscope)  
(Cold Target Recoil Ion Momentum Spectroscopy)

Using COLTRIMS an experiment can be performed where the alignment and orientation can be read out afterwards, provided that the molecule dissociates.

Challenge: coincidence measurement → one can study only one/few molecules per laser shot
When it’s hard to use only one molecule....

$\text{N}_2$ ground state orbitals determined by molecular tomography (= HHG)

Pump-probe spectroscopy at emerging XUV and x-ray FELs

Challenges:
- finite repetition rate
- few events despite high intensity
- dynamics = very time-consuming

Let’s try to align/orient all molecules in our sample beforehand

Interaction of a molecule with a DC field and an intense laser field

\[ H = J^2 + V_\mu (\omega, \theta_s) + V_\alpha (\omega_{\text{par}}, \omega_{\text{perp}}, \theta_L) \]

Interaction with a DC field (\( \varepsilon_s \))

\[ V_\mu (\omega, \theta_s) = -\omega \cos \theta_s \]

\[ \omega = \frac{\mu \varepsilon_s}{B} \]

Interaction with an intense laser field (\( I_L \))

\[ V_\alpha (\omega_{\text{par}}, \omega_{\text{perp}}, \theta_L) = -(\Delta \omega \cos^2 \theta_L + \omega_L) \]

\[ \Delta \omega = \omega_{\text{par}} - \omega_{\text{perp}} \]

\[ \omega_{\text{par, perp}} = \frac{\alpha_{\text{par, perp}} I_L}{2B} \]

Alignment/orientation with a DC field

1965: Hexapole state-selection and orientation of polar molecules (Bernstein)

1991: “Brute-force” orientation (Loesch)
J. Chem. Phys. 93, 4779 (1990)
Alignment/orientation with intense laser fields - overture

1991: Ion TOF distributions in Multi-Electron Dissociative Ionization

**FIG. 2.** TOF ion mass spectra of CO with the laser polarization (a) parallel to the drift tube axis and (b) perpendicular to the drift tube axis. The scale for the ion signals is the same for both spectra.

Alignment/orientation with intense laser fields - 1

1998: Adiabatic molecular alignment (Sakai & Stapelfeldt)

\[ I_2 \rightarrow I_{2,\text{aligned}} \rightarrow I^+ I \rightarrow I^{++} I \]

YAG       Pump       Probe

Adiabatic vs. diabatic alignment

Alignment of I$_2$ under adiabatic conditions
Stapelfeldt and Seideman

Orientation (and alignment) under diabatic (impulsive) conditions
Vrakking and Stolte
Probing alignment in real time:
Long pulse IR + Short pulse IR Pump-probe experiments

- **Long pulse:**
  - Alignment, w.o. ionization

- **Short pulse:**
  - Ionization, w.o. alignment

Ionization intensity

Long pulse IR pump (appr. 3 psec)

Short pulse IR probing (appr. 100 fsec)

Elapsed time
Alignment/orientation with intense laser fields - 2

2001: Impulsive molecular alignment (Rosca-Pruna and Vrakking)

Popular activities since these earliest demonstrations of laser-induced alignment

- From diatomic to complexer, polyatomic molecules
- From 2D to 3D dynamic alignment
- Schemes to optimize dynamic alignment
- Alternative probes of molecular alignment
- From molecular alignment to molecular orientation

Laser-induced orientation demonstrated, but not yet better than convention DC techniques
Reach a very high degree of impulsive orientation by combining:

- Hexapole state-selection
- A dc electric field
- Femtosecond laser excitation
- Laser pulse shaping
From Alignment to Orientation

Ghafur et al, submitted
So far, $\langle \cos \theta \rangle = 0.74$ has been demonstrated and $\langle \cos \theta \rangle = 0.95$ may soon become possible!
So what are we doing this for?

Pump-probe spectroscopy at emerging XUV and x-ray FELs

Ambitions:
1) A time-resolved molecular interferometer
2) Time-resolved intra-molecular electron diffraction
So what are we doing this for? - a molecular interferometer -

Photoelectron spectra

- I + I-
- I$_2^-$

Kinetic energy (eV)

Pump-probe delay (fs)

Photoelectron momentum distributions

Anisotropy parameter

So what are we doing this for?
- intra-molecular electron diffraction -

C(1s) core-shell photo-emission from CO using 294 to 326 eV radiation.

Away from the Carbon atom (black) the angular distribution is relatively unstructured.

In the direction of the Oxygen atom (red) a diffraction structure is observed.

The AMOLF VMIS

Interaction chamber

Intermediate chamber

Source chamber

LN$_2$ cooled copper shield and $\mu$-metal shield

Entrance slit-pair

FEL

Pneumatic valve

Skimmer

Pneumatic valve

LN$_2$ cooled copper shield

Available for user experiments

Pulsed valve with access from outside
Pump-probe experiment on $\text{CO}_2$ alignment (FLASH Campaign 2008, BL2)
Pump-probe experiment on CO₂ alignment (FLASH Campaign 2008, BL2)

Finding the two-color overlap

- Use bond-softening in H₂
- XUV-production of H₂⁺
- IR-dissociation into H⁺ + H
- Velocity and angle-resolved detection of H⁺
Pump-probe experiment on CO$_2$ alignment (FLASH Campaign 2008, BL2)

Time-dependent alignment of CO$_2$

- Use IR to align the molecule
- Use FLASH FEL to dissociatively ionize
- Velocity and angle-resolved detection of O$^+$
- Step towards molecular frame dynamics (fragmentation, imaging)

Next step: photodissociation of Br$_2$ (spring 2009)
Conclusions and outlook

Molecular alignment and orientation techniques are able to provide high-quality samples for experiments at FLASH & XFEL (est. \( <\cos\theta> = 0.95 \) possible).

Molecular alignment at FLASH has been demonstrated in CO\(_2\).

Alignment and orientation provide the link between laboratory-frame and molecular-frame experiments, and thus enable new experimental methodologies (based on intra-molecular electron diffraction & interference).

Our next experiment at FLASH will be an attempt to follow dissociation dynamics of Br\(_2\) using these methods.

We have constructed a Velocity Map Imaging Spectrometer (VMIS) that has been optimized for experiments at FLASH, and that is available for experiments by other users.