

# 自由電子雷射化學動力學和分子成像應用 (Application of FEL in chemical dynamics and molecule imaging)

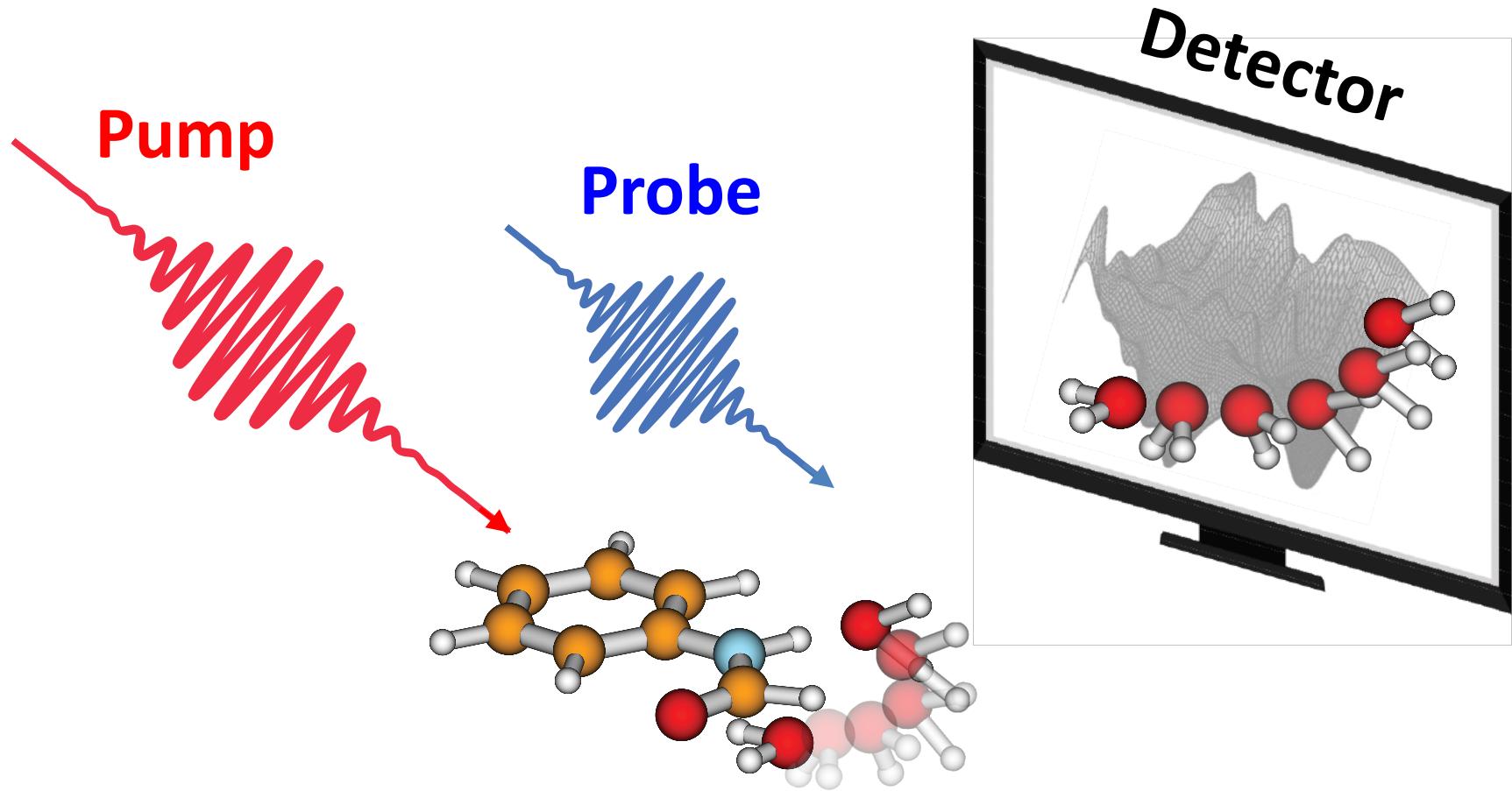
張元賓 (Yuan-Pin Chang)

國立中山大學化學系

# Outline

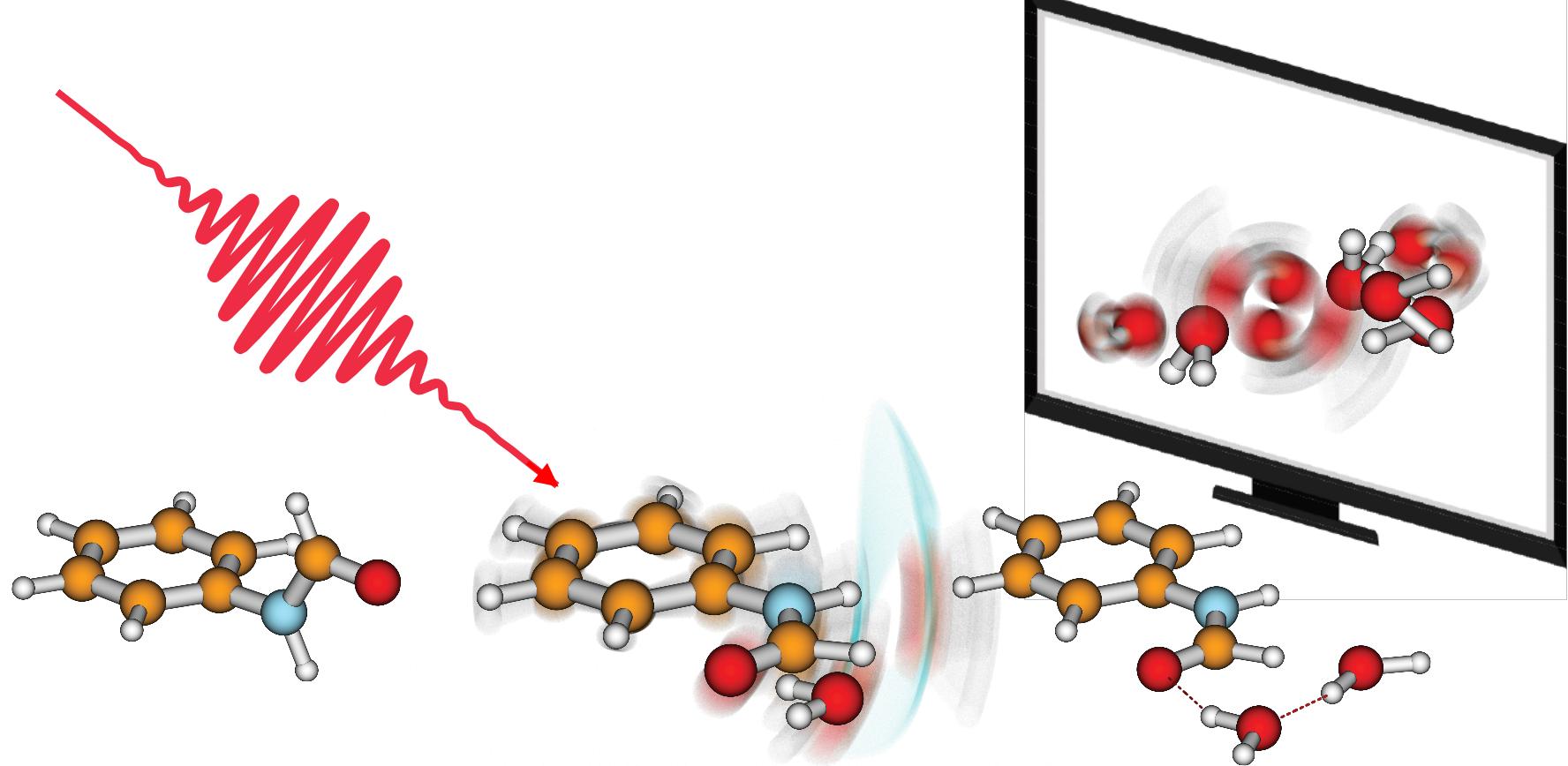
- Part 1: Diffractive imaging of isolated molecules with X-ray free-electron lasers (FEL)
  - State and structure selection of molecules (量子態與結構篩選)
  - Mix-field orientation of molecules (分子空間排序)
  - FEL x-ray diffraction of molecules (X光繞射)
- Part 2: Imaging molecular structure through femtosecond photoelectron diffraction on aligned and oriented gas-phase molecules
  - Photoelectron diffraction of molecules
- Part 3: Trapping single particles for imaging and spectroscopic applications
  - Optically trapping of particles

# Motivation: study molecular frame dynamics

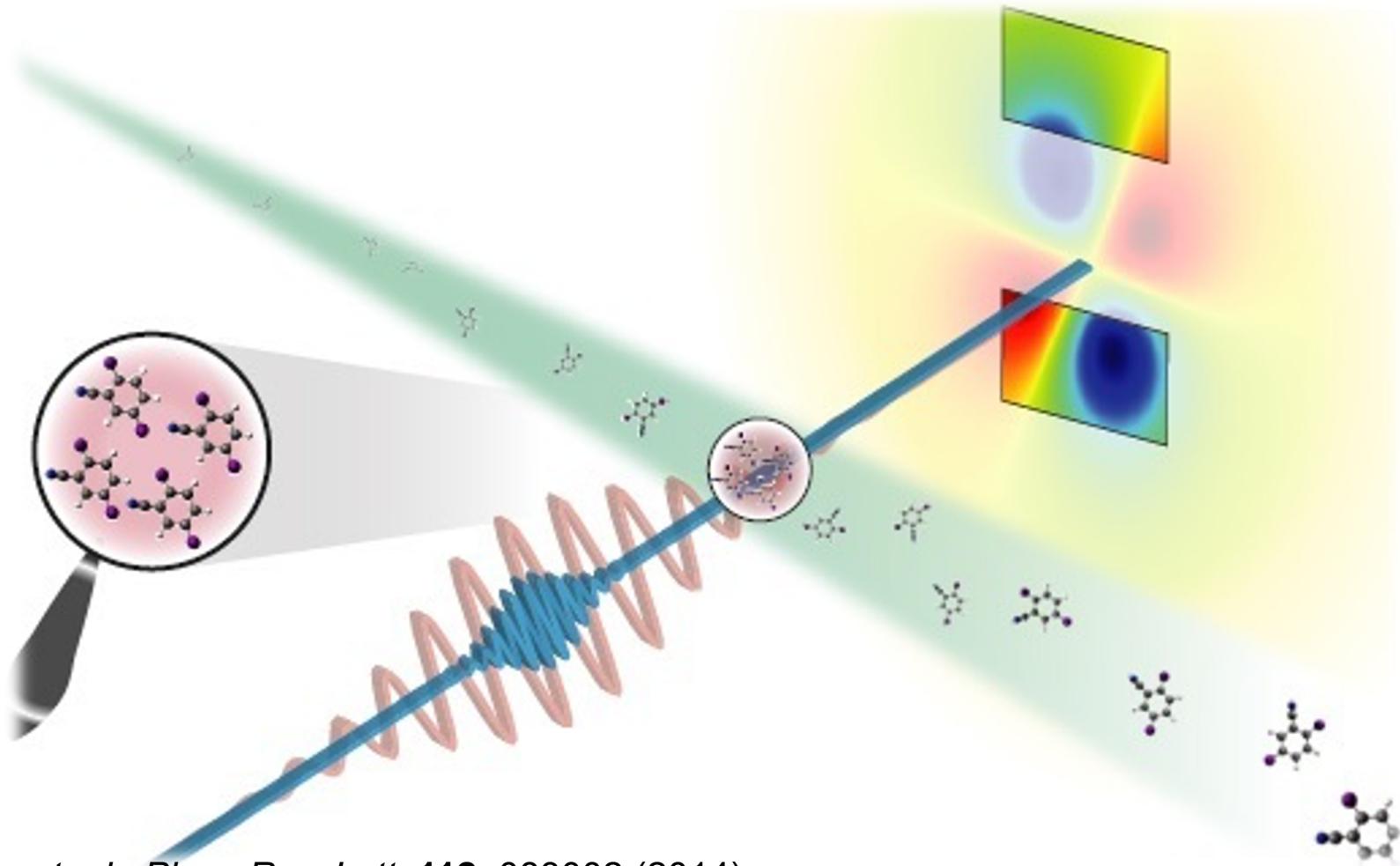


Study 1) intermolecular interaction dynamics in the 2) molecular frame of a complex system by using 3) controlled molecular samples

# Where is my “controller”?



# Part I – single molecule X-ray diffraction



J. Küpper et. al., *Phys. Rev. Lett.* **112**, 083002 (2014)

S. Stern et. al., *Faraday Discuss.* **171**, 393 (2014)

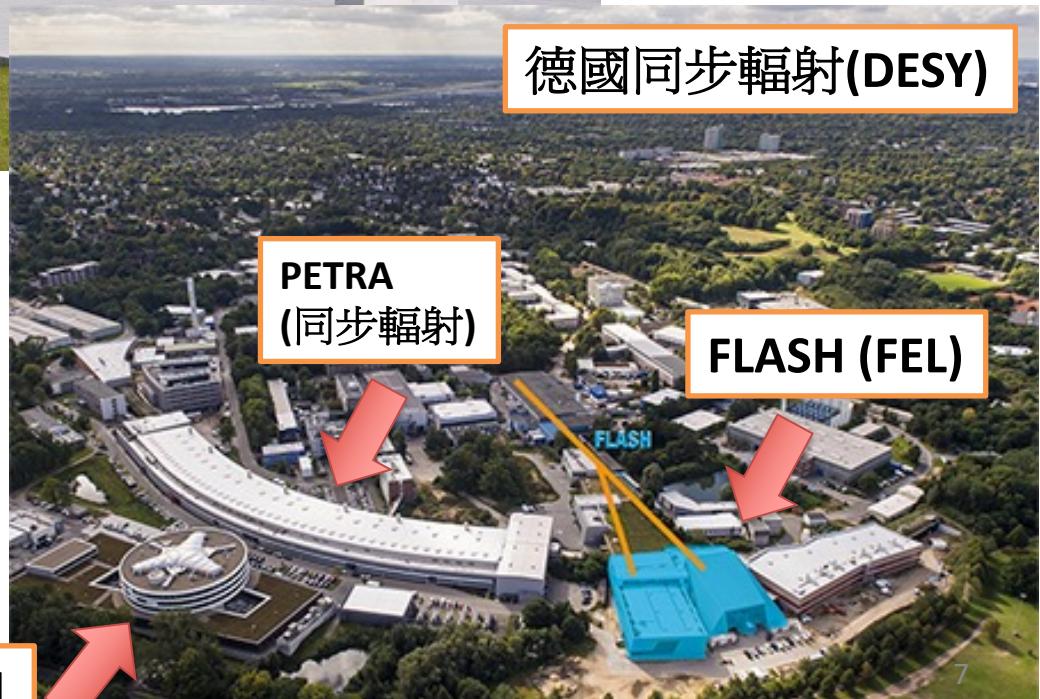
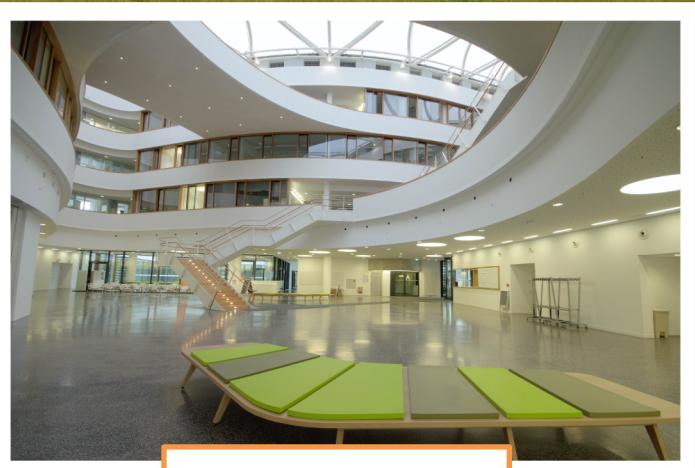
T. Kierspel et. al., *J. Chem. Phys.* **152**, 084307 (2020)

# Center for free-electron laser science (CFEL), DESY, Hamburg, Germany



FLASH (FEL)

- 4.2 nm – 45 nm
- 50 fs – 200 fs



# People involved in this work

Jochen Küpper,<sup>1,2,3,4,5,\*</sup> Stephan Stern,<sup>1,2</sup> Lotte Holmegaard,<sup>1,6</sup> Frank Filsinger,<sup>4,5,a</sup> Arnaud Rouzée,<sup>7,8</sup> Artem Rudenko,<sup>5,9,10</sup> Per Johnsson,<sup>11</sup> Andrew V. Martin,<sup>1,b</sup> Marcus Adolph,<sup>12</sup> Andrew Aquila,<sup>1,21</sup> Saša Bajt,<sup>21</sup> Anton Barty,<sup>1</sup> Christoph Bostedt,<sup>13</sup> John Bozek,<sup>13</sup> Carl Caleman,<sup>1,14</sup> Ryan Coffee,<sup>13</sup> Nicola Coppola,<sup>1</sup> Tjark Delmas,<sup>1</sup> Sascha Epp,<sup>5,9</sup> Benjamin Erk,<sup>5,9,c</sup> Lutz Foucar,<sup>5,15</sup> Tais Gorkhover,<sup>12</sup> Lars Gumprecht,<sup>1</sup> Andreas Hartmann,<sup>16</sup> Robert Hartmann,<sup>16</sup> Günter Hauser,<sup>17,18</sup> Peter Holl,<sup>16</sup> Andre Hömke,<sup>5,9</sup> Nils Kimmel,<sup>17</sup> Faton Krasniqi,<sup>5,15</sup> Kai-Uwe Kühnle,<sup>9</sup> Jochen Maurer,<sup>6</sup> Marc Messerschmidt,<sup>13</sup> Robert Moshammer,<sup>9,5</sup> Christian Reich,<sup>16</sup> Benedikt Rudek,<sup>5,9,d</sup> Robin Santra,<sup>1,2,3</sup> Ilme Schlichting,<sup>15,5</sup> Carlo Schmidt,<sup>5</sup> Sebastian Schorb,<sup>12</sup> Joachim Schulz,<sup>1,e</sup> Heike Soltau,<sup>16</sup> John C. H. Spence,<sup>19</sup> Dmitri Starodub,<sup>19,f</sup> Lothar Strüder,<sup>17,20,g</sup> Jan Thøgersen,<sup>6</sup> Marc J. J. Vrakking,<sup>7,8</sup> Georg Weidenspointner,<sup>17,18</sup> Thomas A. White,<sup>1</sup> Cornelia Wunderer,<sup>21</sup> Gerard Meijer,<sup>4,h</sup> Joachim Ullrich,<sup>9,5,d</sup> Henrik Stapelfeldt,<sup>6,22</sup> Daniel Rolles,<sup>5,15,21</sup> and Henry N. Chapman<sup>1,2,3</sup>

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<sup>4</sup>Fritz Haber Institute of the

<sup>5</sup>Max Planck Advanced Study Gro

<sup>6</sup>Department of Chemistr

<sup>7</sup>FOM Institute AMOLF, Sc

<sup>8</sup>Max-Born-Institute, M

<sup>9</sup>Max Planck Institute for

<sup>10</sup>J. R. Macdonald Laboratory, Department o

<sup>11</sup>Department of Physics, Lu

<sup>12</sup>Technical Univ

<sup>13</sup>Linac Coherent Light Source, SLAC National Accele

<sup>14</sup>Uppsala University, Department of

<sup>15</sup>Max Planck Institute for

<sup>16</sup>PNSensor

<sup>17</sup>Max Planck Semicon

<sup>18</sup>Max Planck Institute for

<sup>19</sup>Department of Physics, Ari

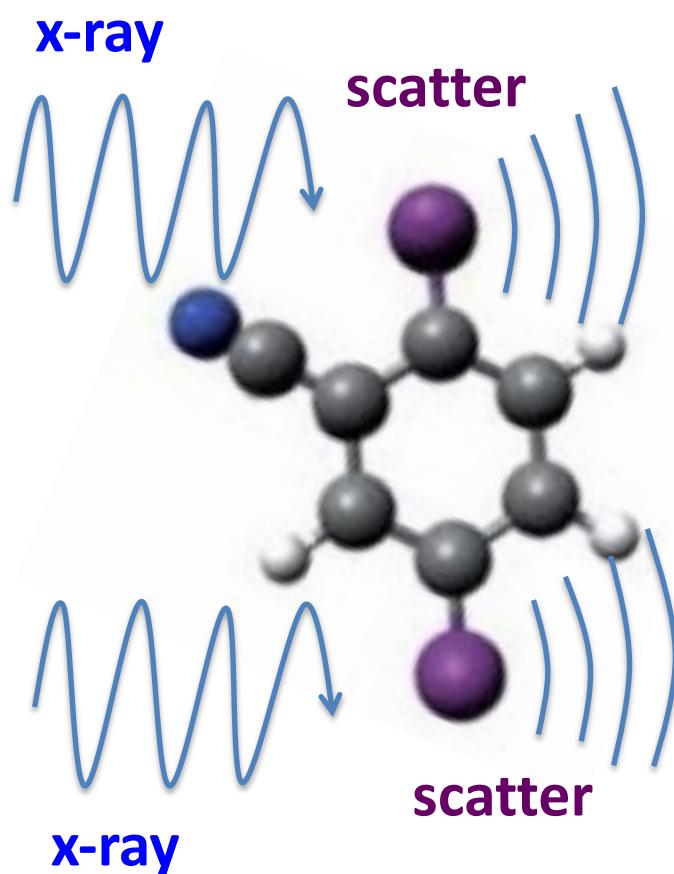
<sup>20</sup>University of Siegen, Emmy-Noe

<sup>21</sup>Deutsches Elektronen-S

<sup>22</sup>Interdisciplinary Nanoscience Center (INANO), Aarhus University,

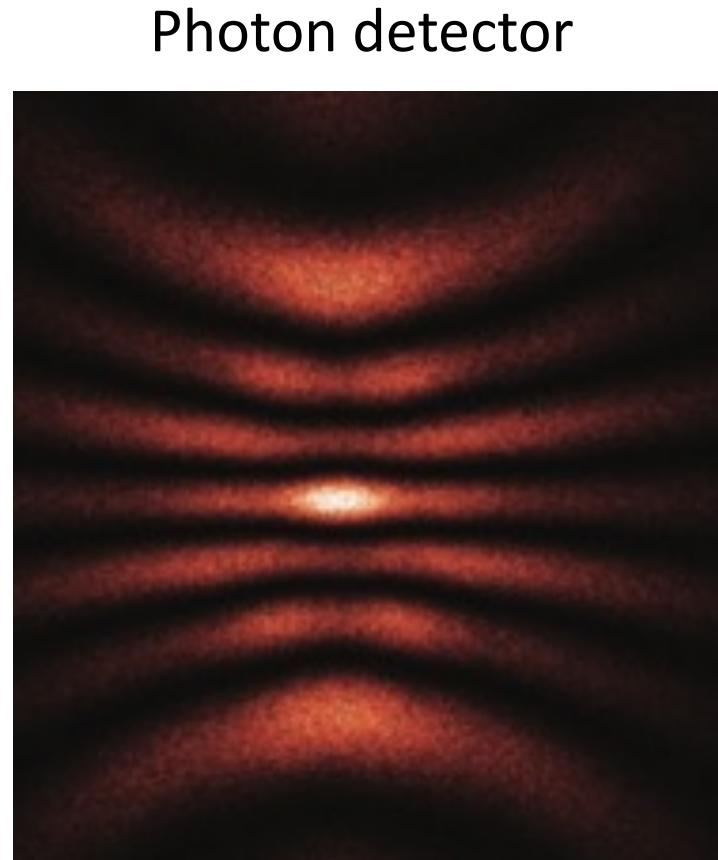


# Motivation: molecular frame information from X-ray diffraction

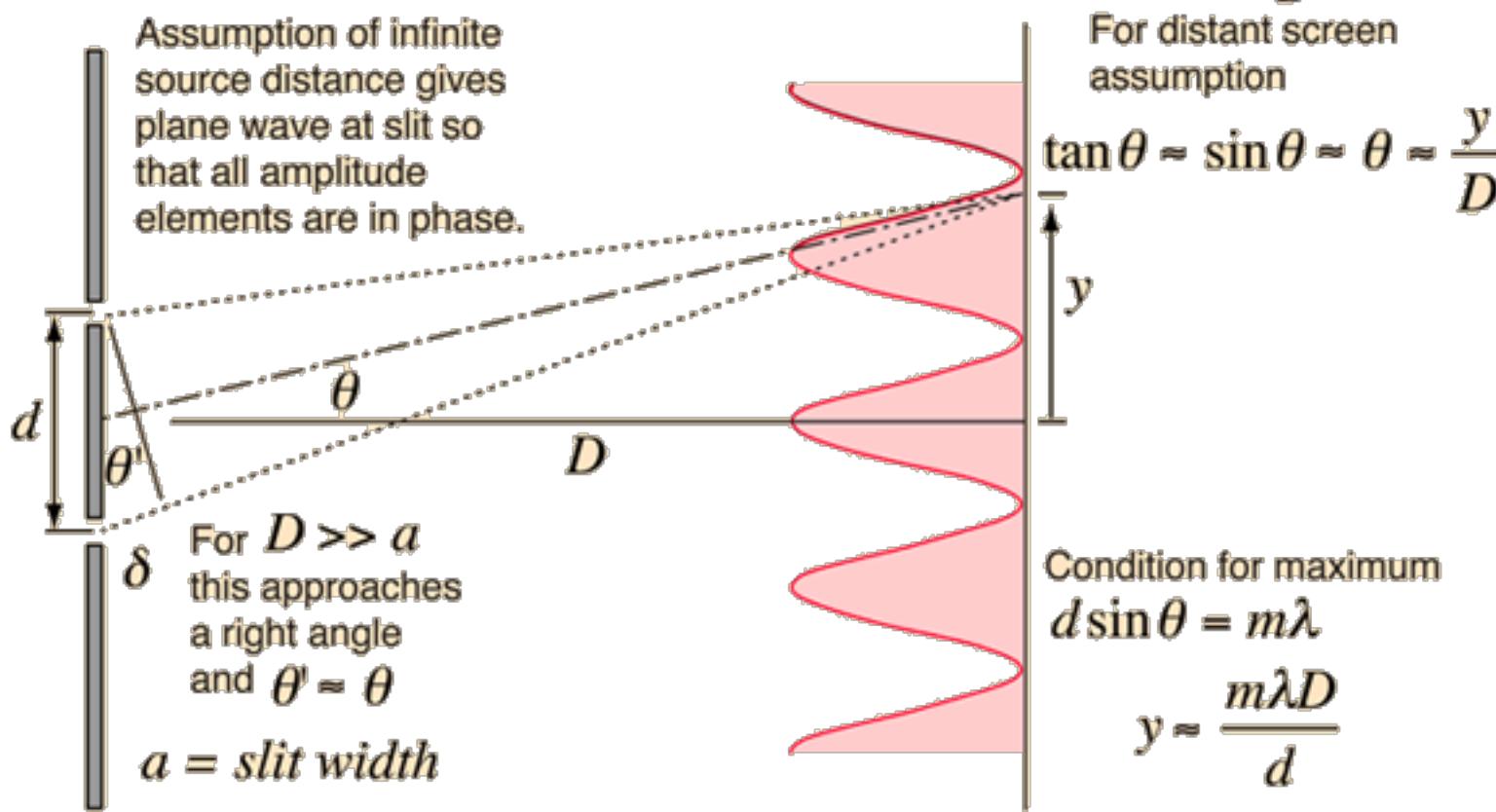


Spatially fixed

2,5-diiodobenzonitrile (DIBN)

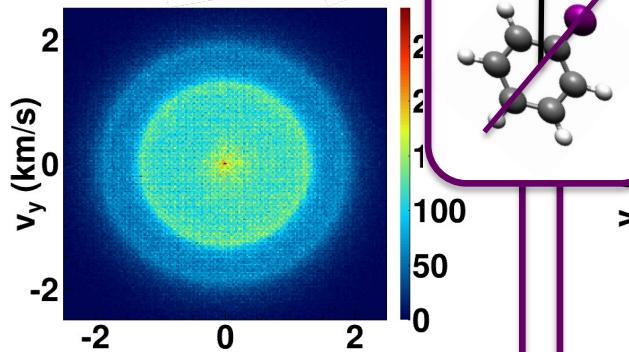
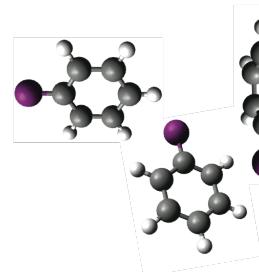


# Double slit interference



# Technique 1: spatial Control of molecules (分子空間排序)

Random Orientation

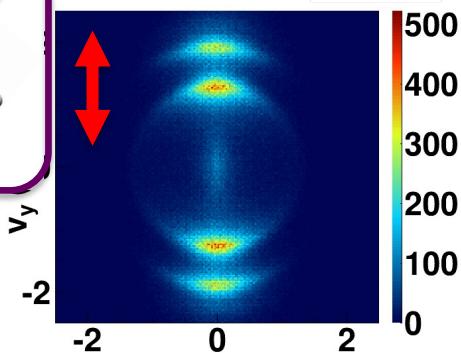
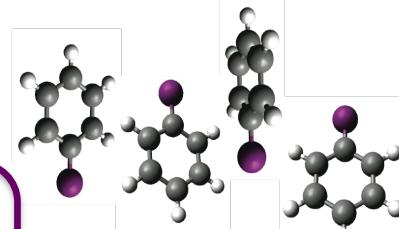


$$\langle \cos^2 \theta \rangle_{2D} = 1/2$$

$$\langle \cos^2 \theta \rangle_{3D} = 1/3$$

$$\langle \cos \theta \rangle = 0$$

Laser Alignment

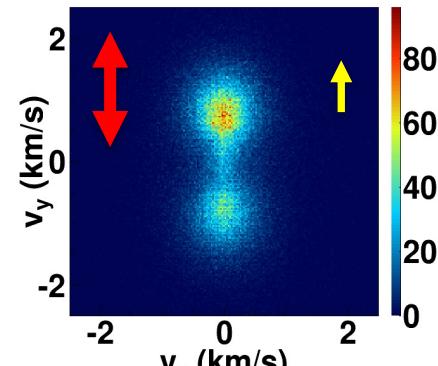
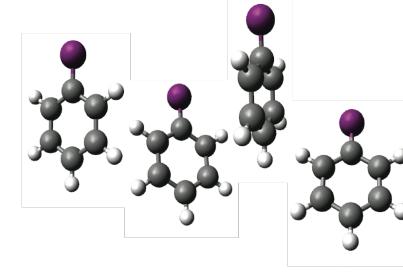


$$1/2 < \langle \cos^2 \theta \rangle_{2D} < 1$$

$$1/3 < \langle \cos^2 \theta \rangle_{3D} < 1$$

$$\langle \cos \theta \rangle = 0$$

Mixed field orientation



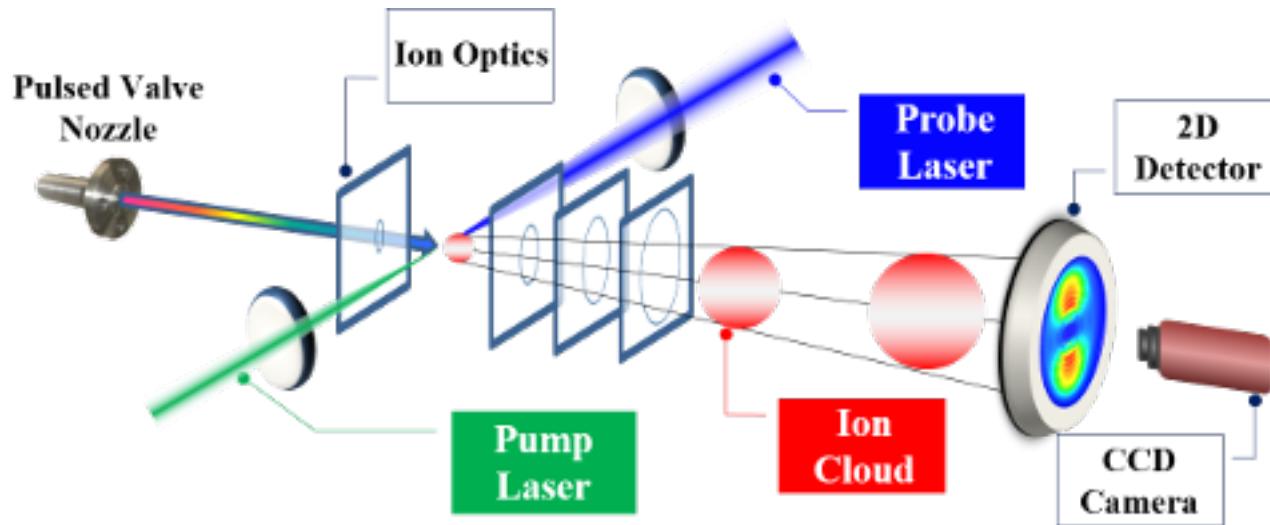
$$1/2 < \langle \cos^2 \theta \rangle_{2D} < 1$$

$$1/3 < \langle \cos^2 \theta \rangle_{3D} < 1$$

$$\langle \cos \theta \rangle > 0$$

Probing scheme: **Coulomb explosion**  $\Rightarrow$  Ion velocity parallel to the C-I bond

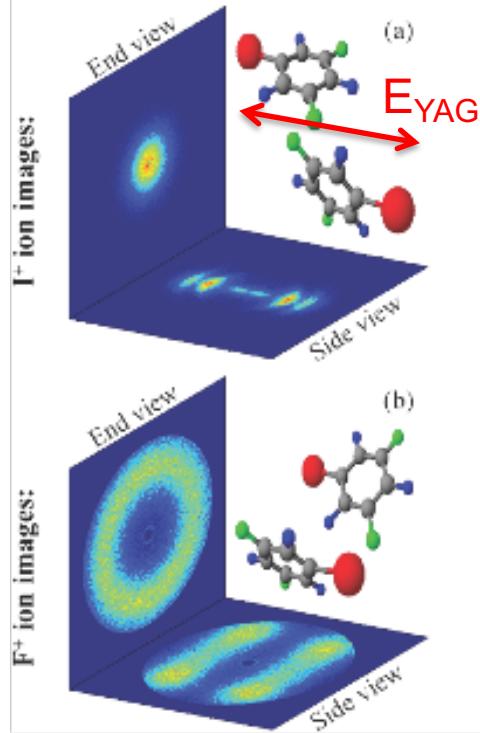
# Velocity map imaging



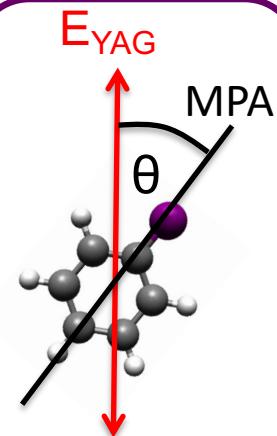
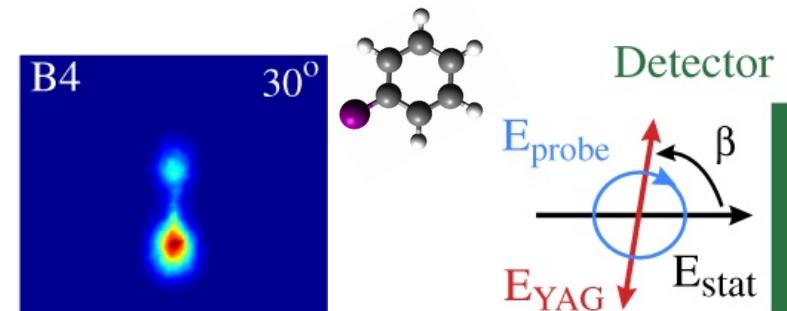
(曾建銘老師會有更精彩的介紹)

# Technique 1: Laser alignment / mix-field orientation

## 1D Alignment



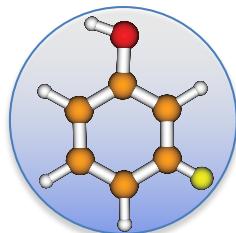
## Mix-field orientation



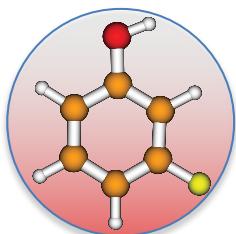
$$\text{Laser alignment: } H = -\frac{1}{4}\epsilon^2(\alpha_{||} - \alpha_{\perp}) \cos^2 \theta$$

$$\text{Mixed field orientation: } H = -\vec{\mu} \cdot \vec{E} - \frac{1}{4}\epsilon^2(\alpha_{||} - \alpha_{\perp}) \cos^2 \theta$$

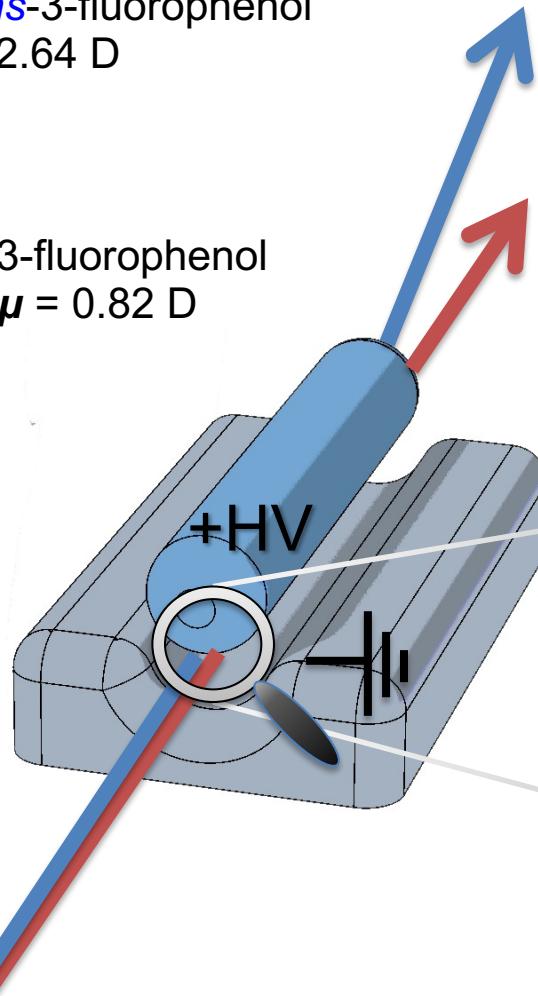
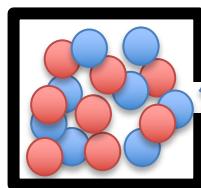
# Technique 2: state and structure separation (量子態與結構篩選)



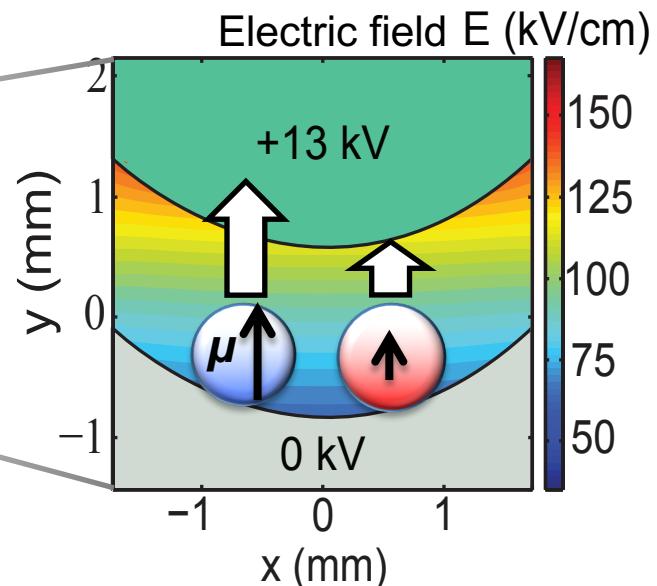
Trans-3-fluorophenol  
 $\mu = 2.64 \text{ D}$



Cis-3-fluorophenol  
 $\mu = 0.82 \text{ D}$



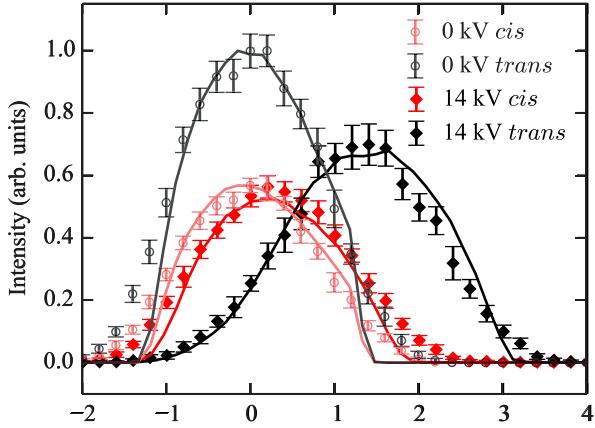
Stark energy  $W = -\mu \cdot E$   
Deflection force  $F = -\nabla(\mu \cdot E)$



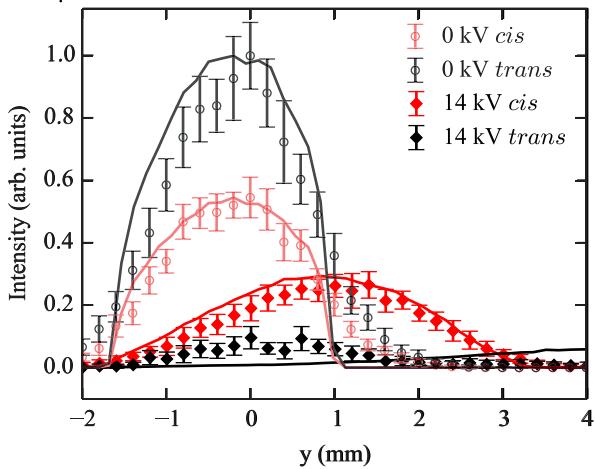
# Technique 2: spatial separation of conformers and rotational states

## Molecular beam intensity profiles

### Helium expansion

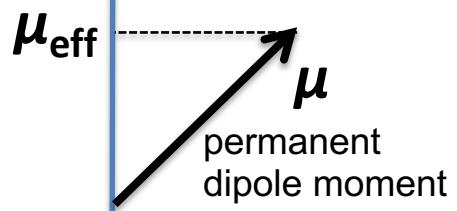


### Neon expansion



## Theory (Stark effect of polar molecules)

$E$  (electric field)



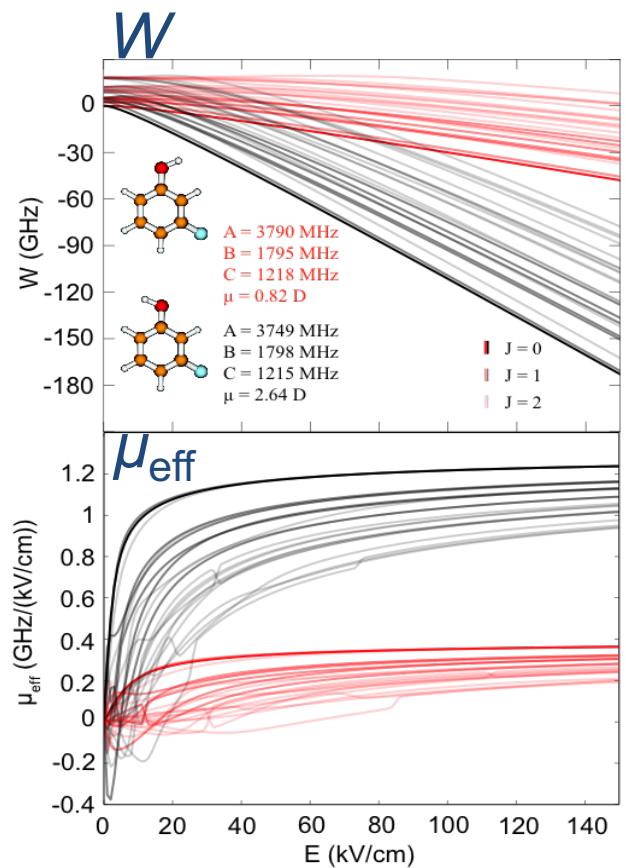
$$\text{Stark energy } W = -\mu \cdot E$$

Deflection force:

$$F = -\nabla(\mu \cdot E) = \mu_{\text{eff}} \nabla E$$

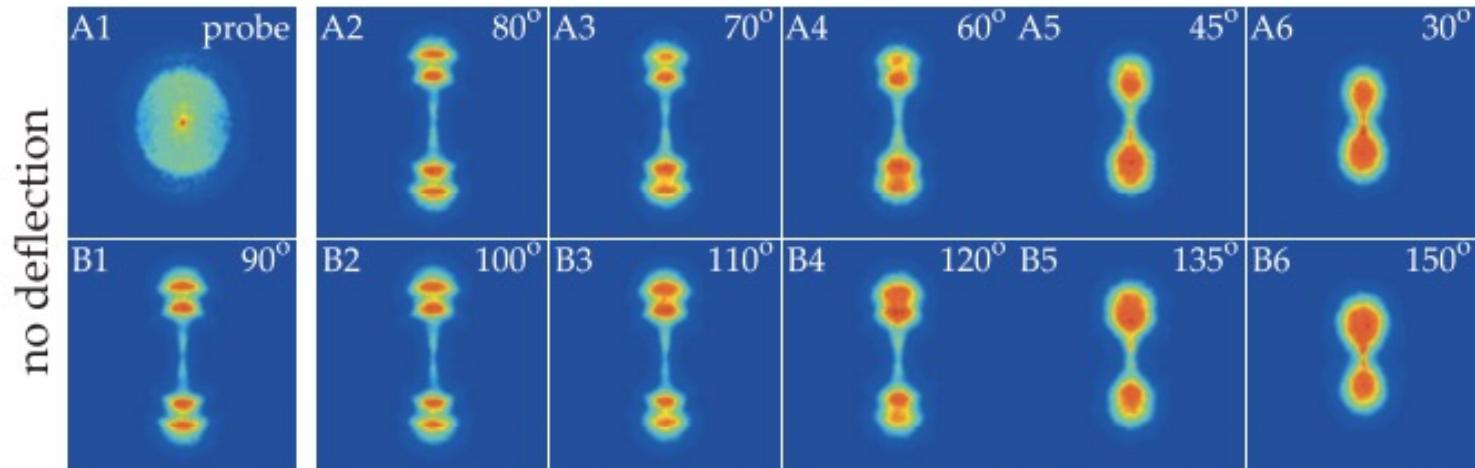
Effective dipole moment:

$$\mu_{\text{eff}} = -\frac{dW}{dE}$$

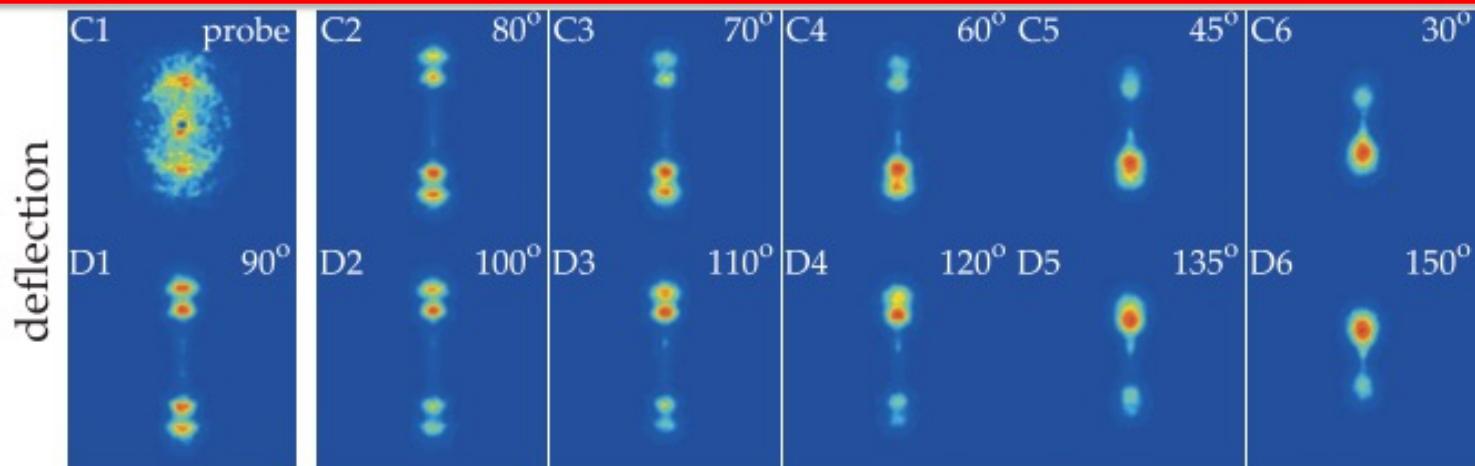


# Improved laser alignment due to state selection

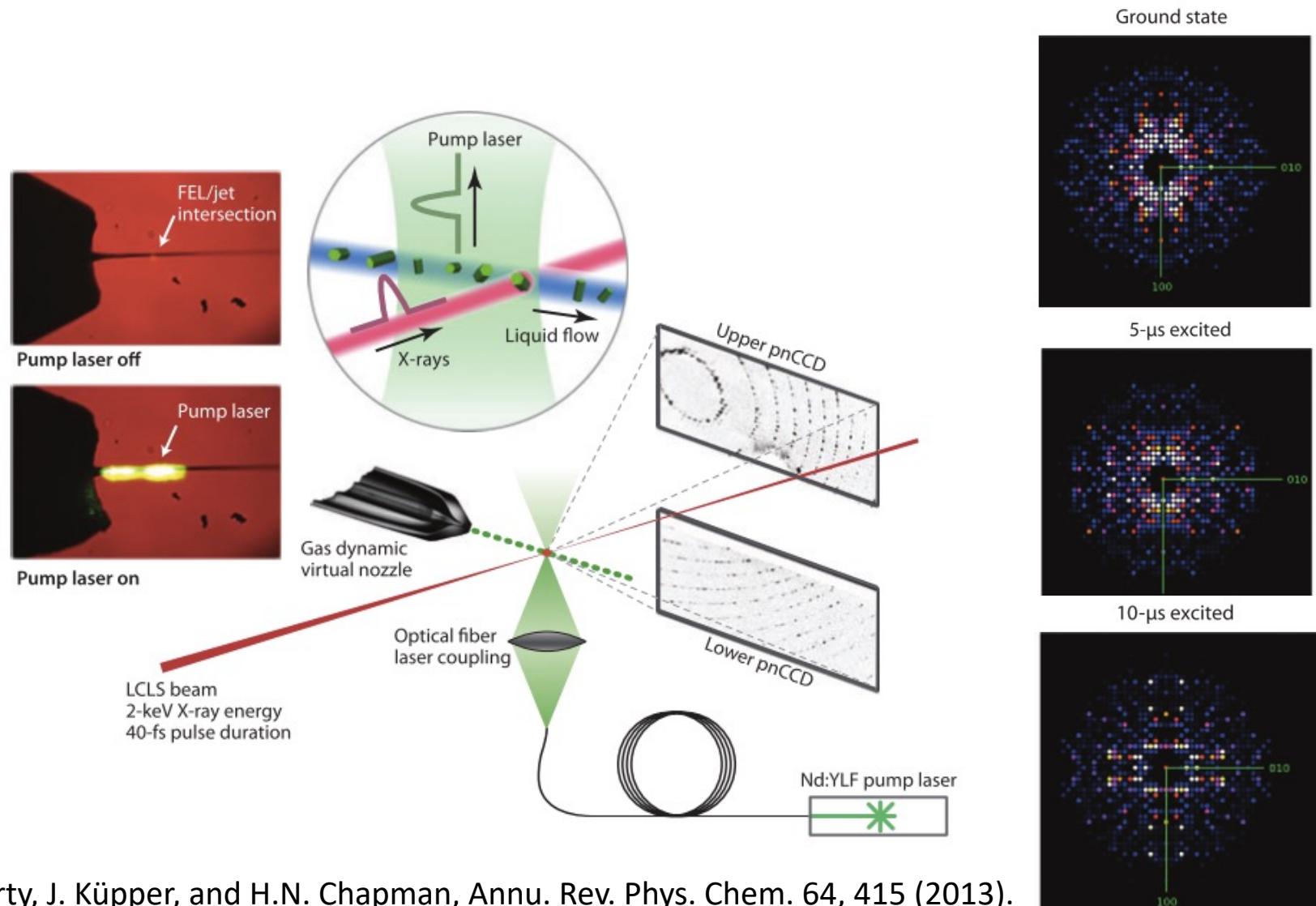
No state selection



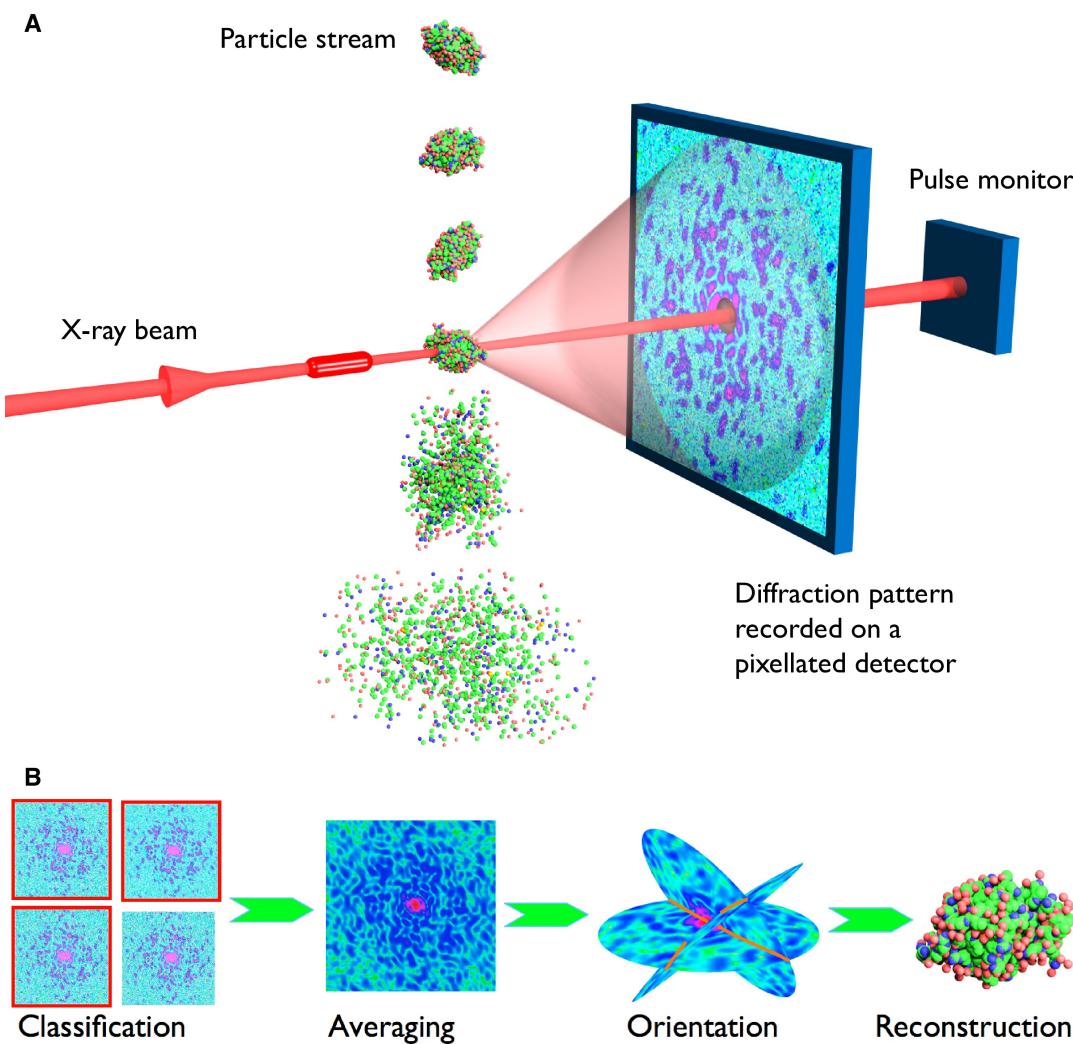
State-selected samples



# Technique 3: X-ray diffraction - protein nanocrystals for determining protein structures



# XFEL single-particle diffractive imaging pipeline

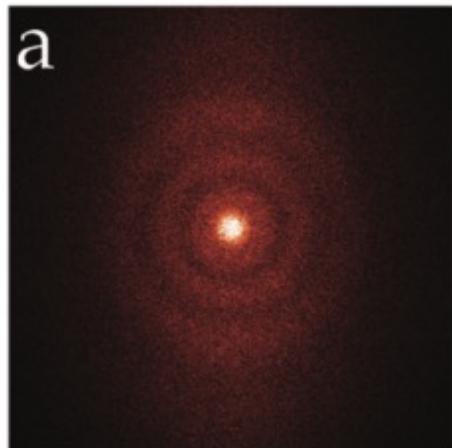


# Technique 3: X-ray diffractive image pattern simulations of isolated molecules

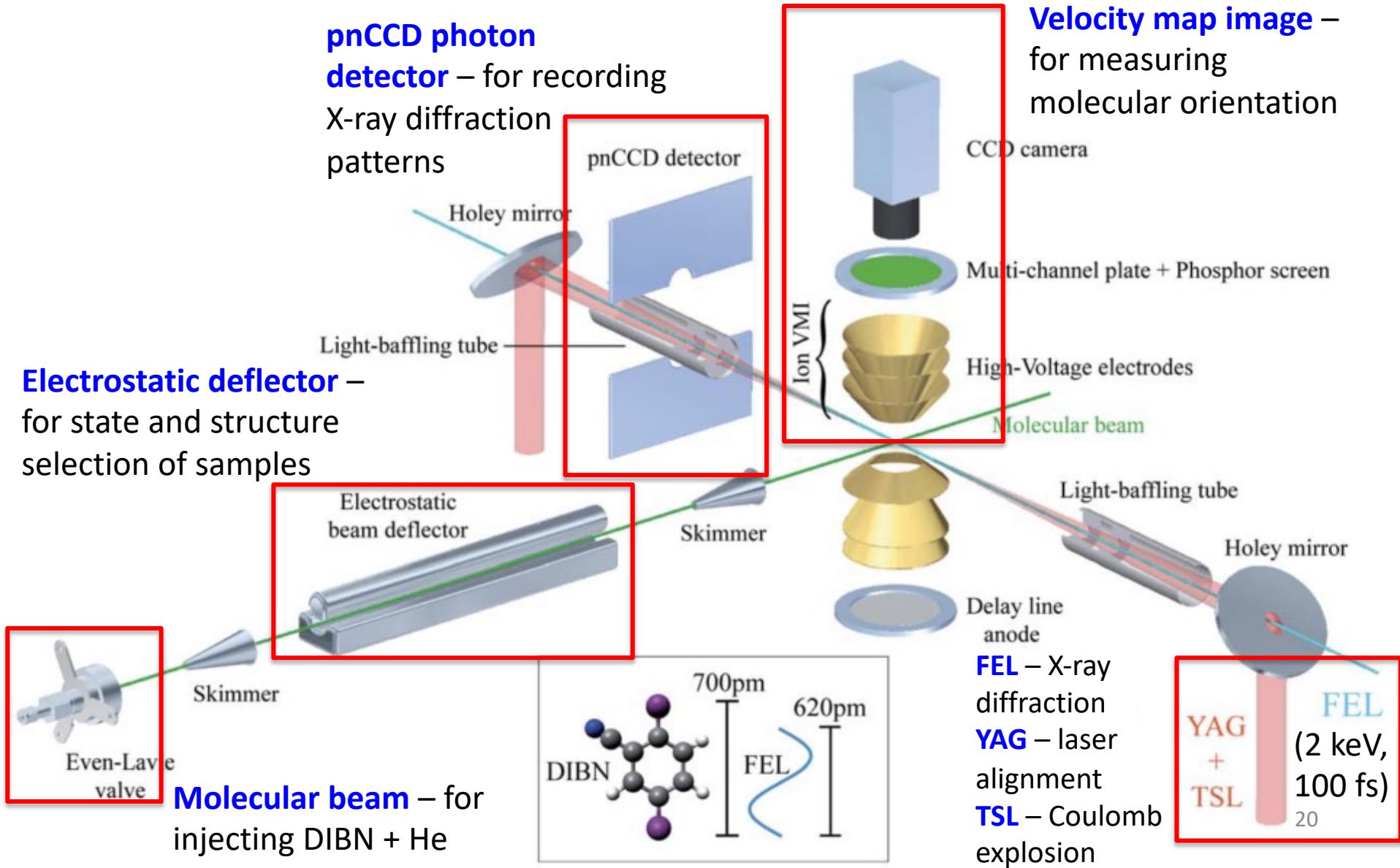


Isotropic sample

$$\langle \cos^2 \theta \rangle_{2D} = 0$$



# Experimental setup



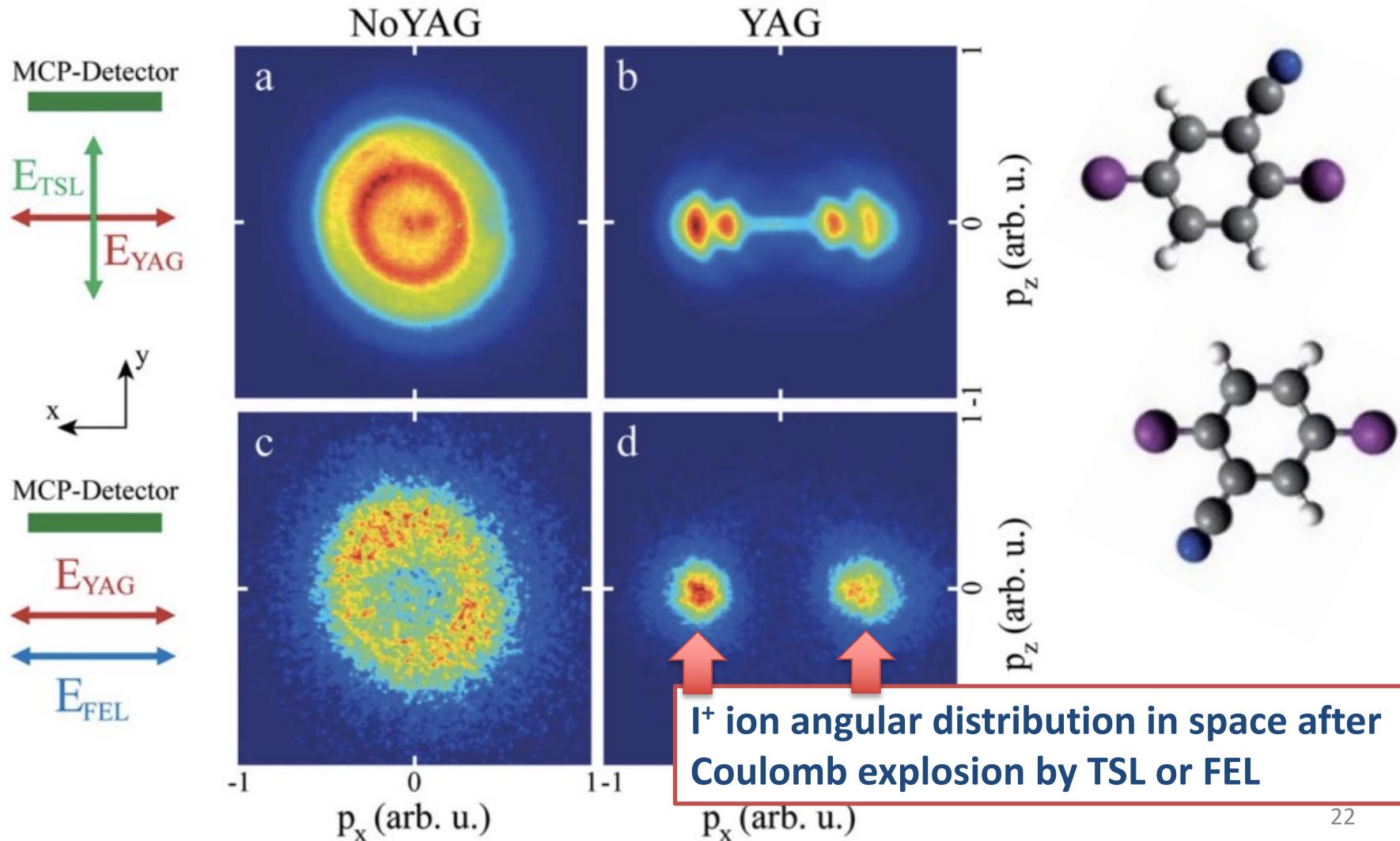
# Linac Coherent Light Source (LCLS) / SLAC National Accelerator Laboratory, US



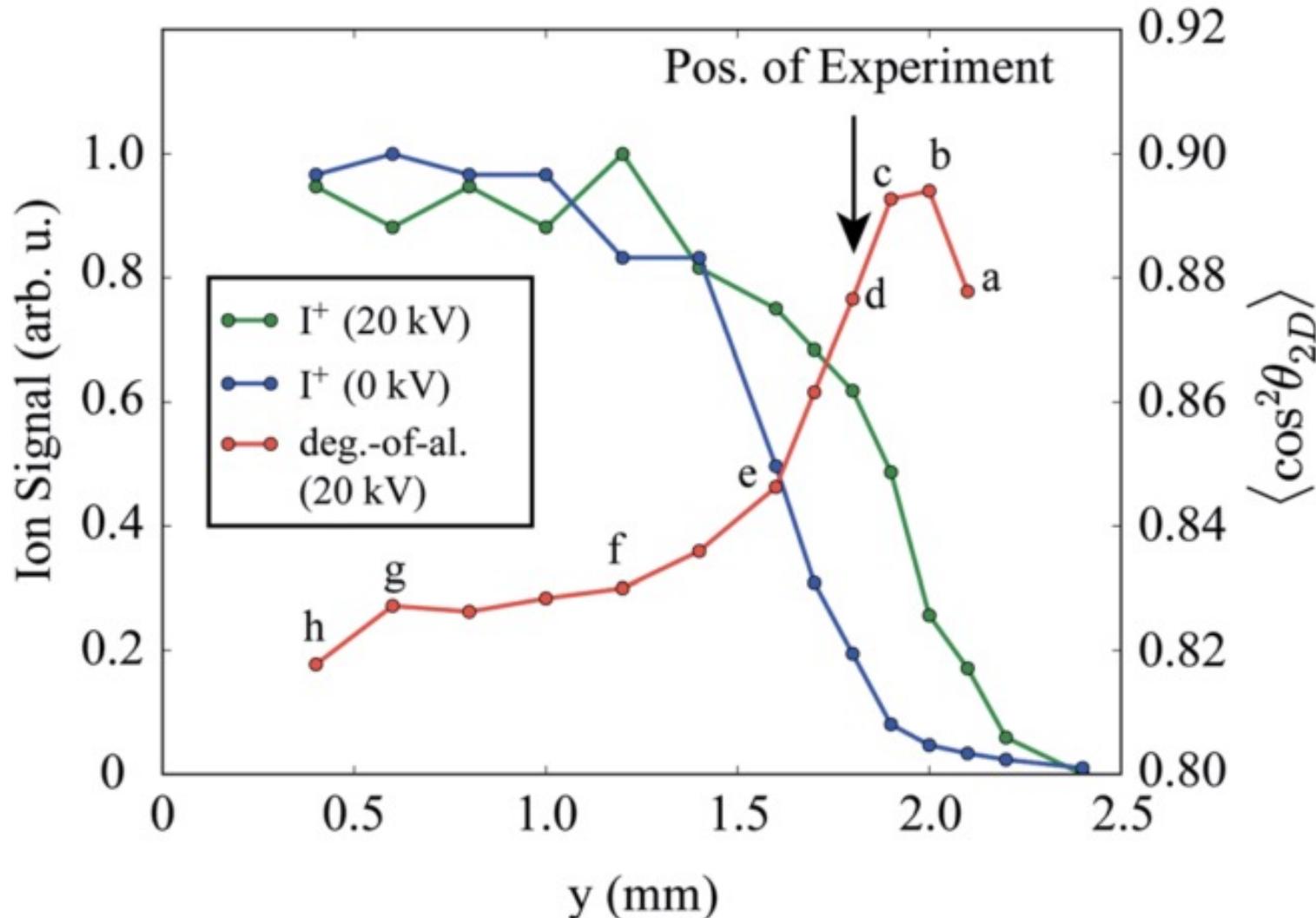
## Atomic, Molecular, and Optical Physics beamline

- $\lambda = 620 \text{ pm}$  (2 keV)
- $E_{\text{pulse}} = 4 \text{ mJ}$
- Beam size =  $30 \mu\text{m}$
- $I_0 \approx 2 \times 10^{15} \text{ W/cm}^2$
- Photon flux =  $1.35 \times 10^{13} \text{ photons/pulse}$
- Pulse duration = 100 fs,
- Repetition rate = 60 Hz

# Determining spatial confinement of laser-aligned DIBN molecules

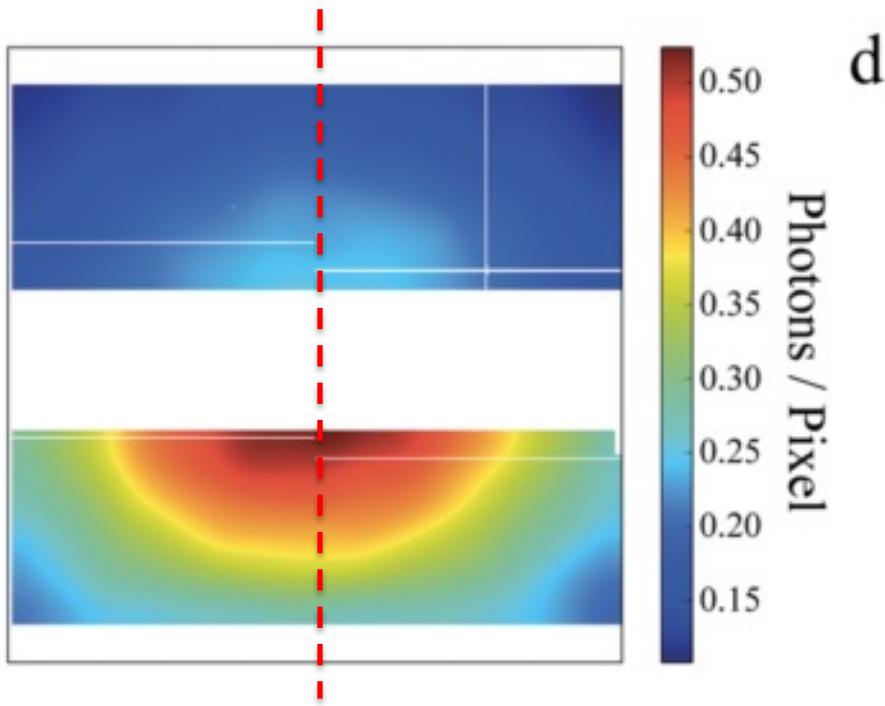


# Alignment at different parts of deflected mol. beam

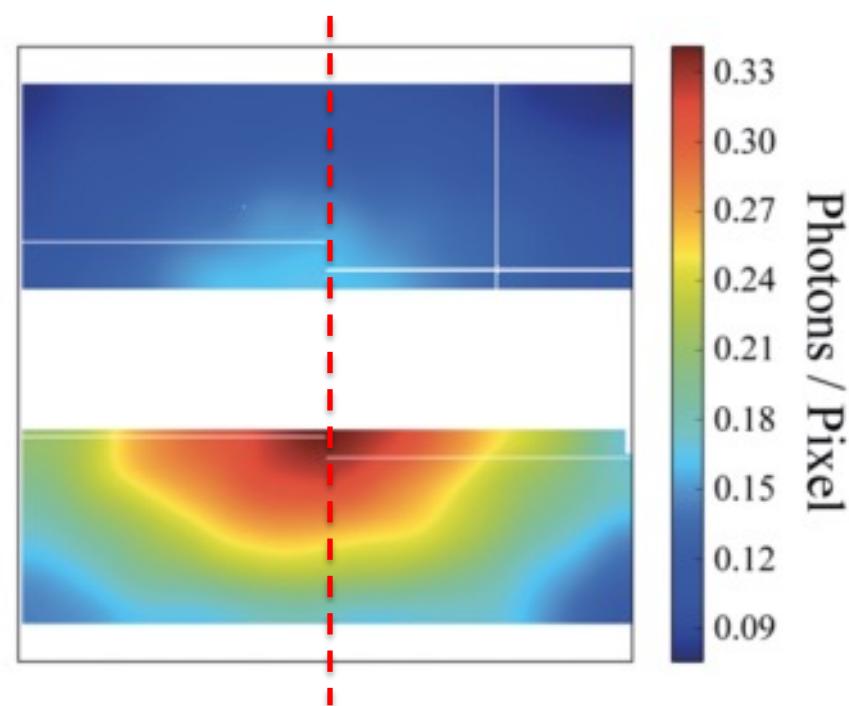


# Experimental (raw) data of X-ray diffraction patterns

No YAG (no aligned)



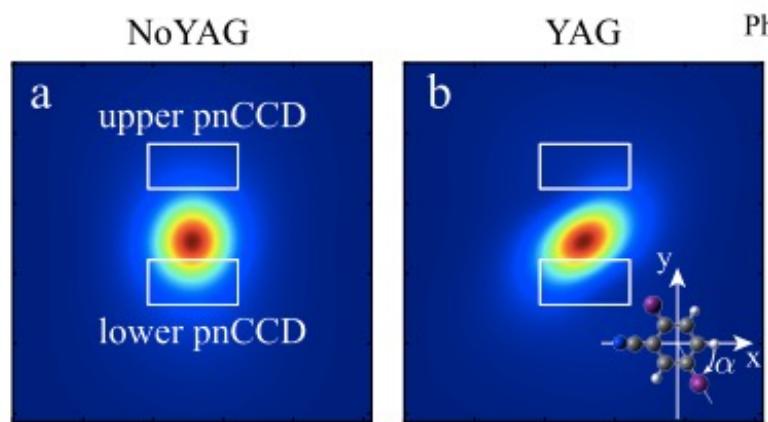
YAG (aligned)



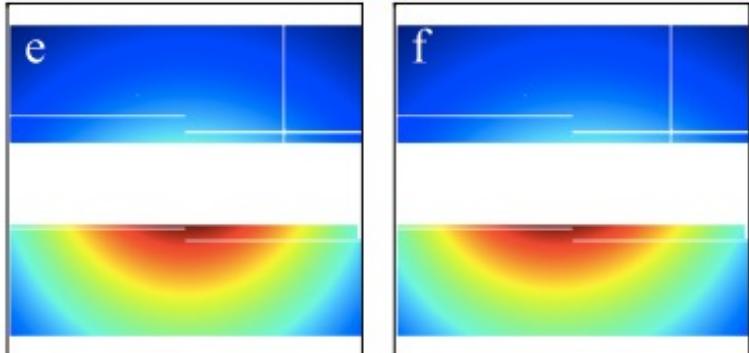
# Simulation of X-ray diffraction data



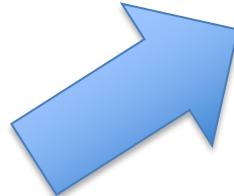
DIBN  
only



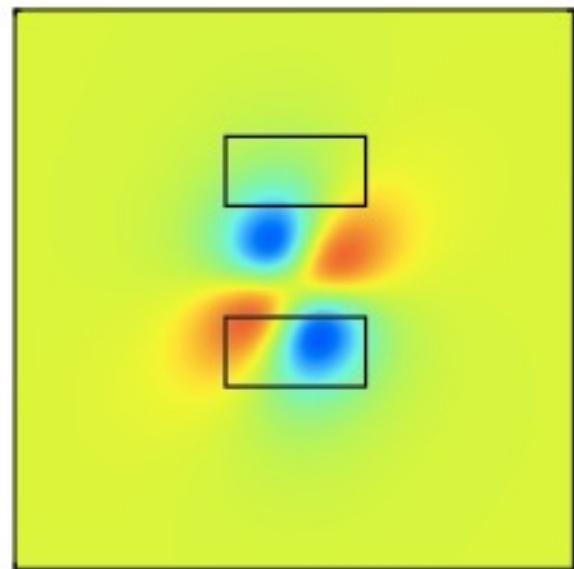
Simulated intensities on pnCCD detector



difference

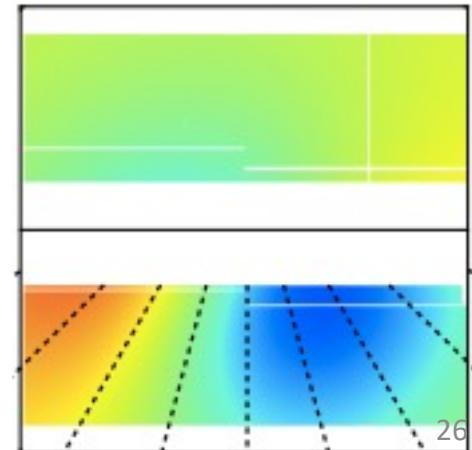
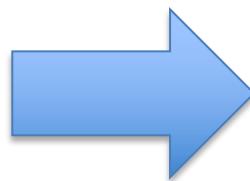


$$I_{\text{YAG}} - I_{\text{NoYAG}}$$

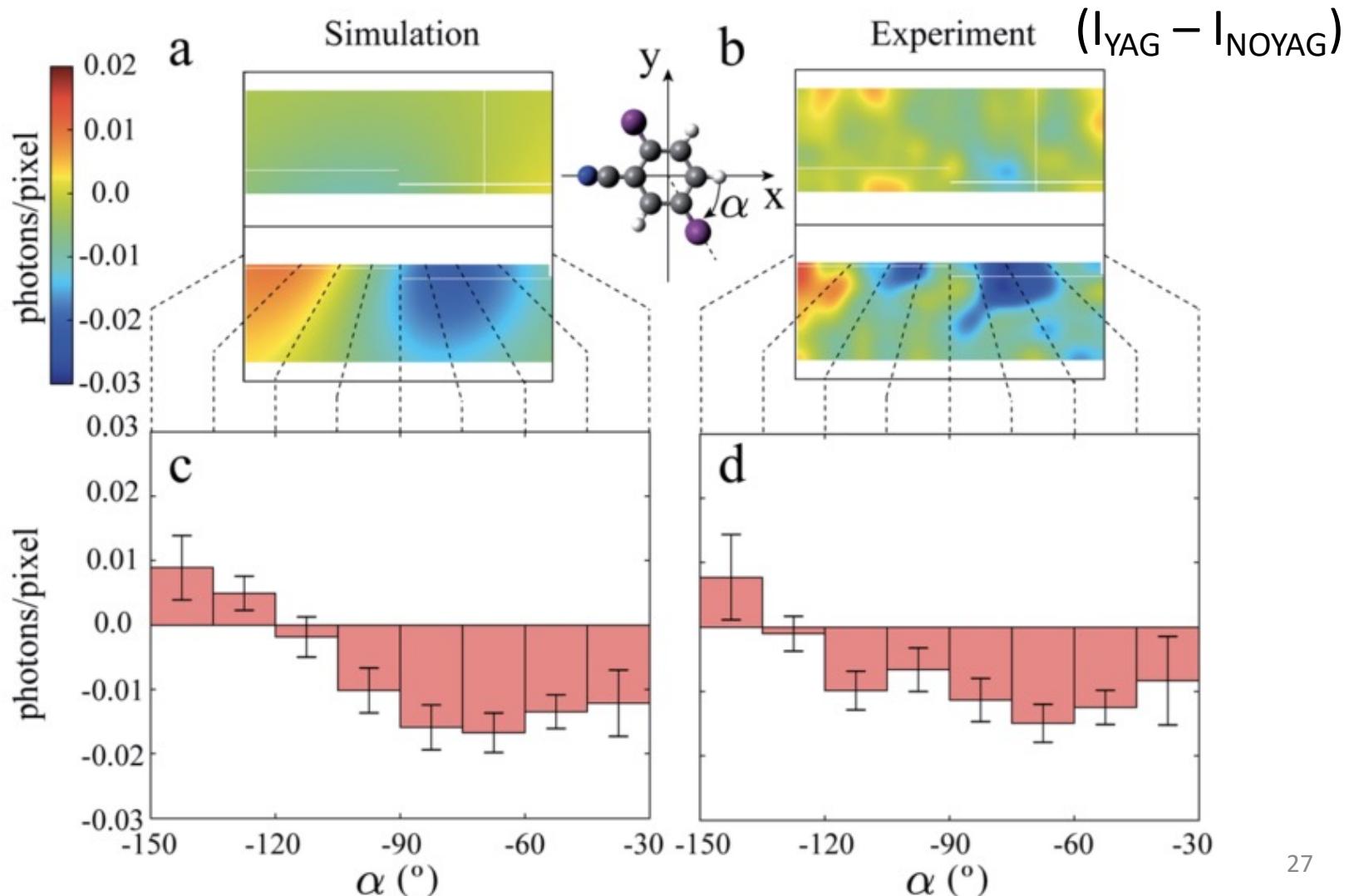


Simulated diffraction difference  
pattern on pnCCD detector

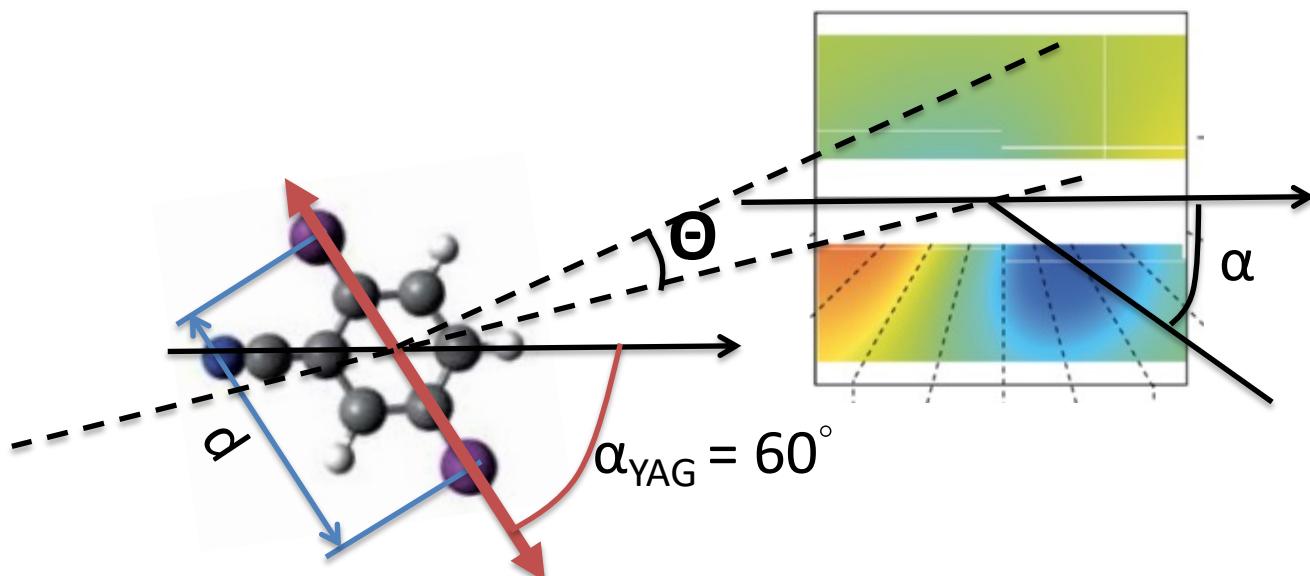
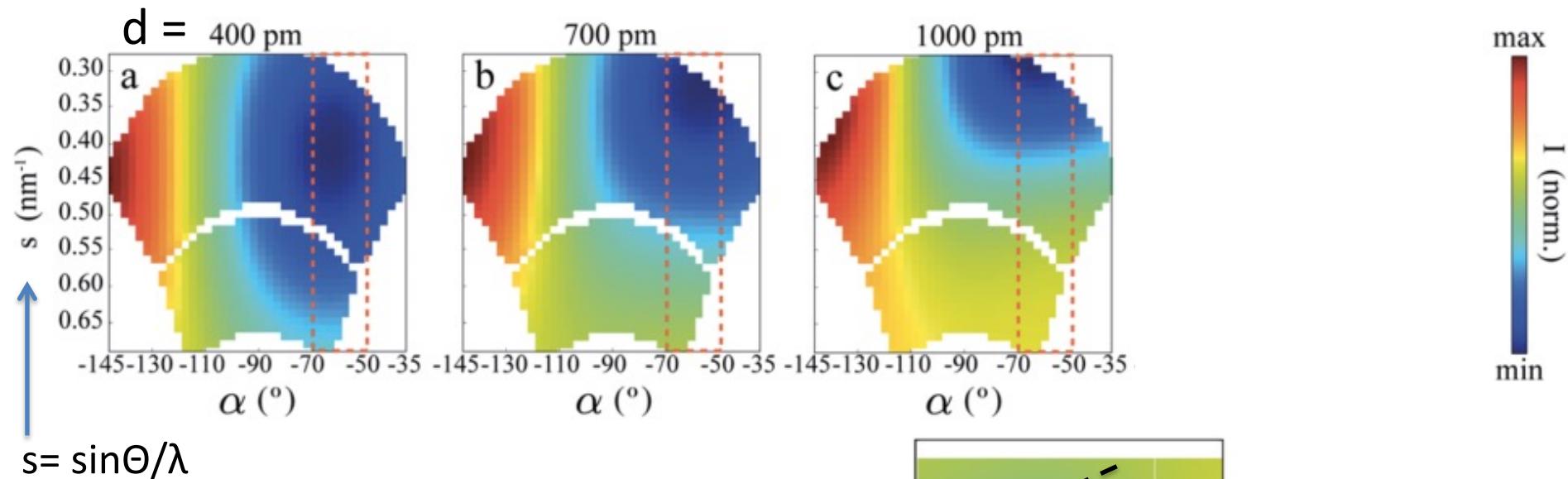
difference



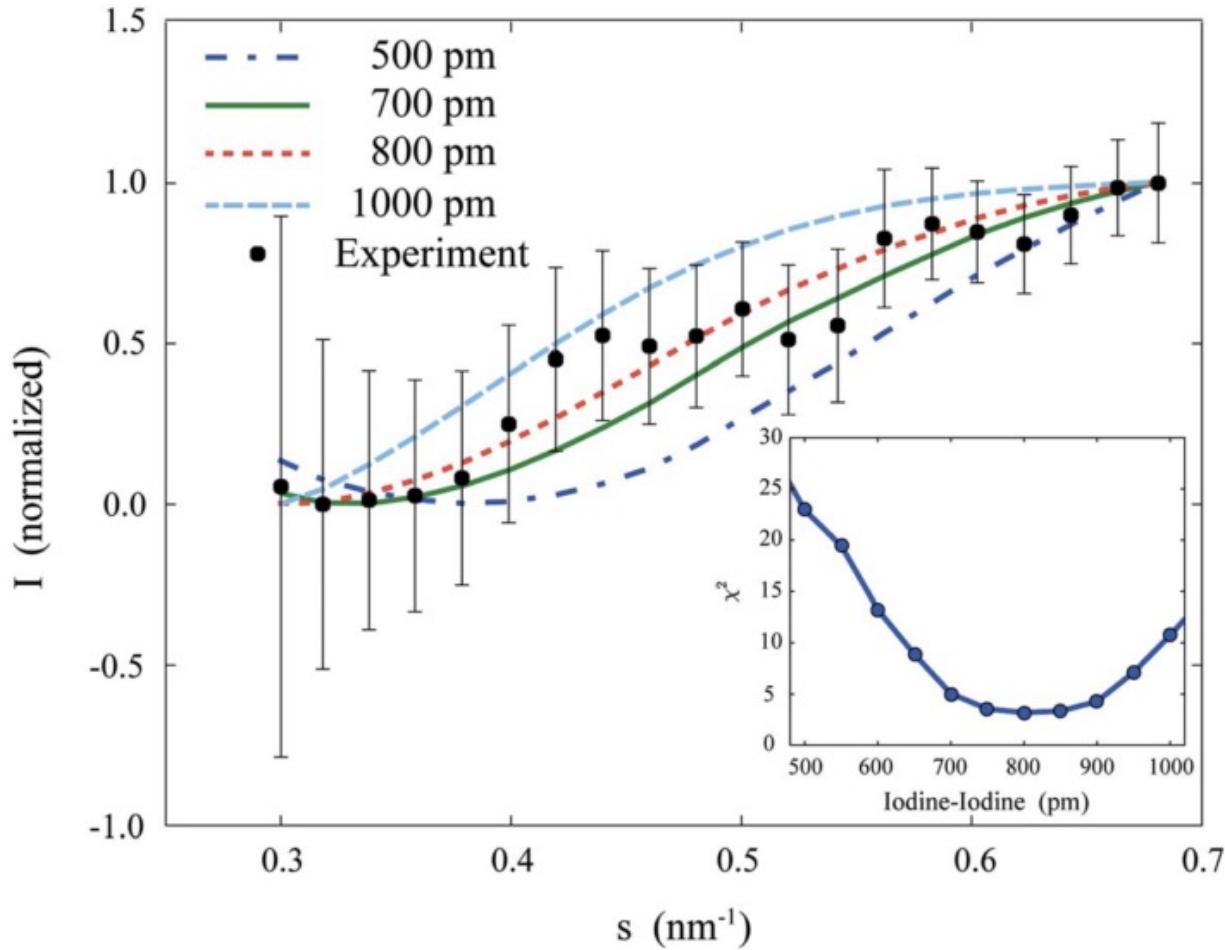
# Experimental & simulation results of diffraction difference



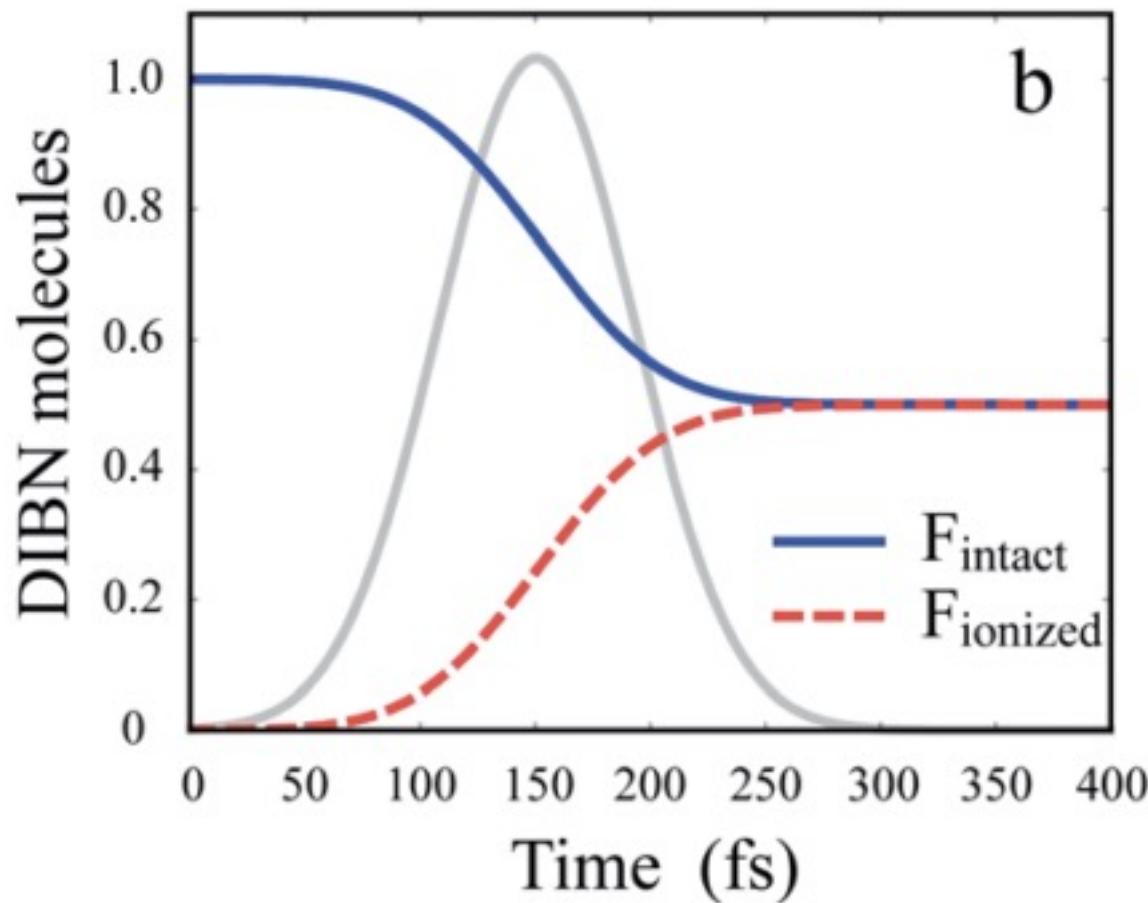
# Simulations with different I – I distances



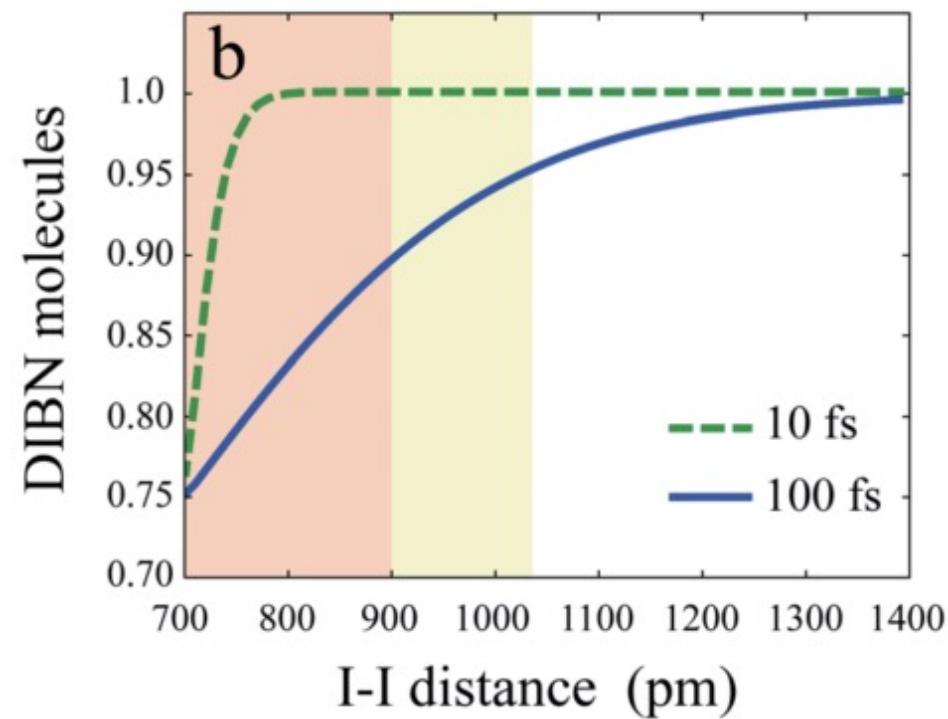
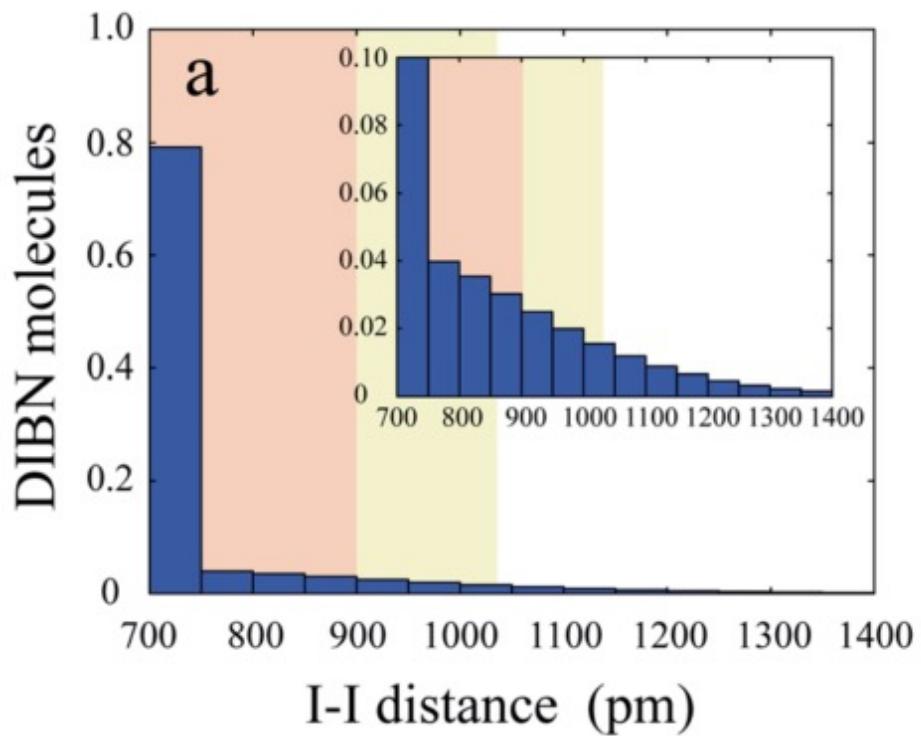
# Comparing exp. and simulated Intensity profiles



# Exploding molecules during a FEL pulse



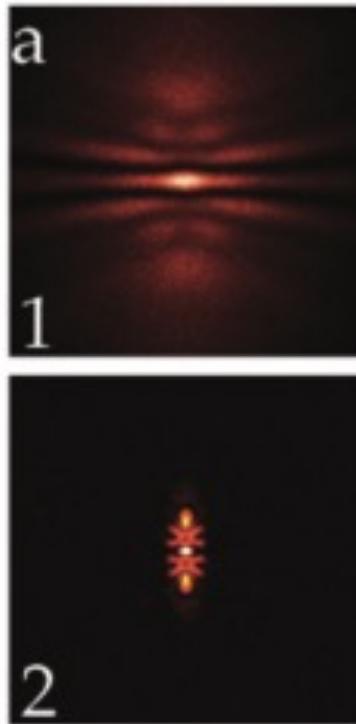
# Changing I – I distance during a FEL pulse



# Outlook 1: imaging dynamics of DIBN photodissociation

Pump-probe delay

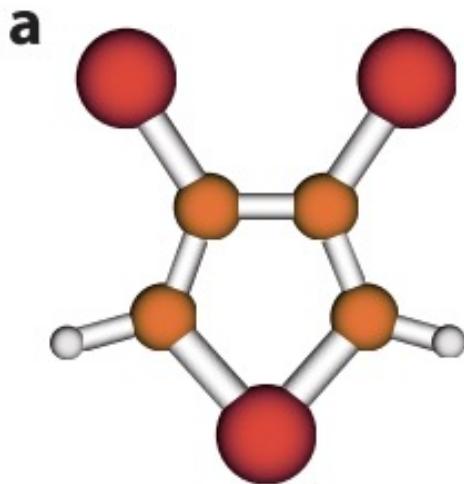
0 fs



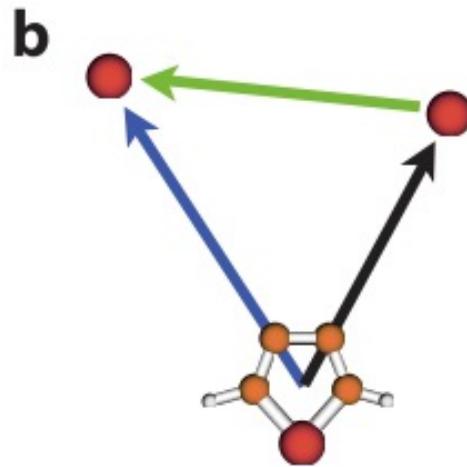
X-ray diffraction  
pattern

Fourier  
transform

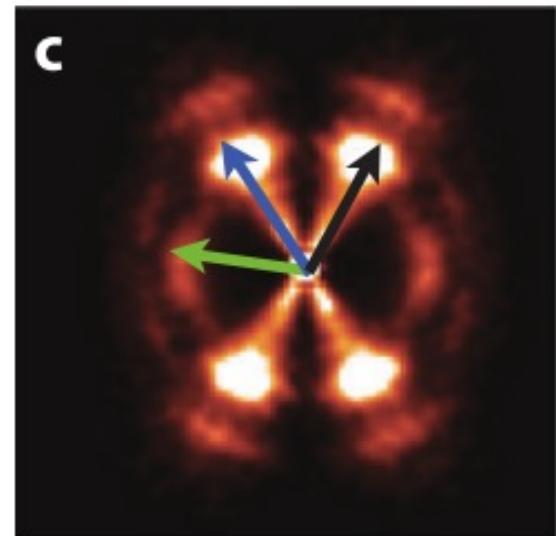
# Outlook 2: vector correlations in photo-fragmentation



3,4-dibromoselenophene



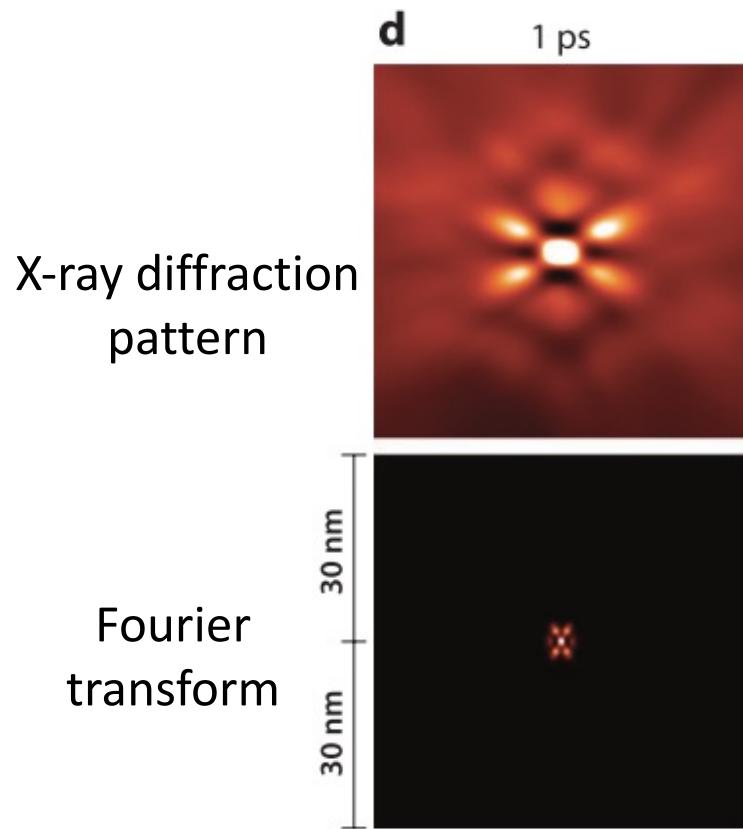
Correlation vectors



Fragmentation hologram

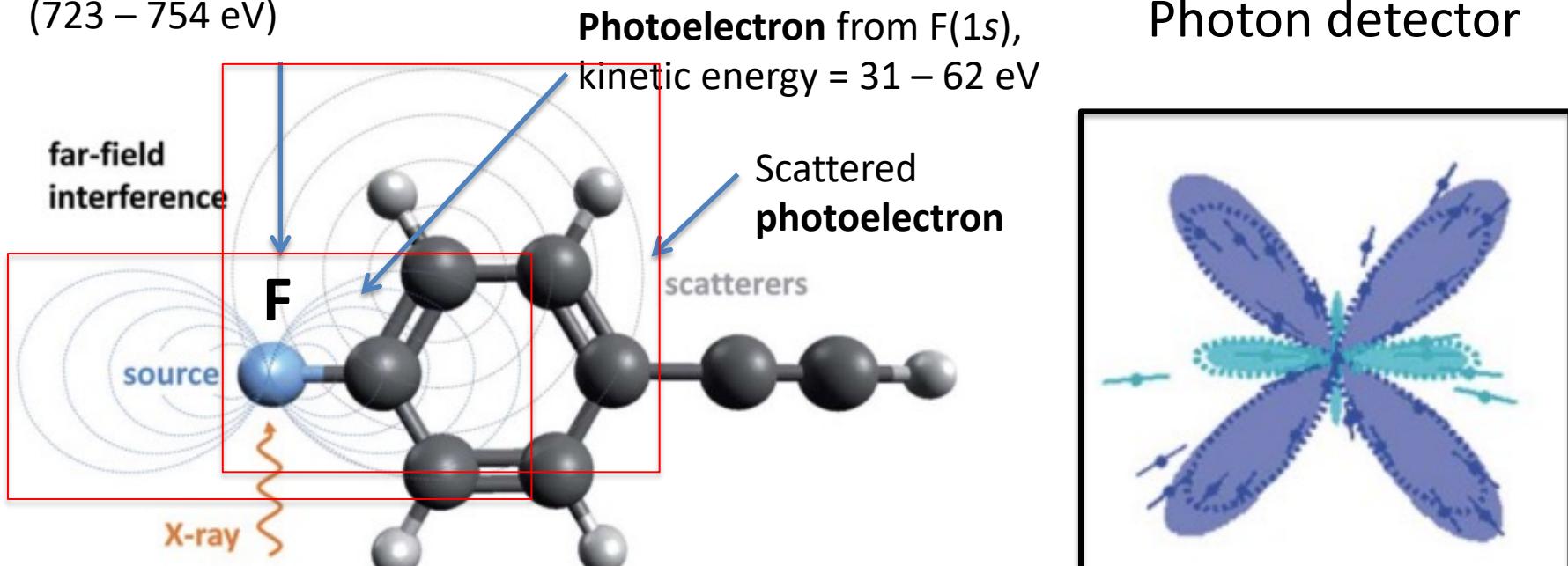
## Outlook 2: fragmentation holography experiment

Pump-probe delay



# Part II - molecular frame information from photoelectron diffraction

F(1s) inner shell (binding energy: 692 eV) photoionization by X-ray (723 – 754 eV)



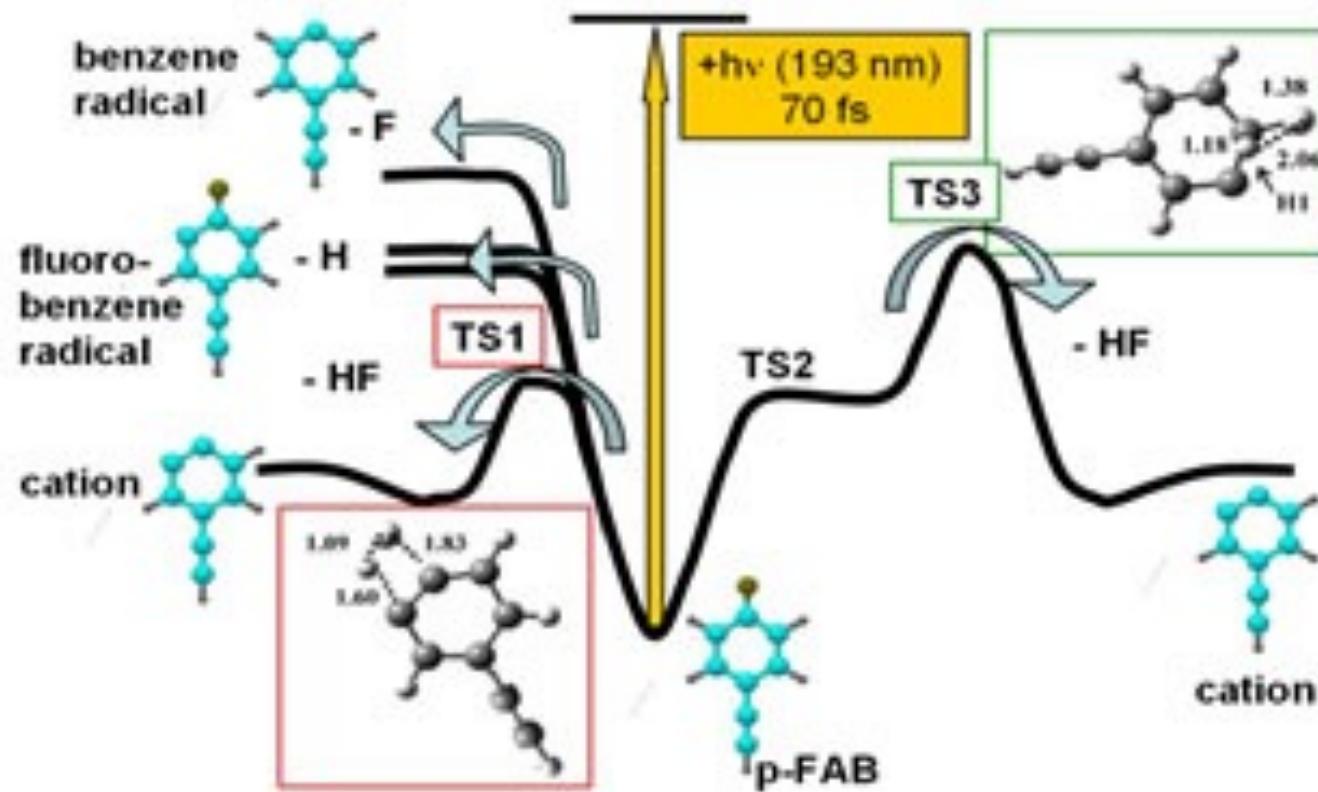
1-ethynyl-fluorobenzene  
(p-FAB)

Molecular frame photoelectron angular distribution (MFPAD)

R. Boll et. al., Phys. Rev. A 68, 061402 (2013)

R. Boll et. al., Faraday Discuss. 171, 57 (2014)

# Motivation: determining structures of transition state in photo-induced dynamics



# People involved in this work

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PHYSICAL REVIEW A **88**, 061402(R) (2013)

## Femtosecond photoelectron diffraction on laser-aligned molecules: Towards time-resolved imaging of molecular structure

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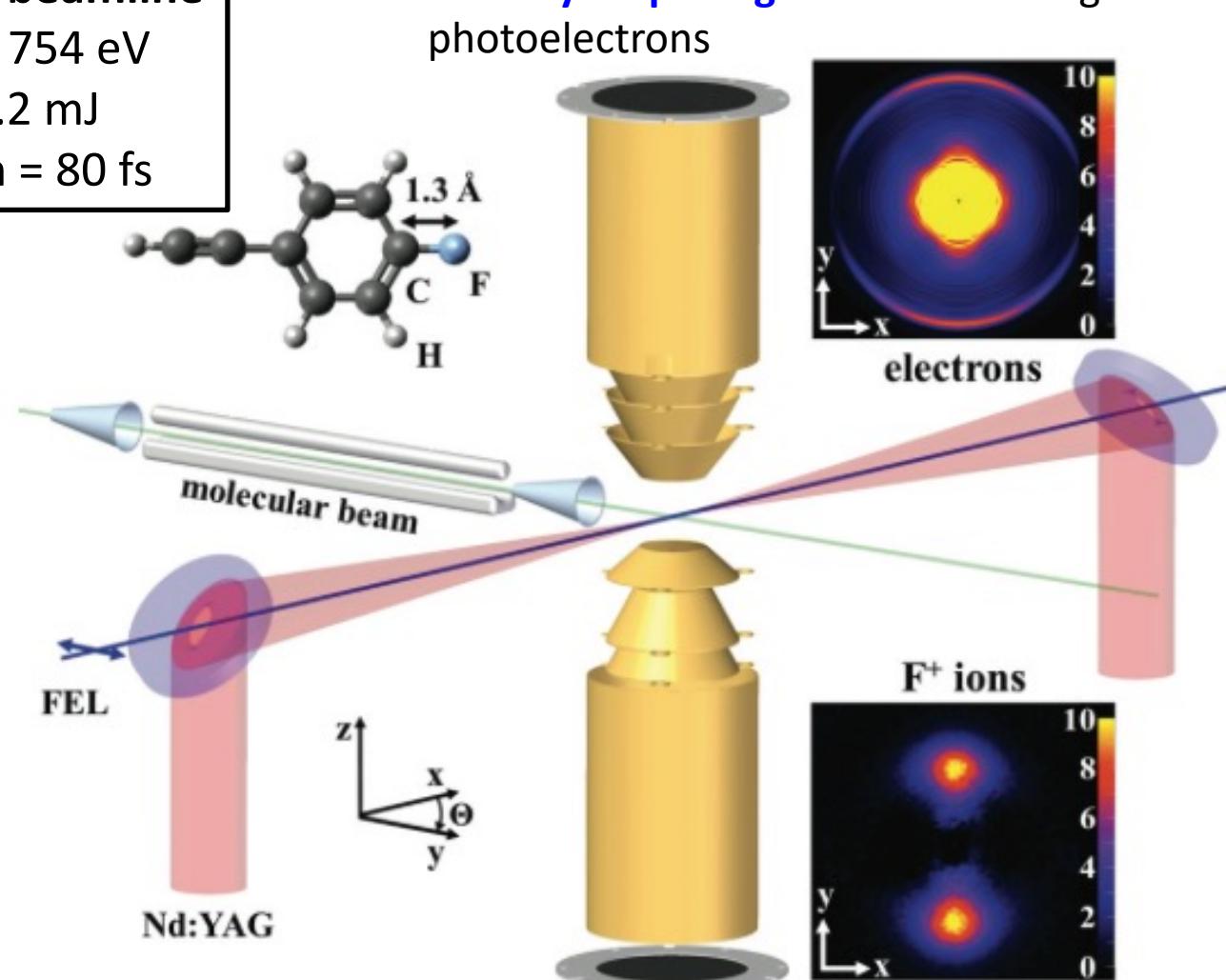
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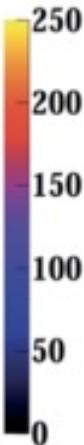
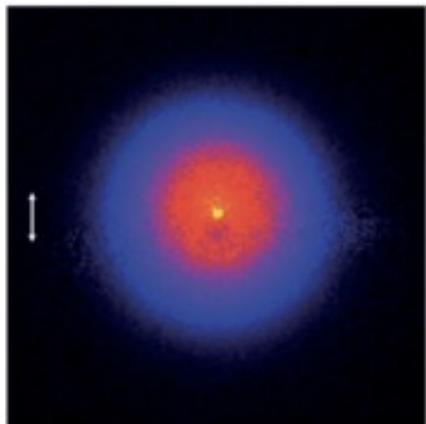
# Experimental setup

## LCLS, SLAC, AMO beamline

- $E_{\text{photon}} = 723 - 754 \text{ eV}$
- $E_{\text{pulse}} = 0.6 - 1.2 \text{ mJ}$
- Pulse duration = 80 fs

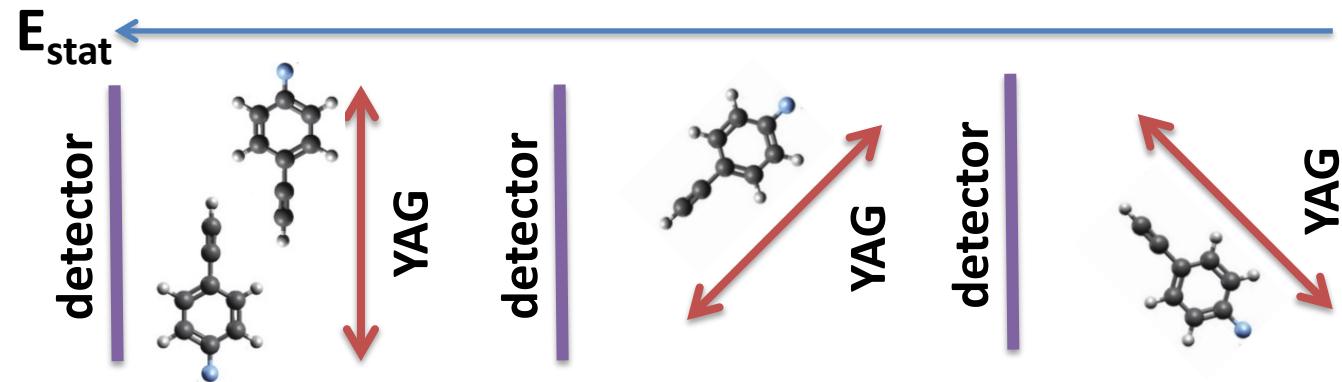


# Exp. results – F<sup>+</sup> ion images

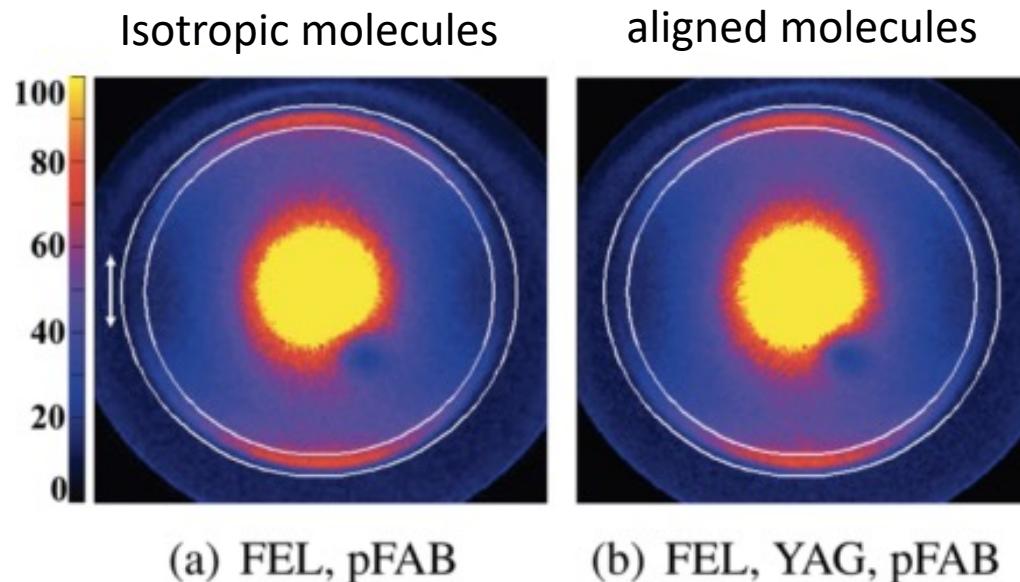


(a) without YAG

(Isotropic molecules)

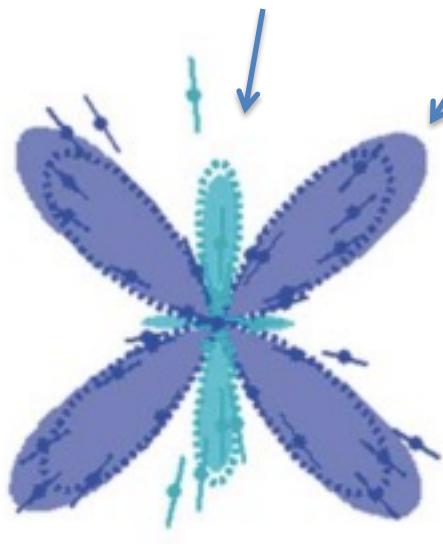


# Exp. Results – photoelectrons



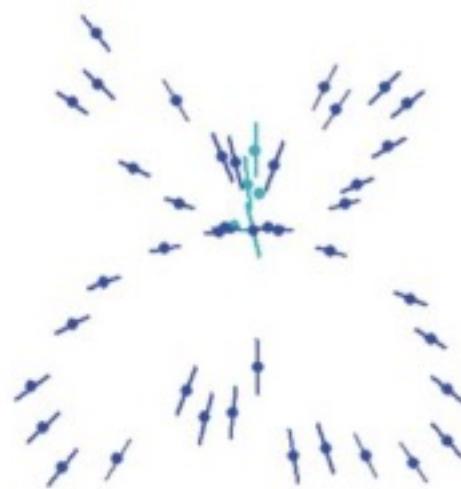
# F (1s) photoelectron angular distribution differences ( $\Delta$ PAD)

Positive difference

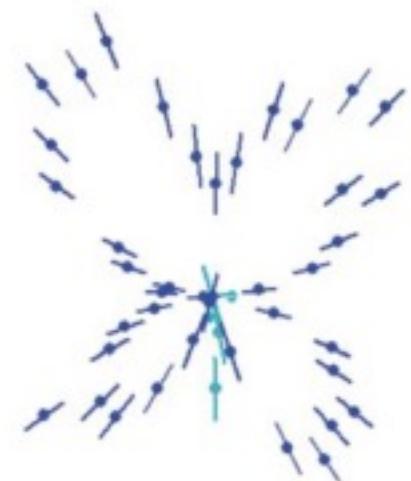


(a) YAG at  $0^\circ$

Negative difference



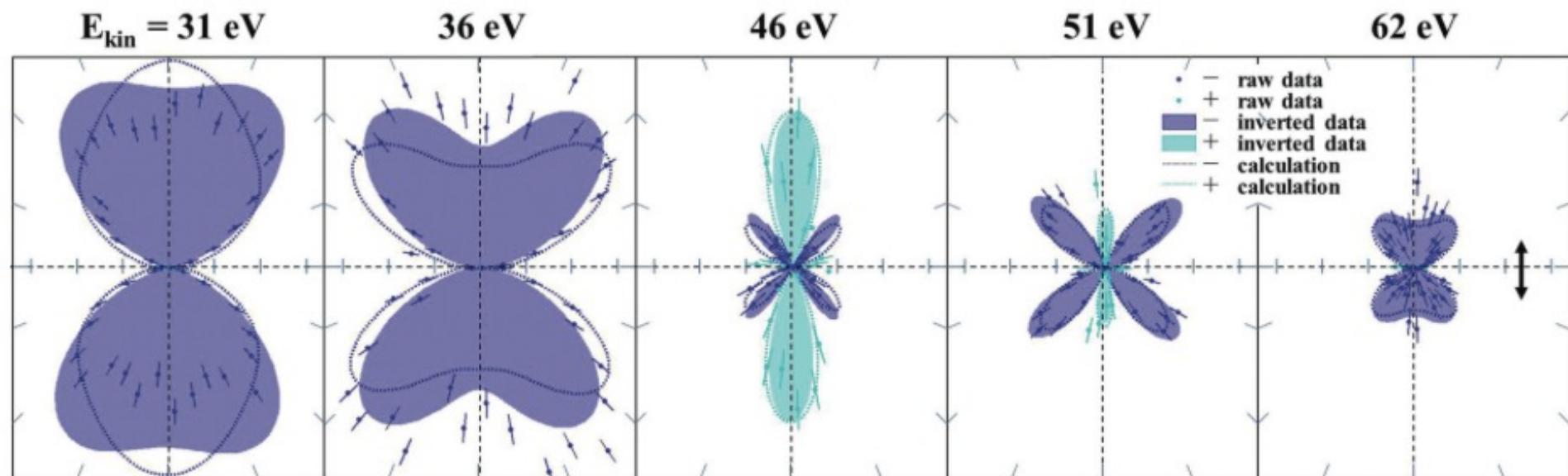
(b) YAG at  $+45^\circ$



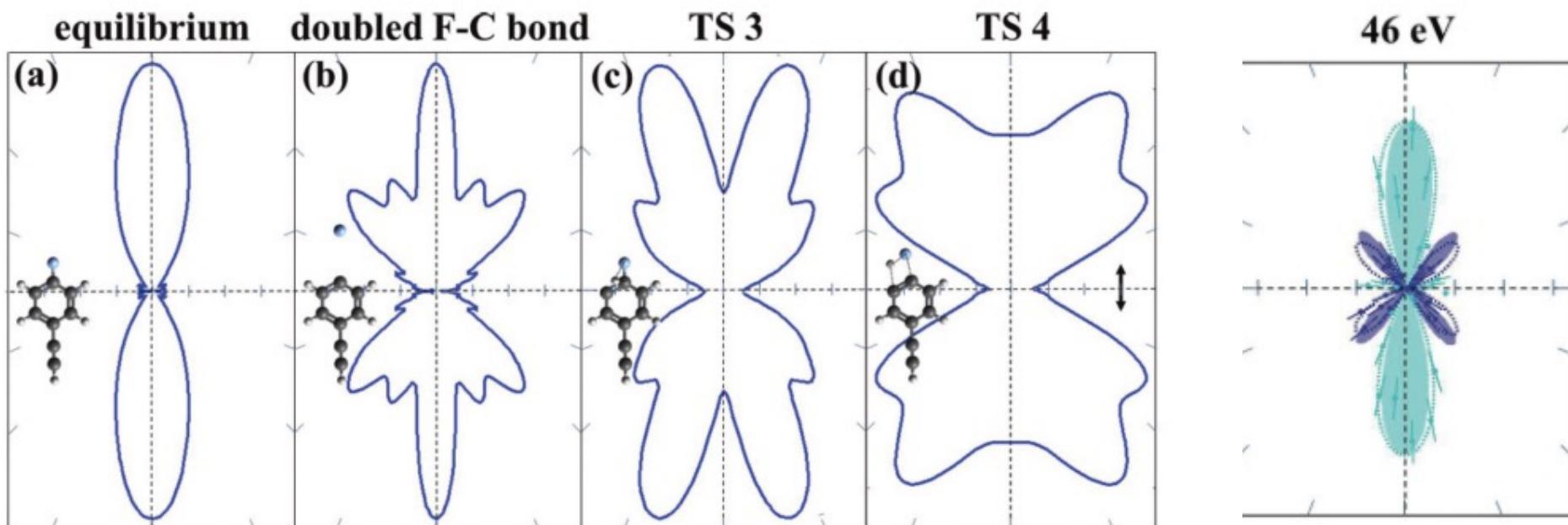
(c) YAG at  $-45^\circ$

Symbol: from non-inverted data  
Area: from inverted data  
Dotted line: DFT calculations

# $\Delta$ PAD as a function of photoelectron kinetic energy



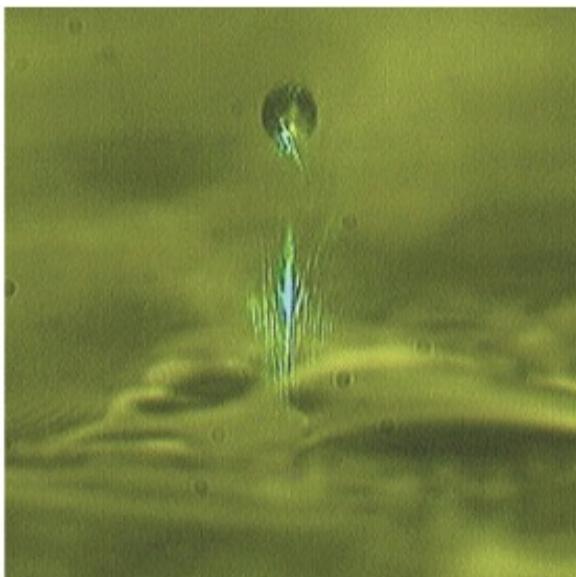
# Calculated PAD for different p-FAB geometries



# Take home messages of part 1 & 2

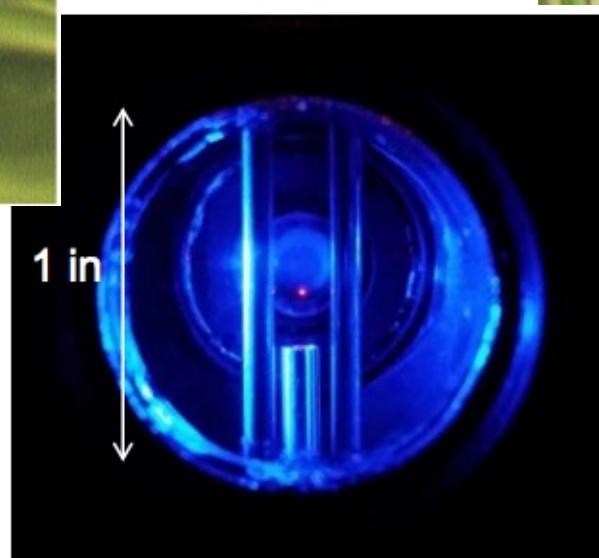
- Experimental demonstration of X-ray FEL diffraction for determining the nuclear structure of a molecule
- Diffraction of photoelectron induced by X-ray FEL for determining the electronic structure of a molecule
- **Advantage of FEL:** high brightness, very short pulse duration (small than the photo-damage / fragmentation time of molecules)
- Promise pump-probe / time-resolved experiment of X-ray / photoelectron diffraction.

# Part III - Single particle measurements via *trapping single particles* for imaging applications

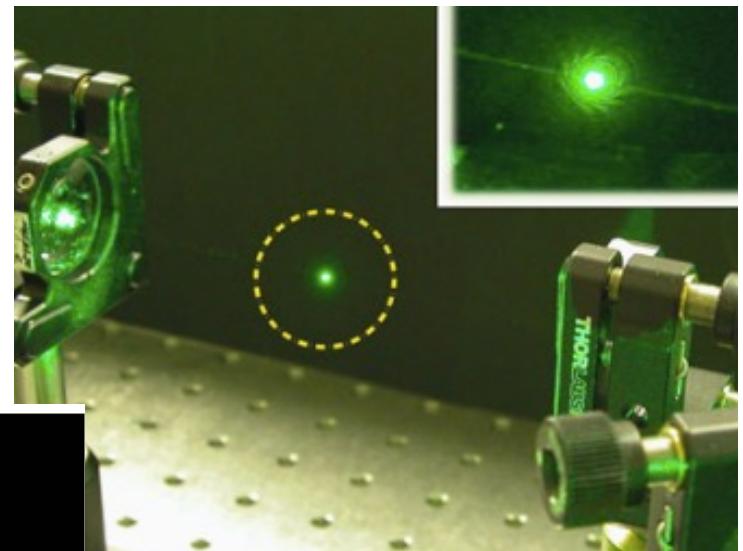


*Gradient force trapping*  
(transparent particles)

Groups: K. Reid, R. Signorell,  
A. D. Ward ... etc.



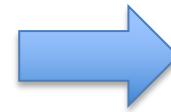
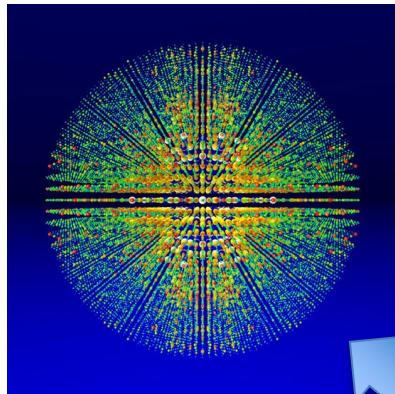
*photophoretic trapping*  
(light absorbing particles)  
Groups: A. V. Rode, Y. L. Pan ... etc



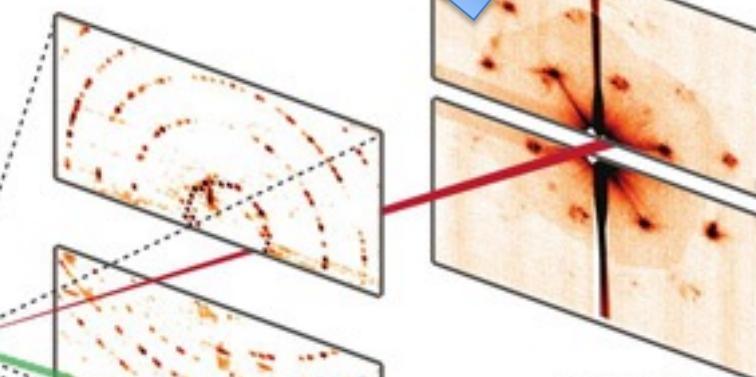
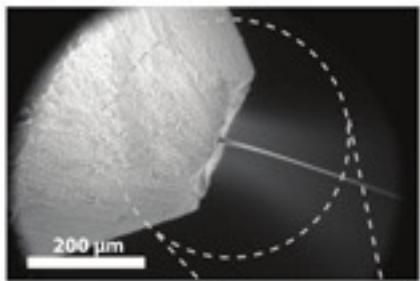
*Electrodynamic balance*  
(Charged particles)  
Groups: C. K. Chan, U. K. Krieger ... etc

# Motivation: femtosecond crystallography of “nanocrystal”

3D diffraction pattern  
(collect 15,000 single shot diffraction images)



Photosystem I complex



Rear pnCCD  
( $z = 564$  mm)

Front pnCCD  
( $z = 68$  mm)

**Issue:** no synchronization between sample and X-ray pulses  
(亂槍打鳥)

# Goal: optical guide for a stream of microscopic particles

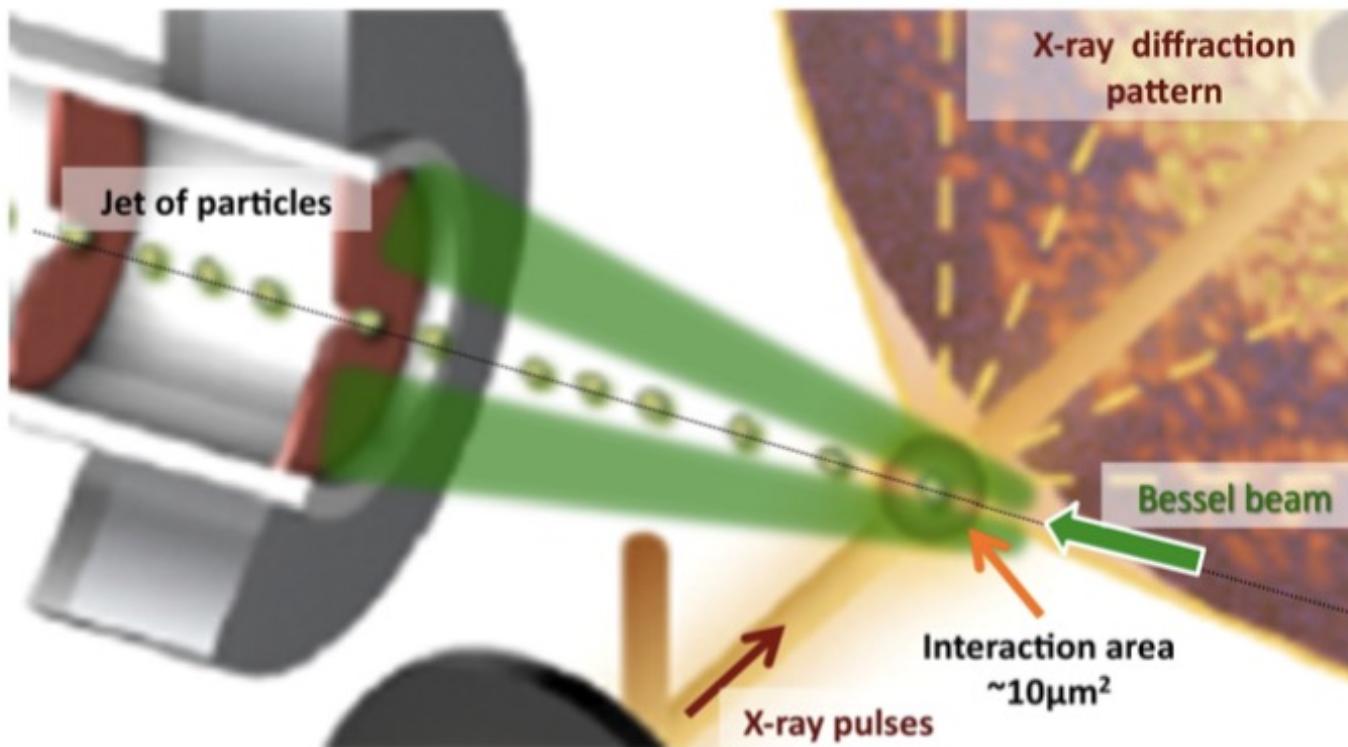
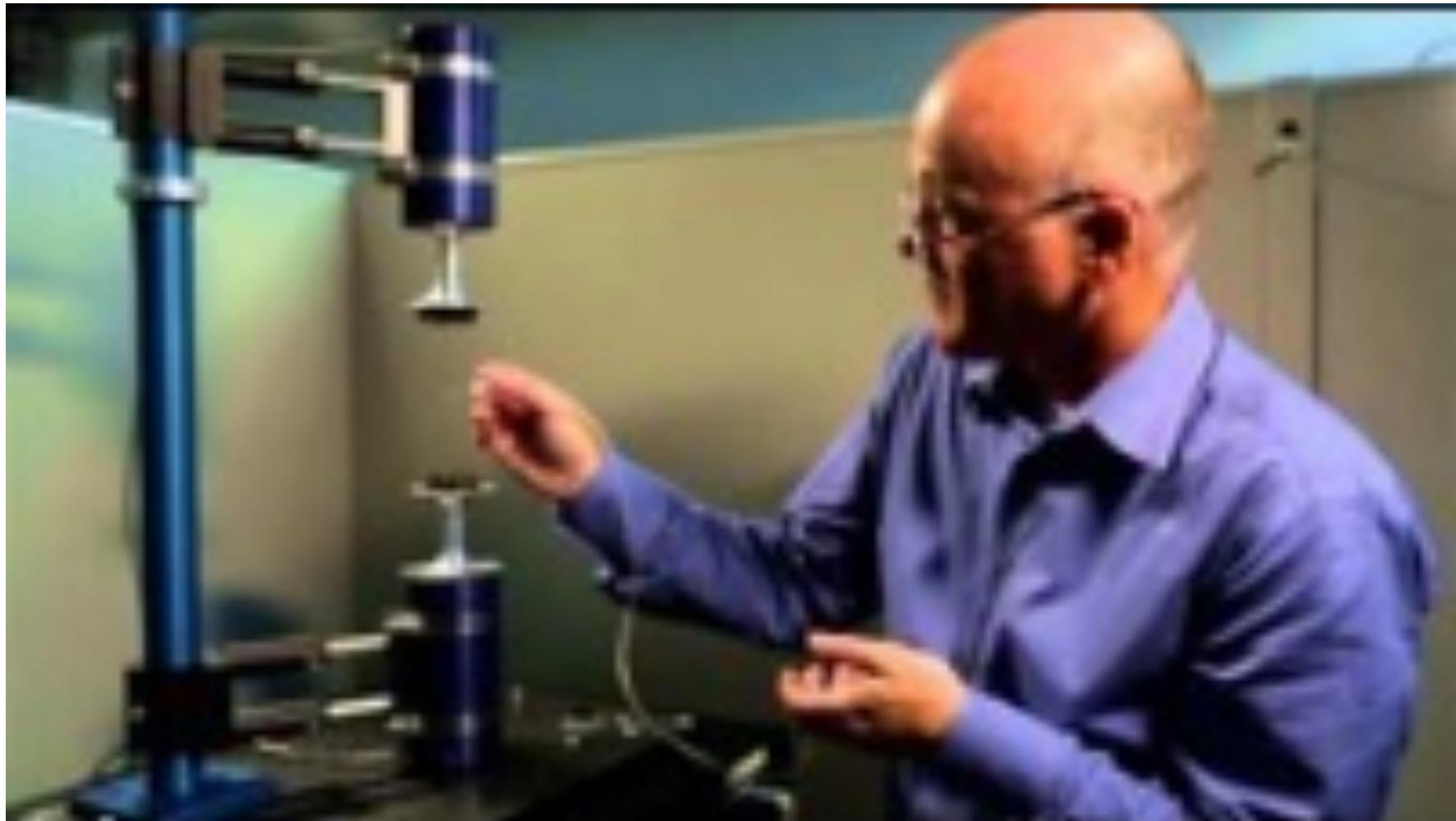


Fig. 1. Conceptual scheme illustrating the compression of a particle stream injected into the interaction chamber with an aerodynamic lens, using a counter-propagating first-order Bessel beam – the ‘funnel’. The background image in this figure is adapted from Ref [19].

# Trapping single particles

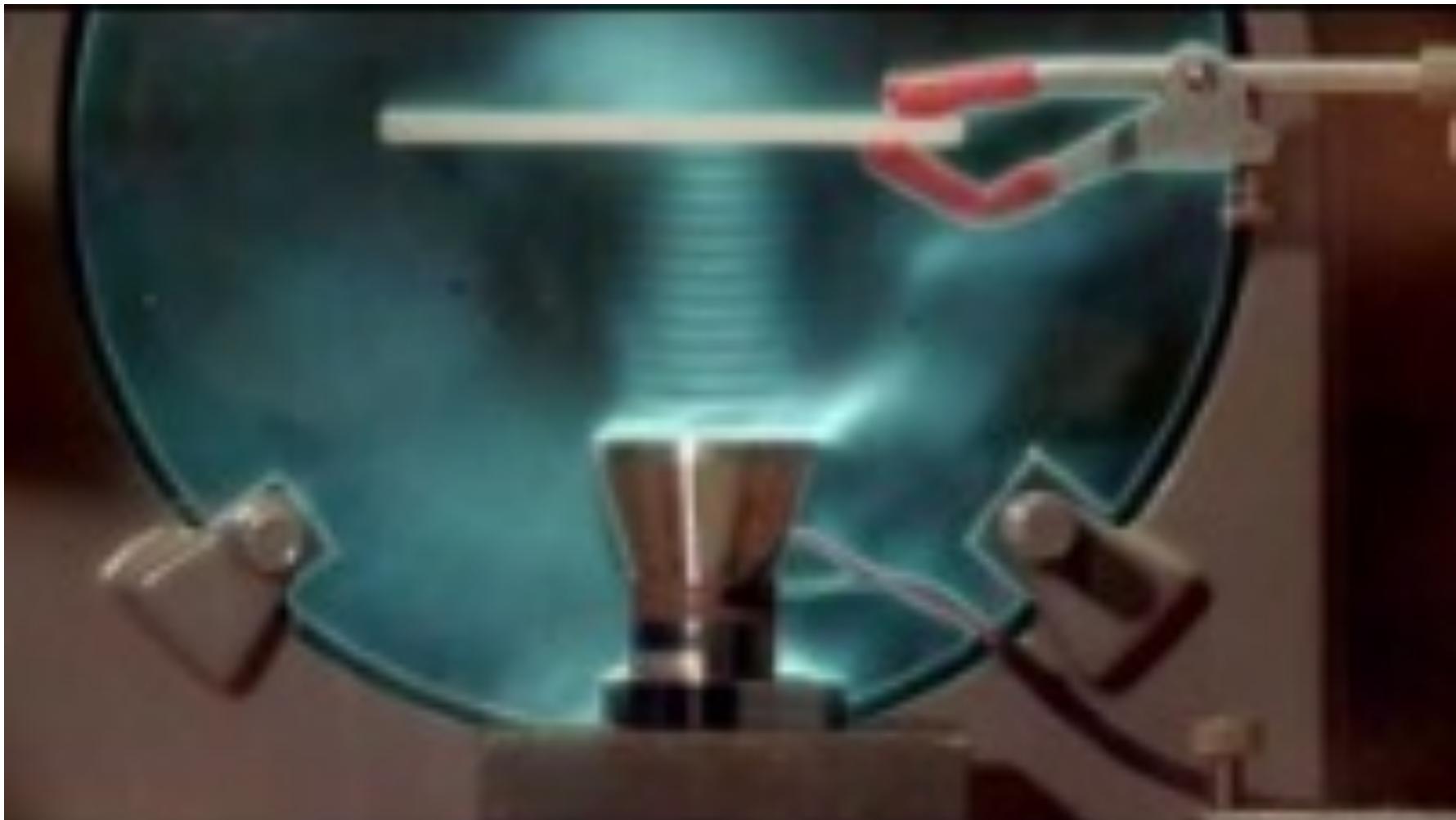
- **Optical trapping**
  - Gradient forces created by focused laser beams
    - Beam shape: Gaussian beam or Bessel beam
    - Type of particle: **transparent to laser wavelength** (few  $\mu\text{m}$ )
  - photophoretic forces created by laser beams
    - Beam shape: Bessel beam
    - Type of particle: **not transparent to laser wavelength**
- **Acoustic levitation**
  - Type of particle: only limited by its size (sub mm to few mm)
- **Electrodynamic balance**
  - Type of particle: charged particle (sub  $\mu\text{m}$  to less 100  $\mu\text{m}$ )

# Acoustic levitation on Youtube



<https://youtu.be/669AcEBpdsY>

# Acoustic levitation on Youtube

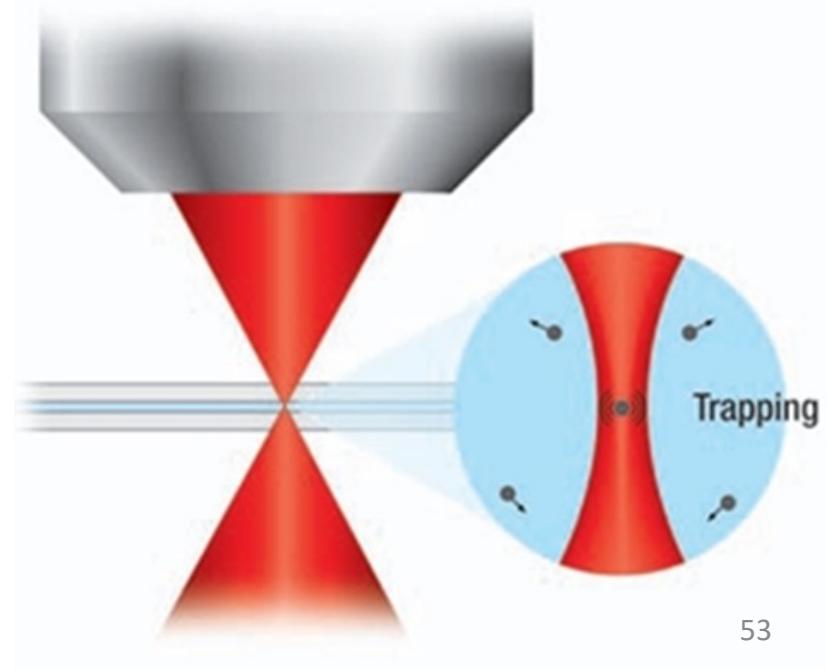


# Optical trapping on youtube

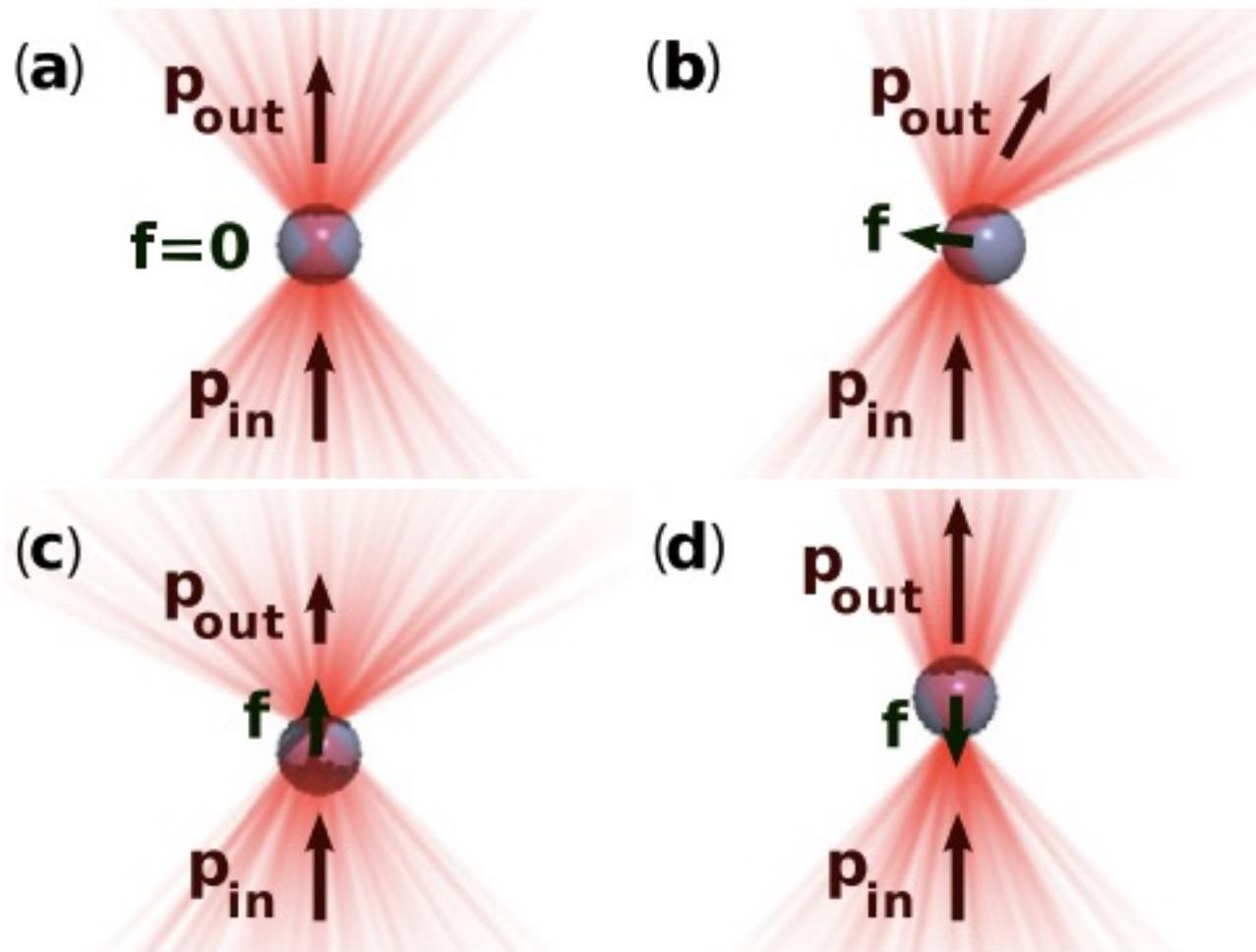


# Optical Tweezers: history

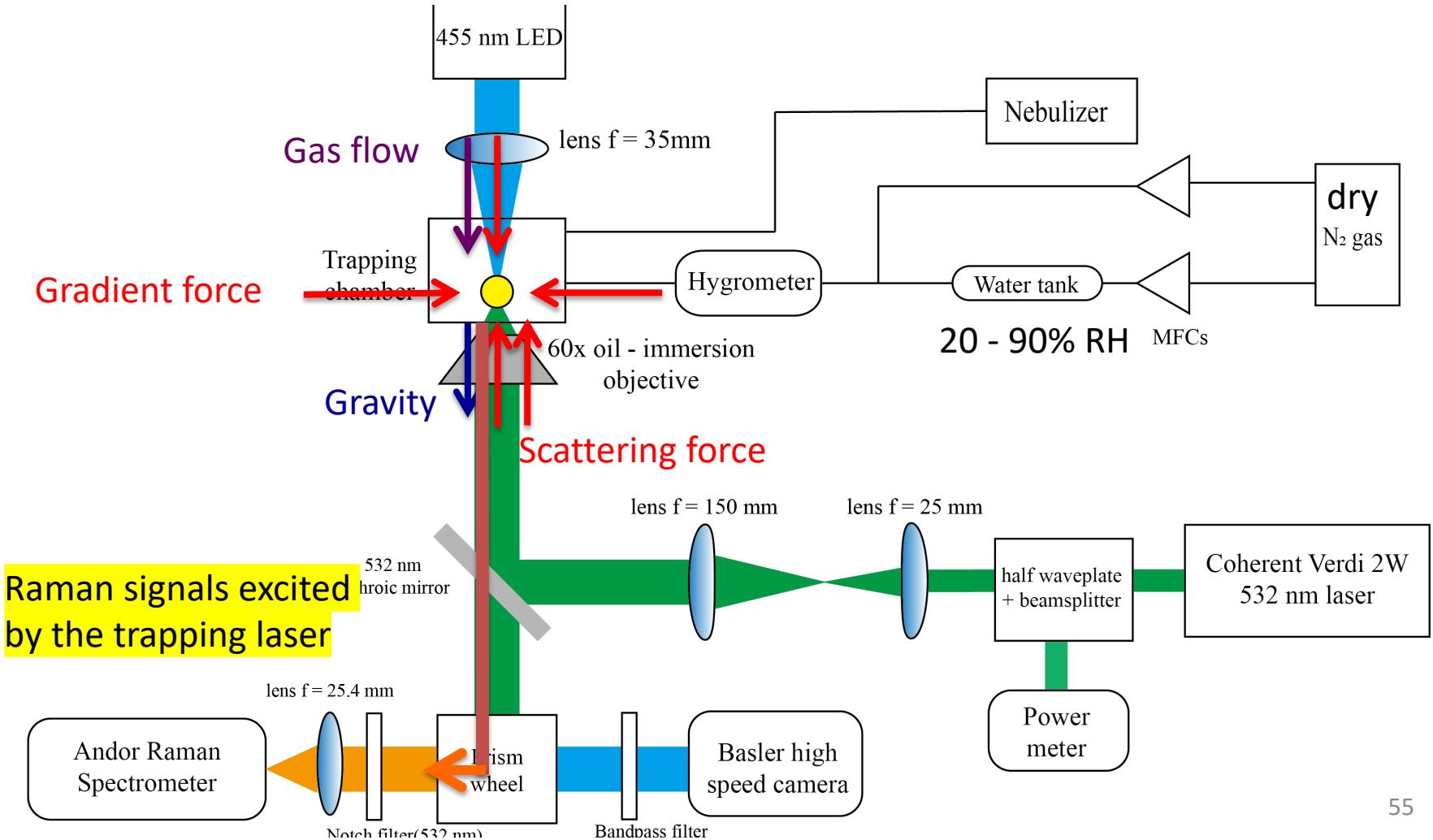
- The detection of optical scattering and gradient forces on micron sized particles was first reported in 1970 by Arthur Ashkin.
- Years later, Ashkin and colleagues reported the first observation of what is now commonly referred to as an optical tweezer: a tightly focused beam of light capable of holding microscopic particles stable in three dimensions.
- In 2018, Ashkin was awarded the Nobel Prize in Physics for this development.
- Optical tweezers have proven useful in other areas of biology as well.



# Principle of optical trapping – gradient force (for transparent particles)

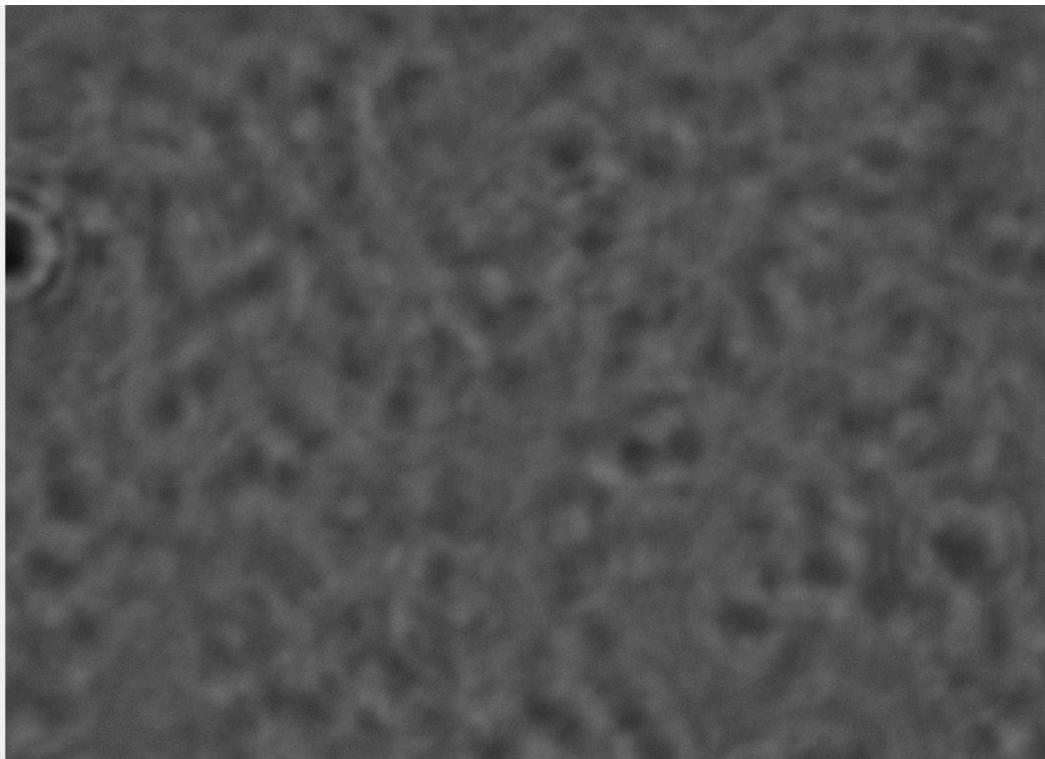


# Use aerosol optical tweezers (AOT) to trap single aerosol droplets (few $\mu\text{m}$ ) in our lab

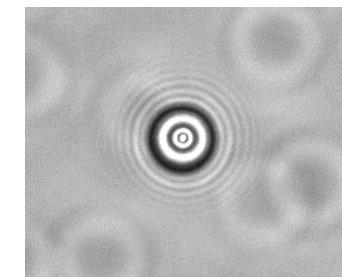
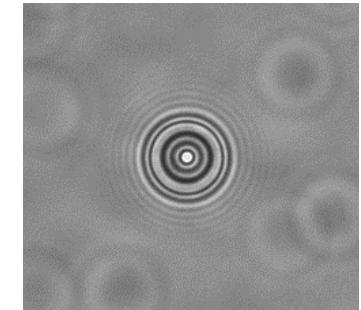


# Single micro-droplet trapping observed by brightfield imaging

Droplet size = few microns

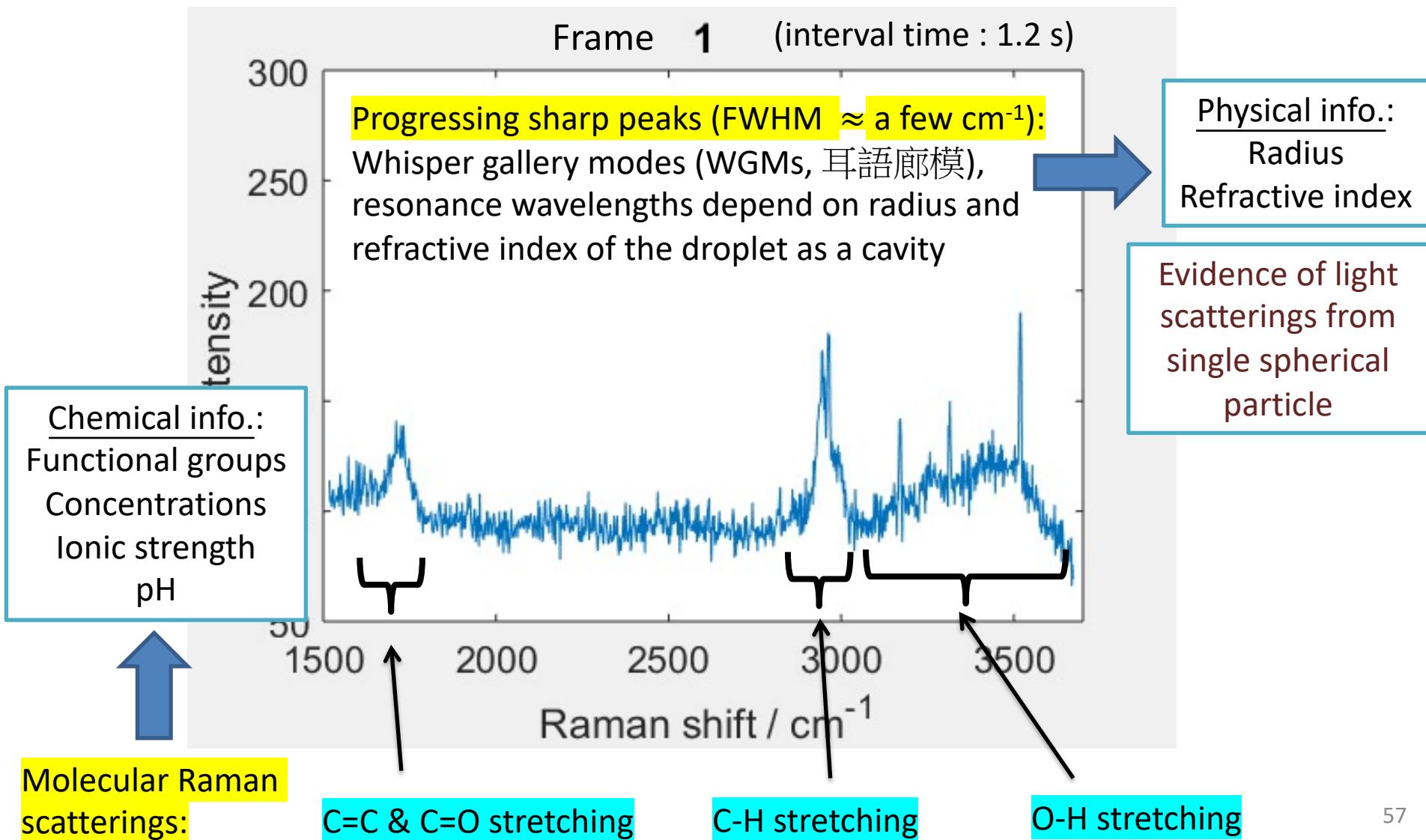


(video replaying)



**After 9 hours**

# Time-resolved Raman spectra of optically trapped single aerosol particle (aqueous citric acid)



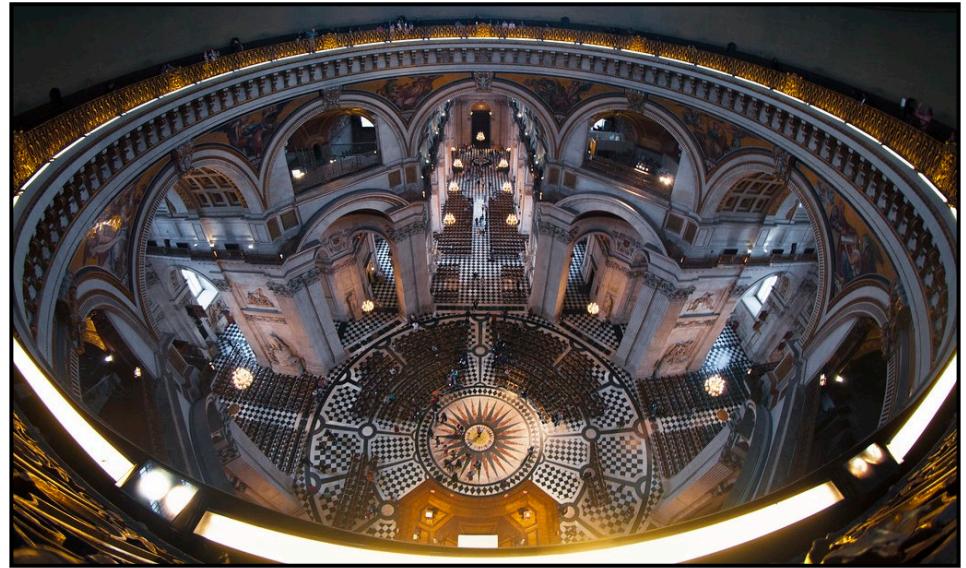
# Whispering-gallery modes (WGMs)

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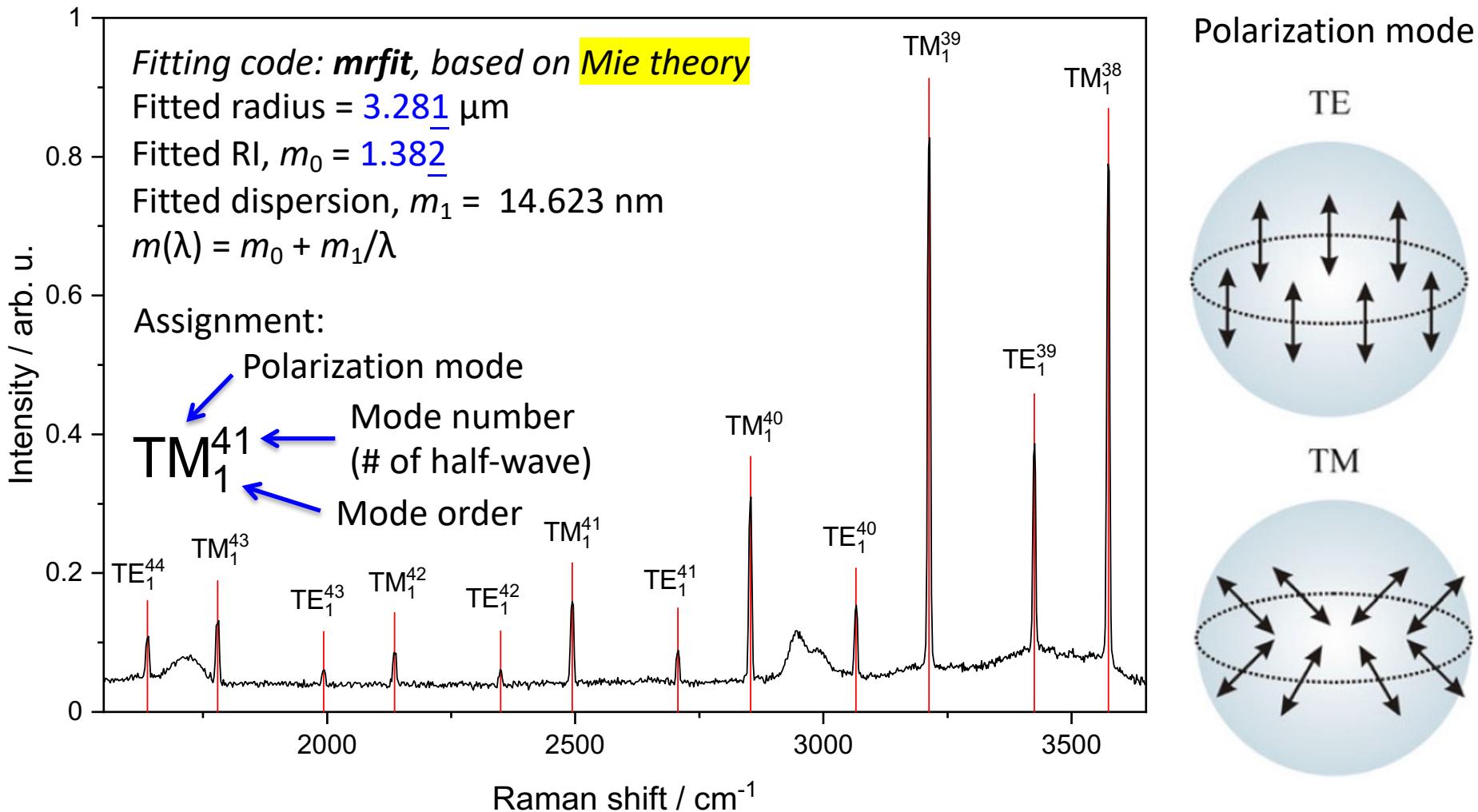
周長 = 駐波半波  
長的整數倍

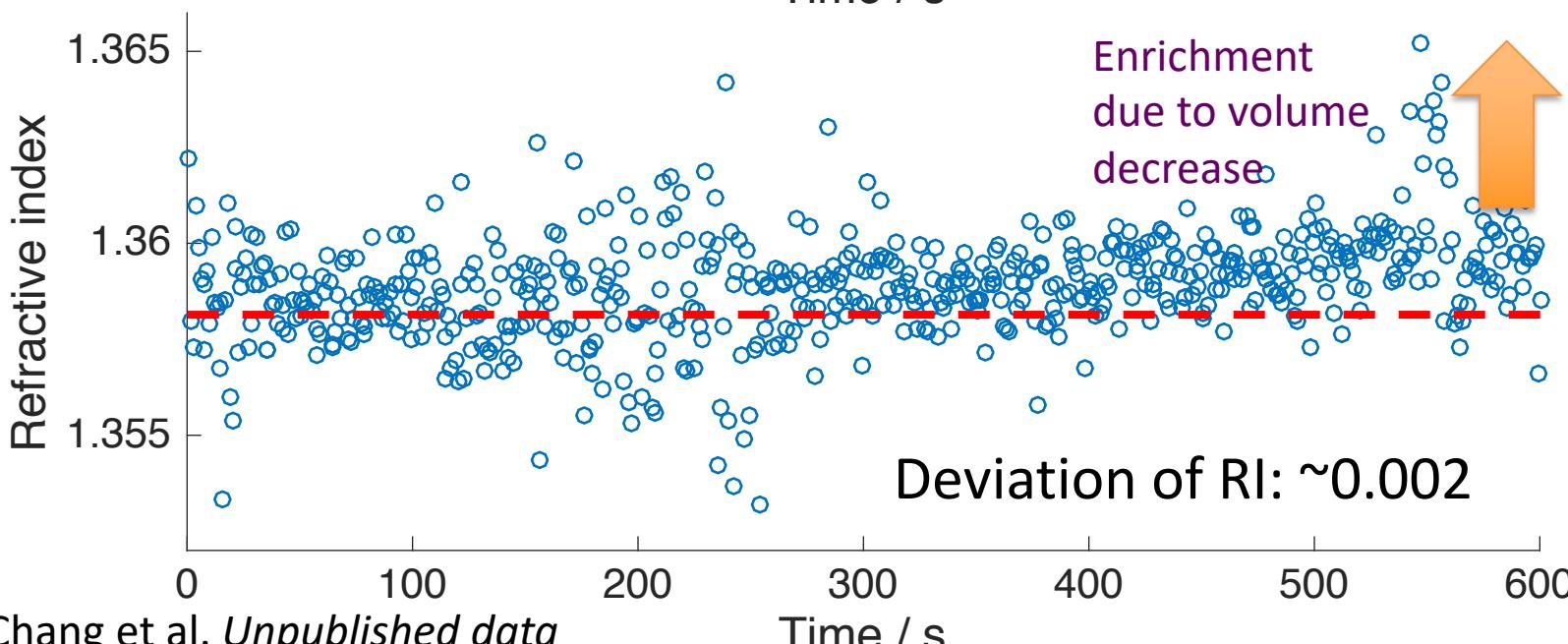
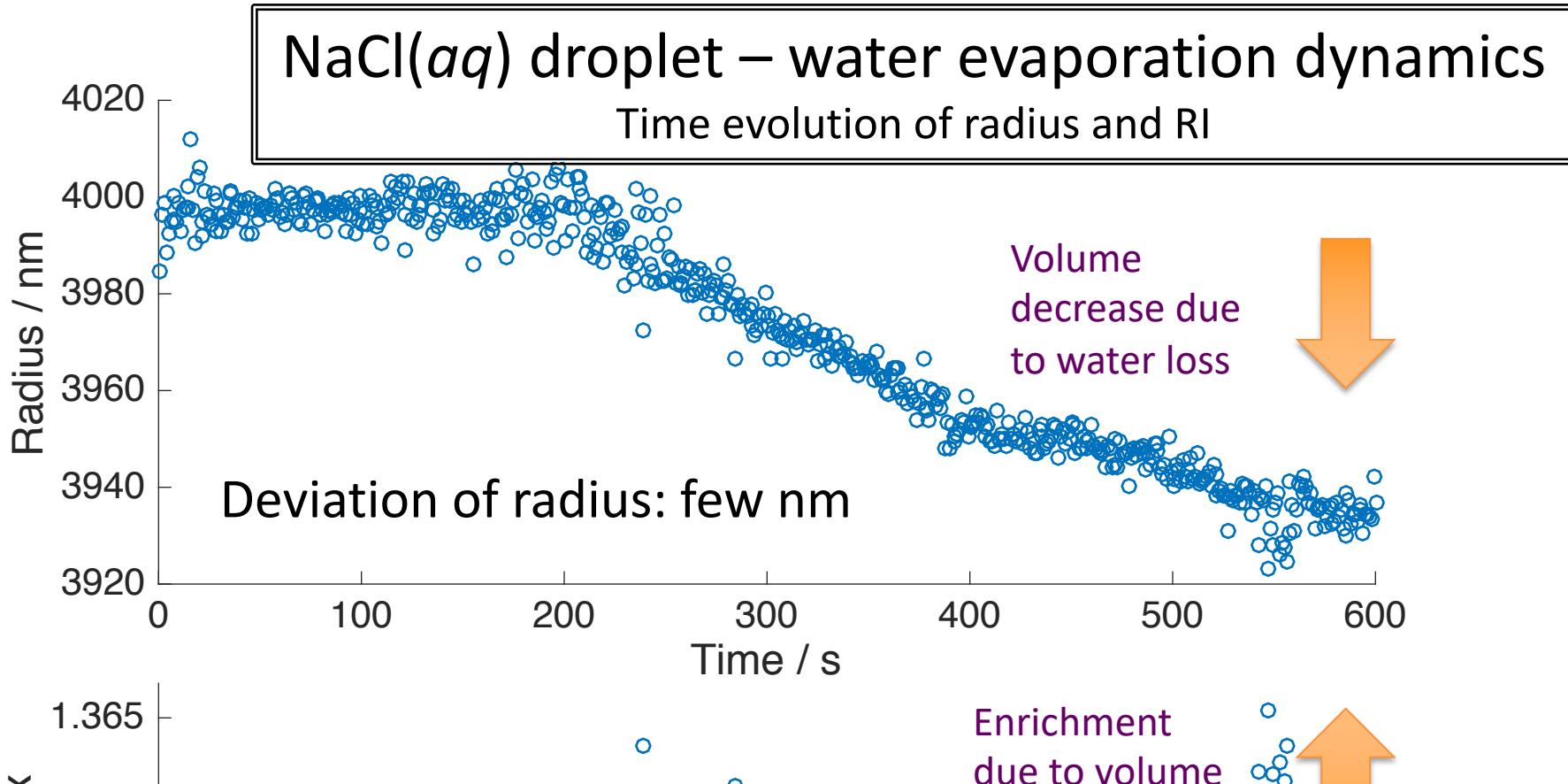
Wave optics



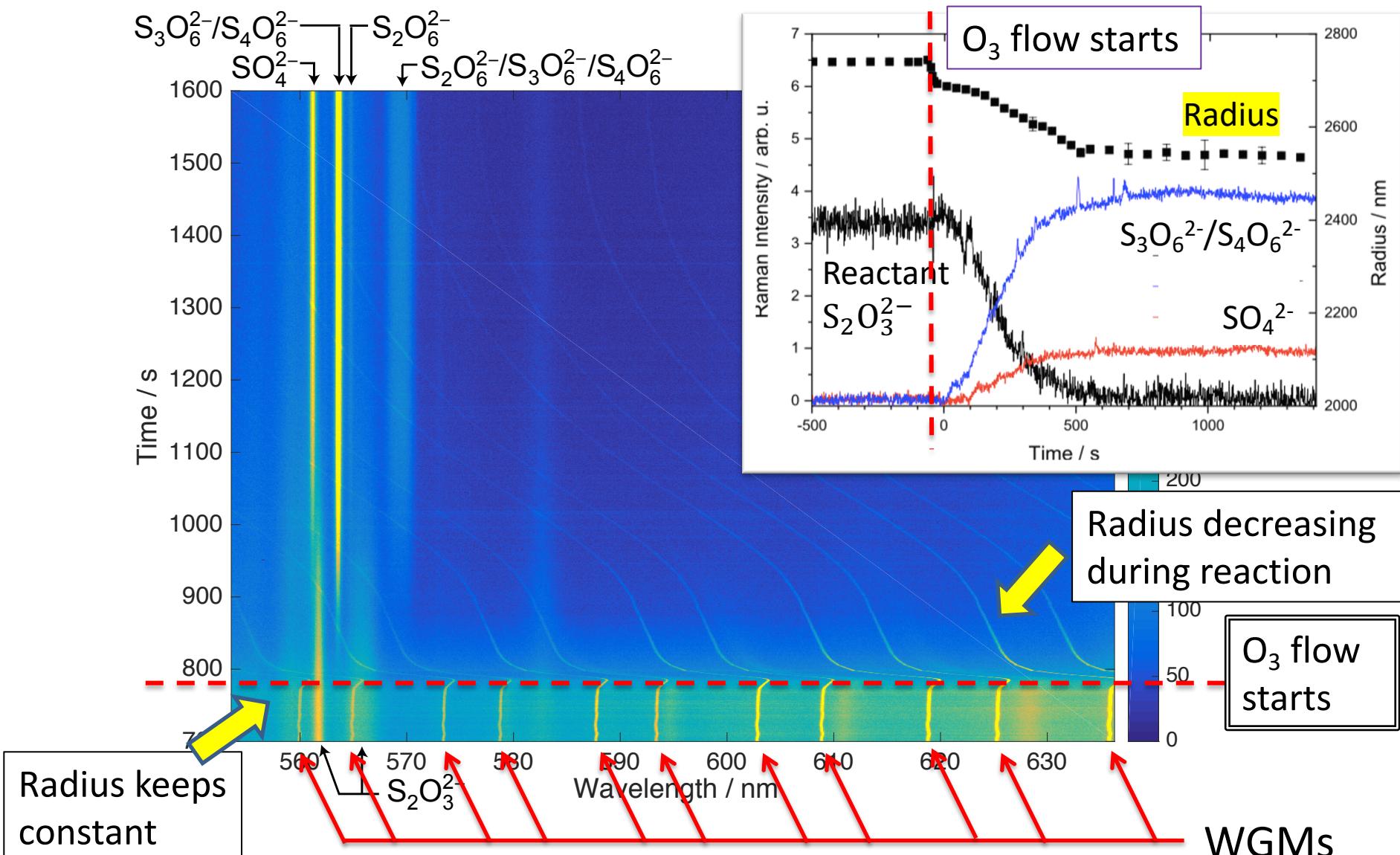
Whispering gallery in St. Paul's Cathedral

# Cavity-enhanced WGMs + Mie theory as an “optical ruler” to measure the size of single microdroplet with an accuracy of nm



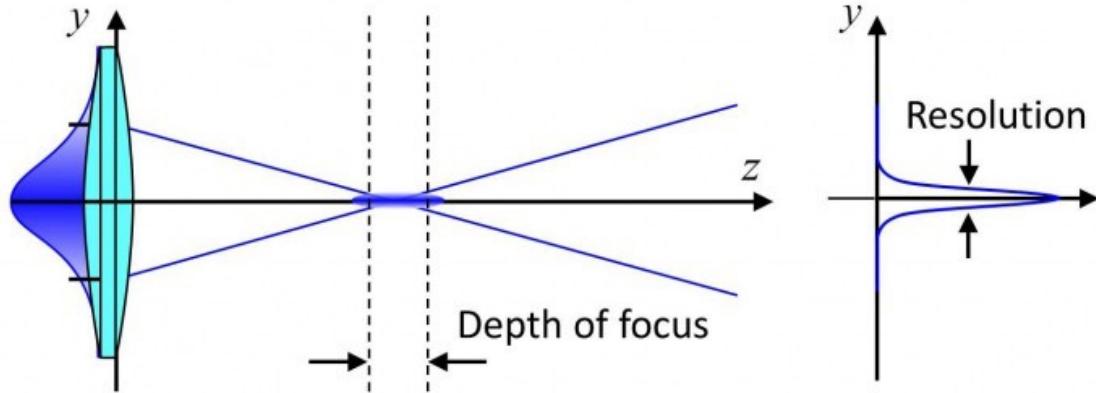


# Take home message: Raman spectra time series as “movie” of physicochemical properties of a single aerosol particle

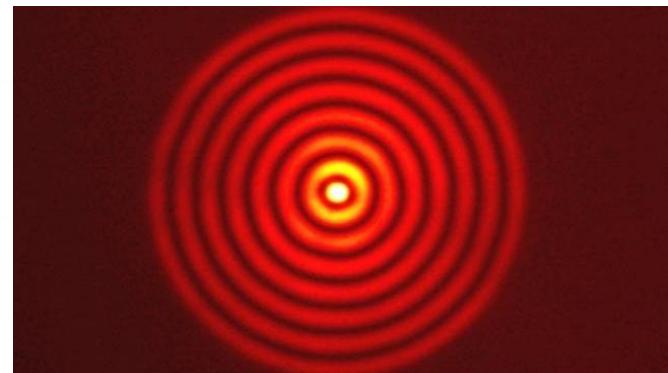
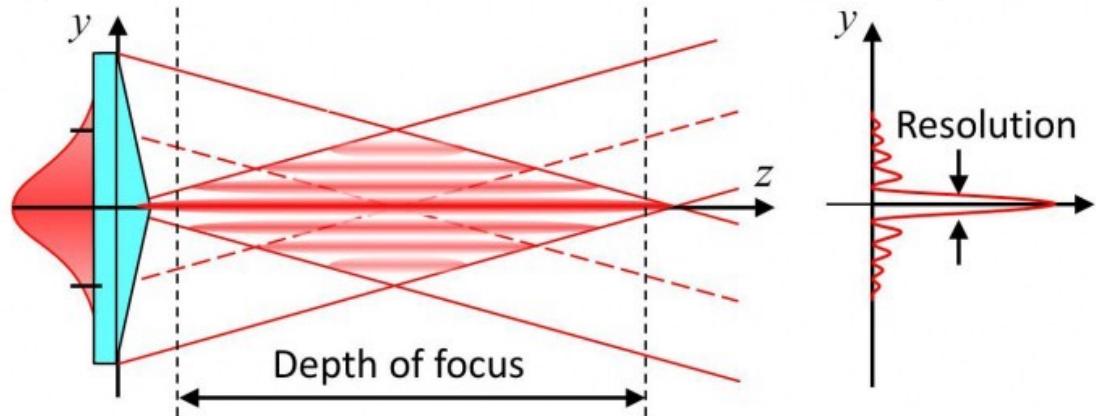


# Optical trapping via Bessel beam

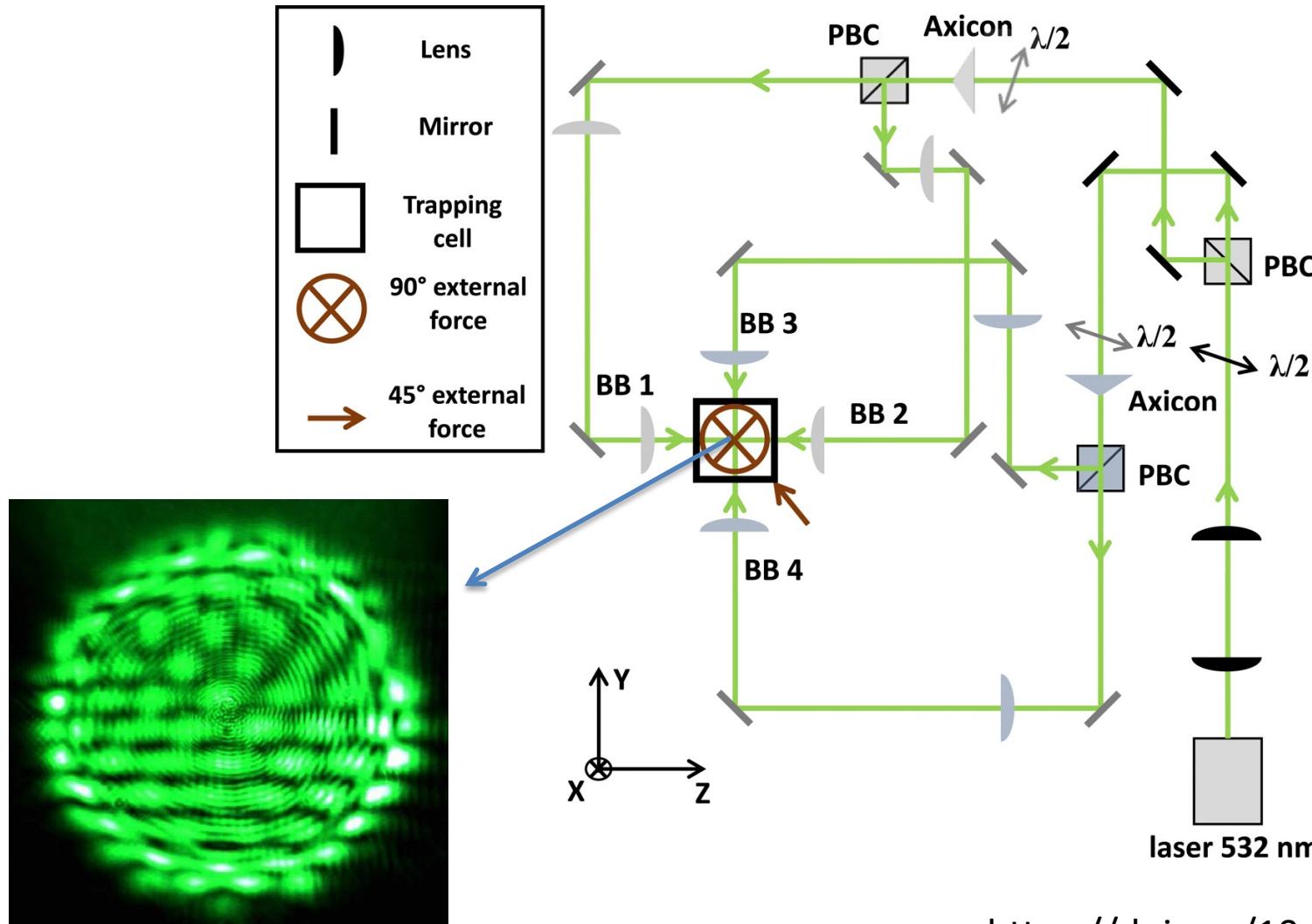
a) Gaussian beam focused with a spherical lens



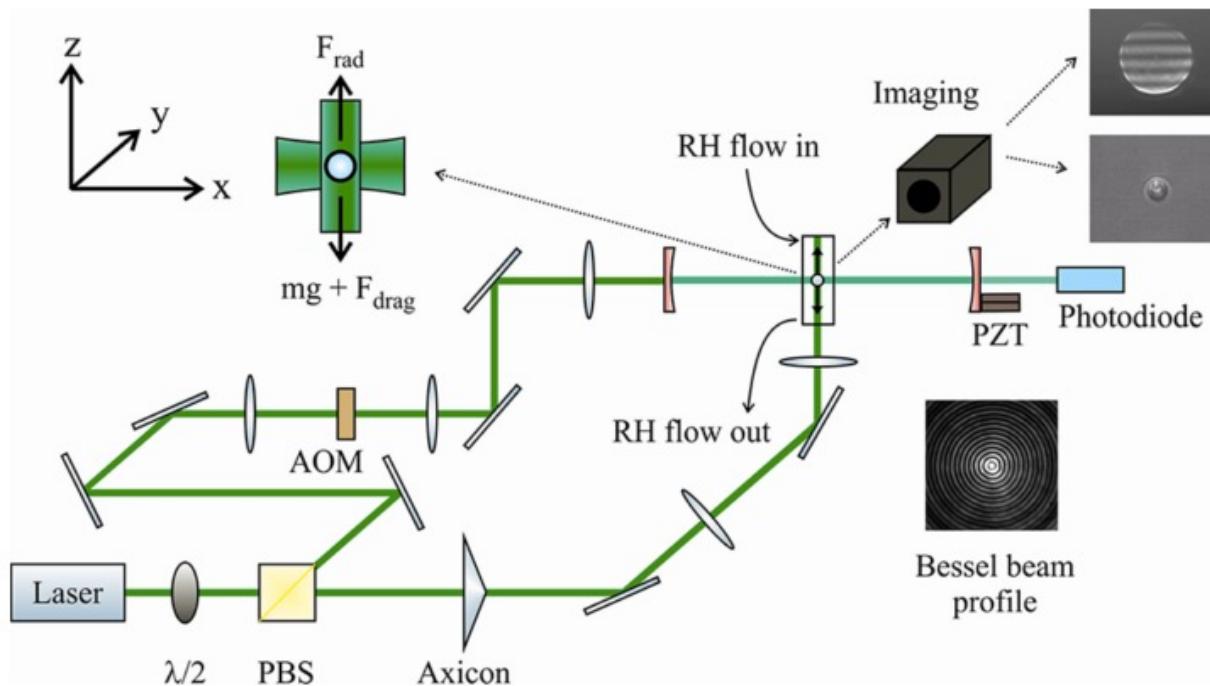
b) Gaussian beam focused with a conical lens (Axicon)



# 3D optical trap

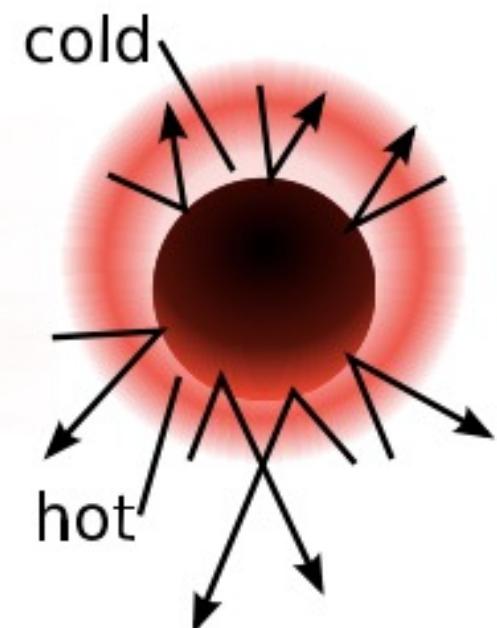
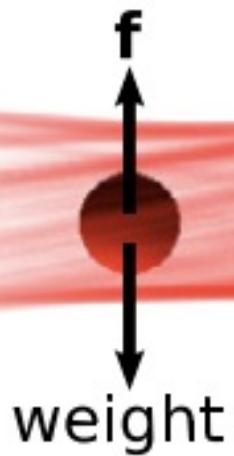


# Bessel beam trap + CRD: single particle spectroscopy

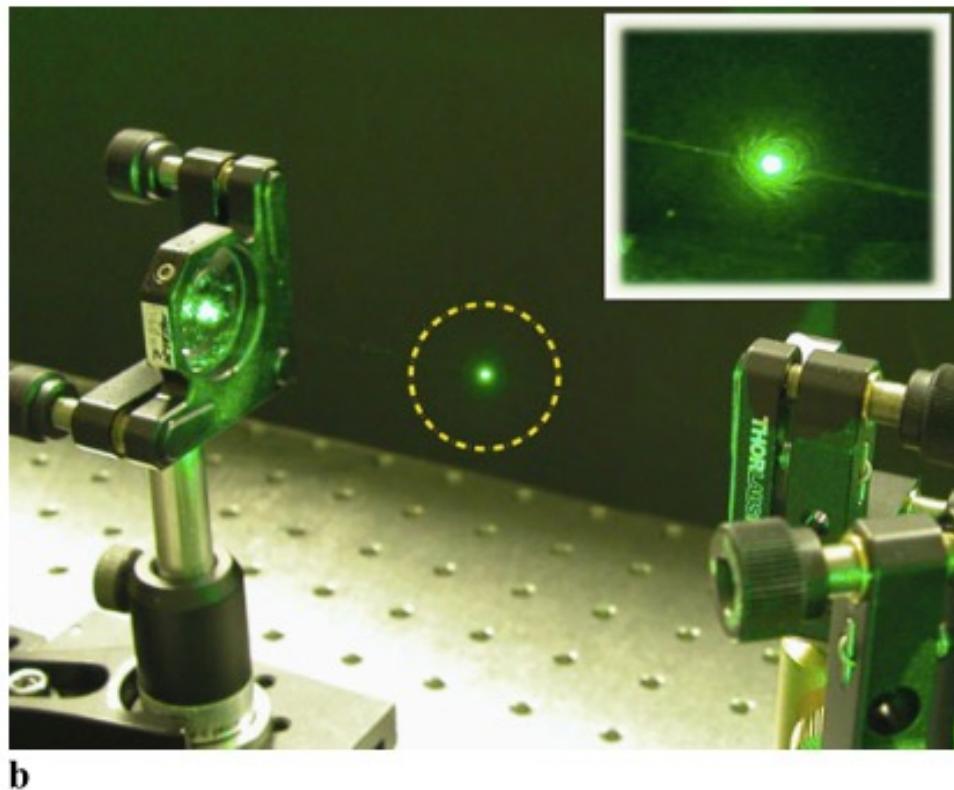
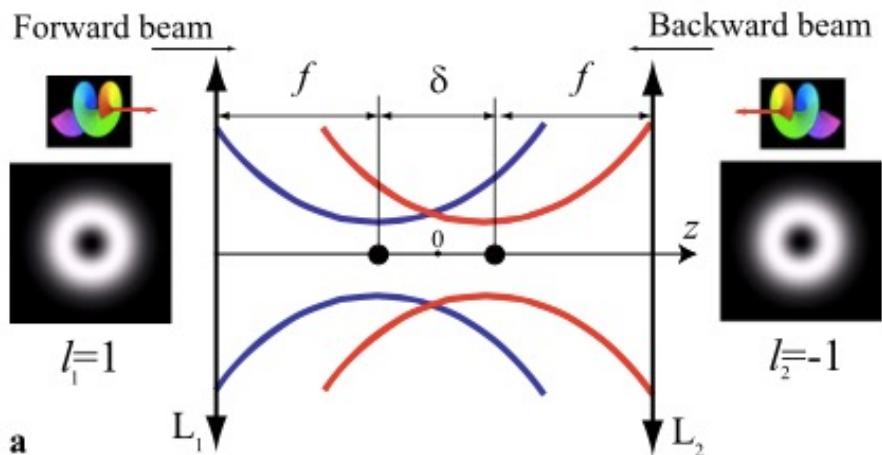


**Figure 1.** Schematic diagram of the single aerosol particle CRDS instrument. The Bessel beam profile is shown with brightfield and elastic scattered light images from an optically trapped droplet. AOM, acousto-optic modulator; PBS, polarizing beam splitter cube.

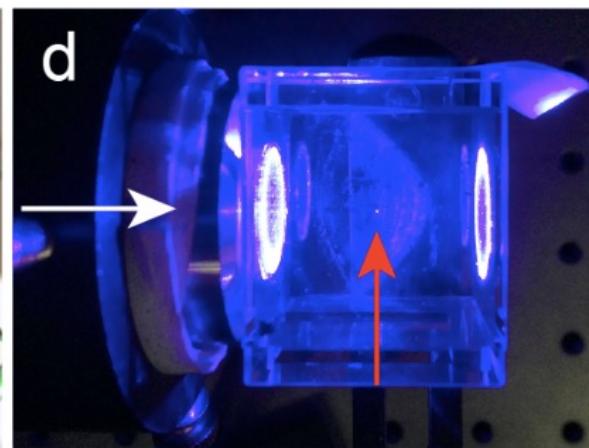
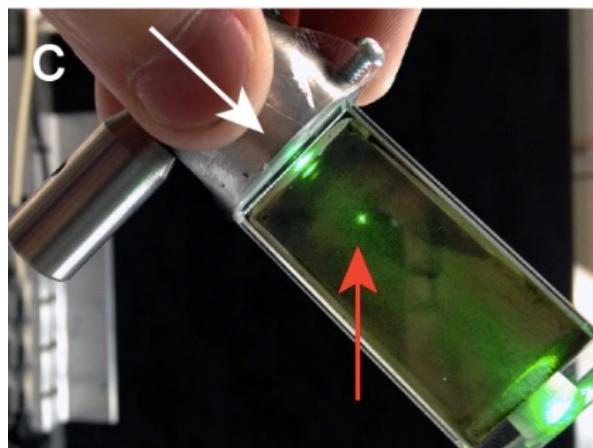
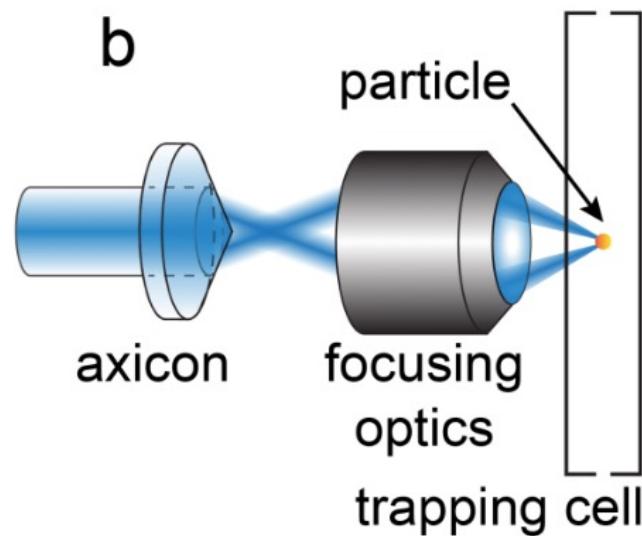
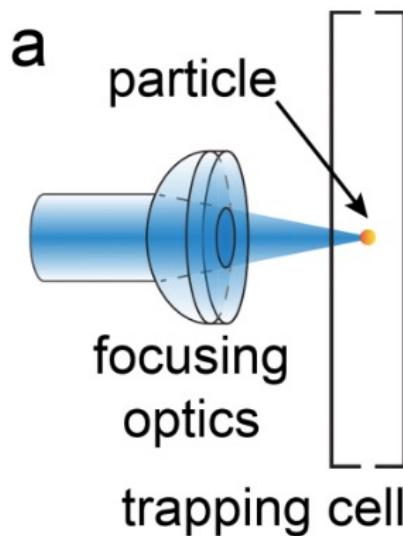
# Principle of trapping non-transparent particles – photophoretic force



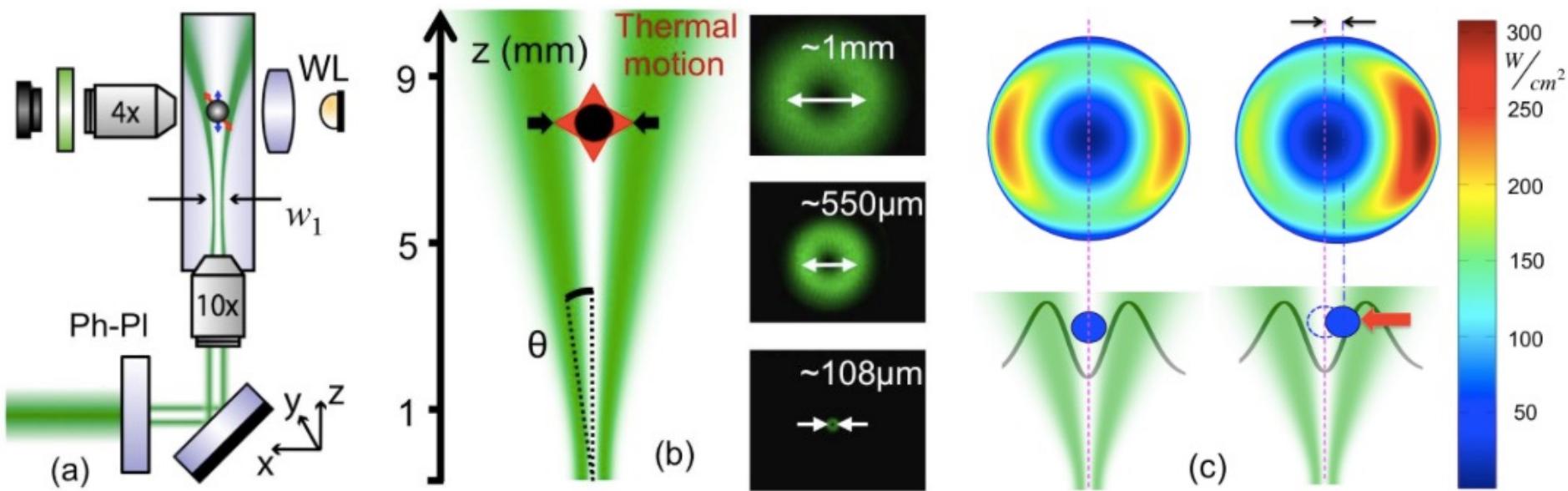
# High-order Bessel beam as a vortex beam trap

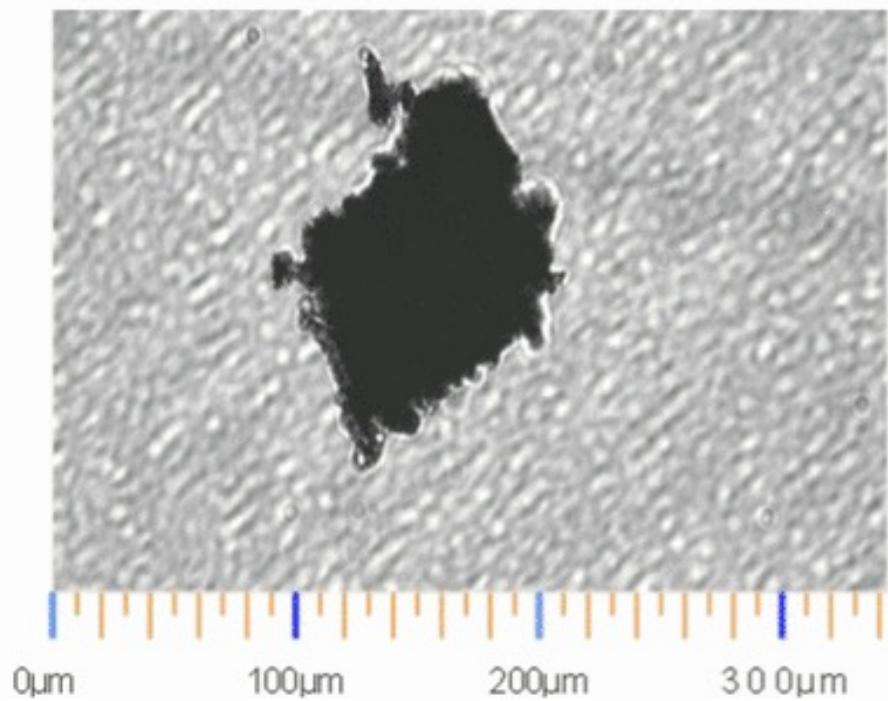
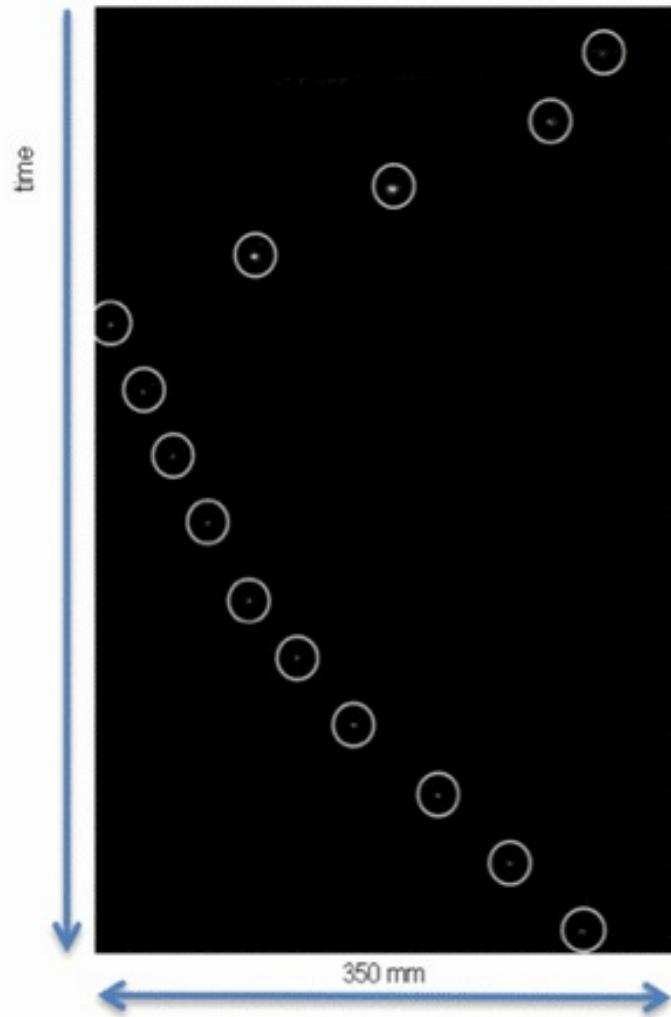
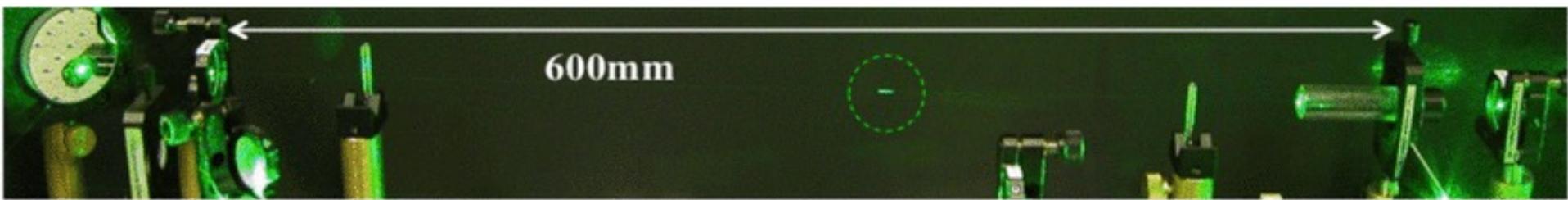


# Trapping carbon nanotubes

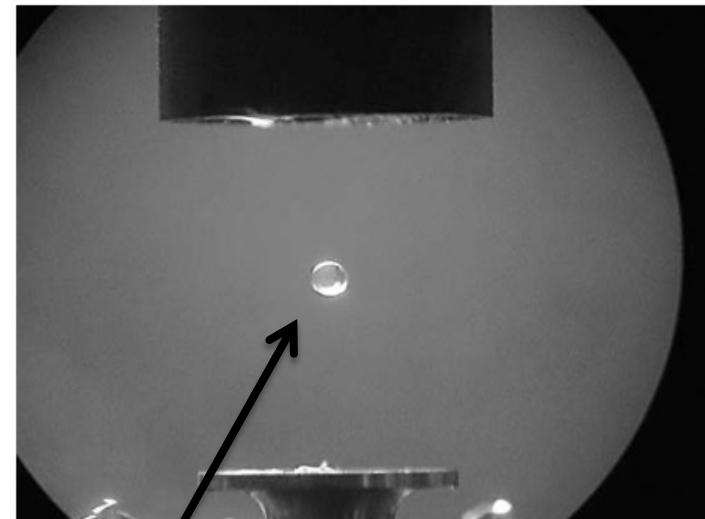
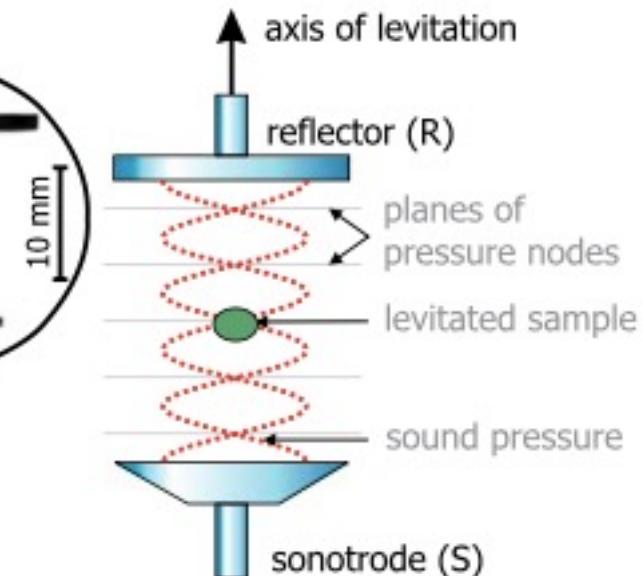
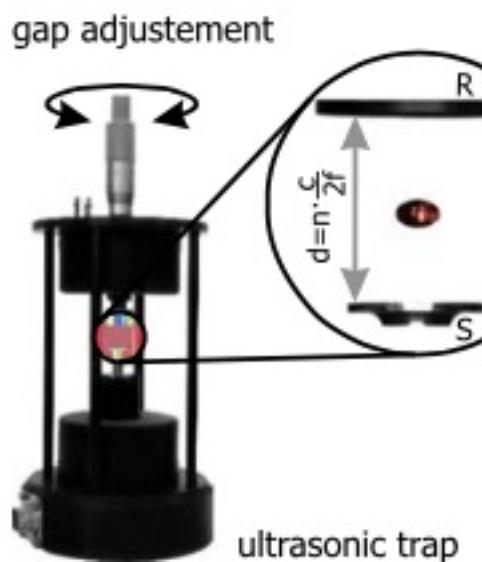


# Optical Funnel on a Stream of Particles in Air or Vacuum





# Acoustic levitation - schematic

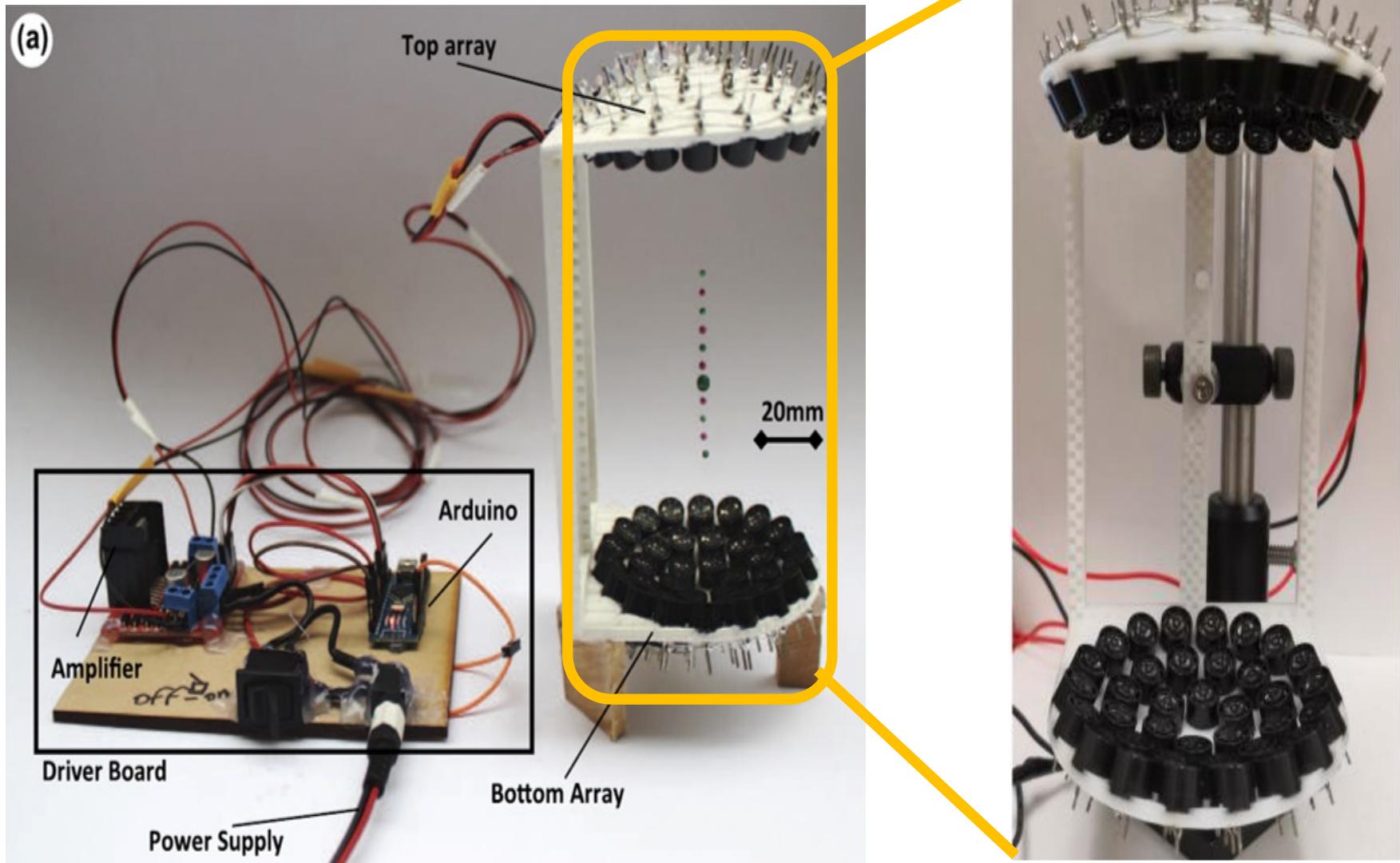


Applications: combine with optical spectroscopy or mass spectrometry

Diameter = 0.2 – 2 mm

# Acoustic Levitation - TinyLev

<http://dx.doi.org/10.1063/1.4989995>



# Application: study interface reaction dynamics via MS

