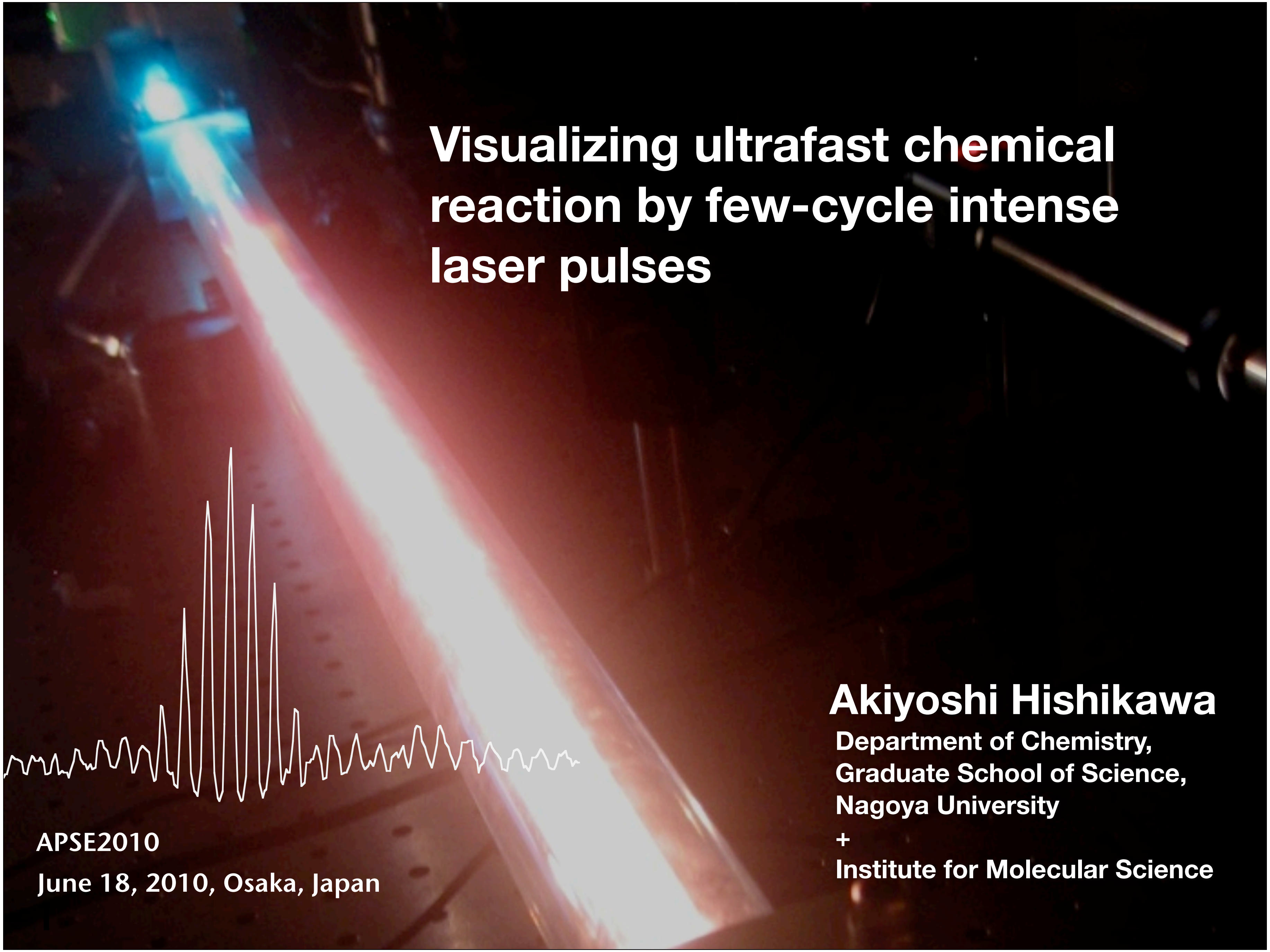


Visualizing ultrafast chemical reaction by few-cycle intense laser pulses

Akiyoshi Hishikawa

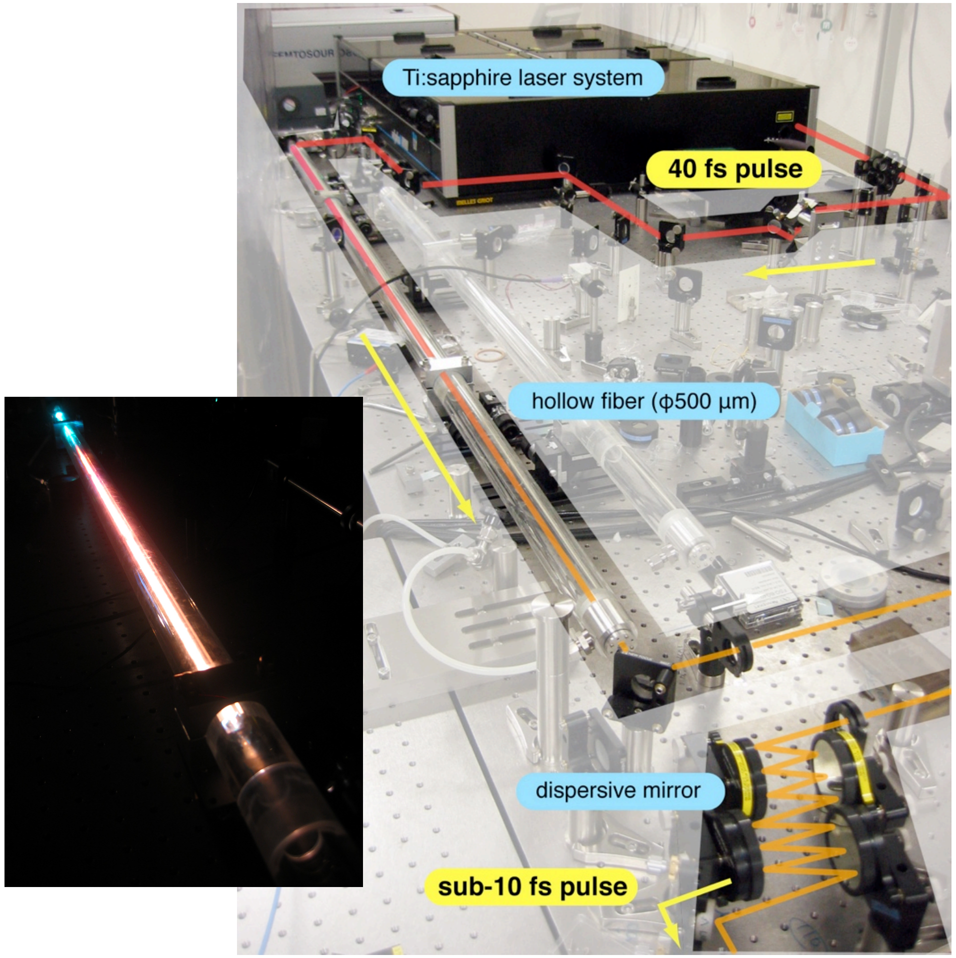
Department of Chemistry,
Graduate School of Science,
Nagoya University
+
Institute for Molecular Science

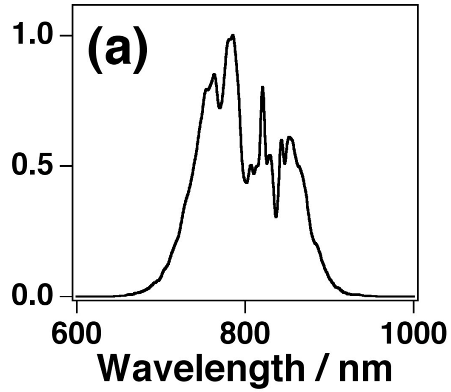
APSE2010

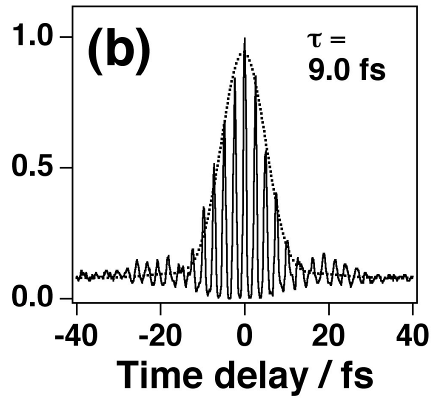
June 18, 2010, Osaka, Japan

Department of Chemistry
Nagoya University
Graduate School of Science

Generation of ultrashort laser pulse





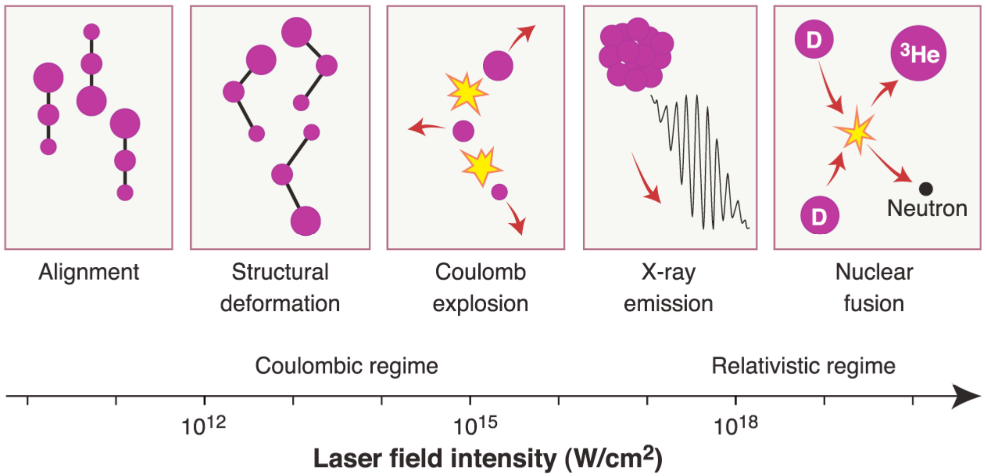


>400μJ/pulse

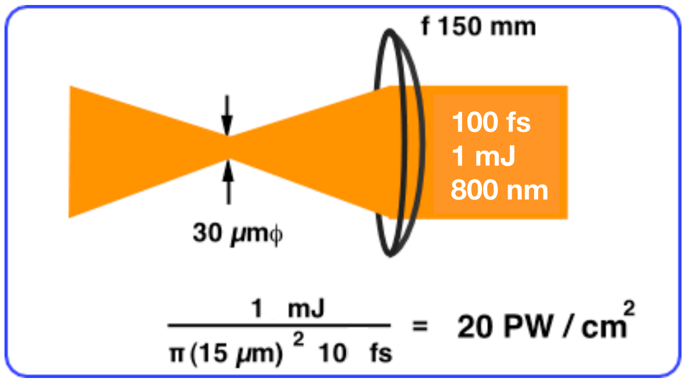
→ > 10^{16}W/cm^2

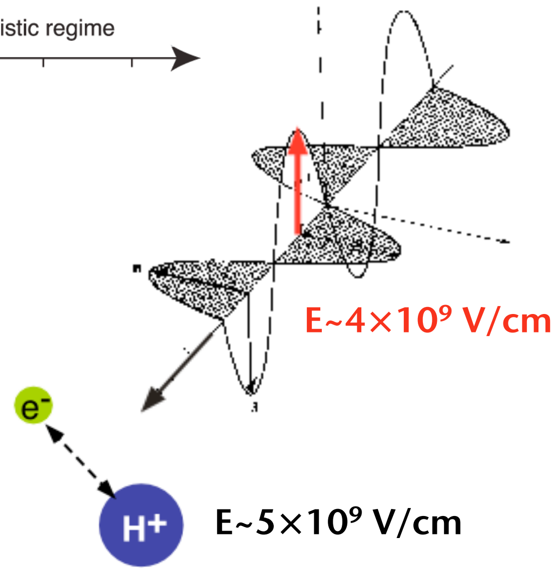
Intense laser fields

Molecular response to intense laser fields



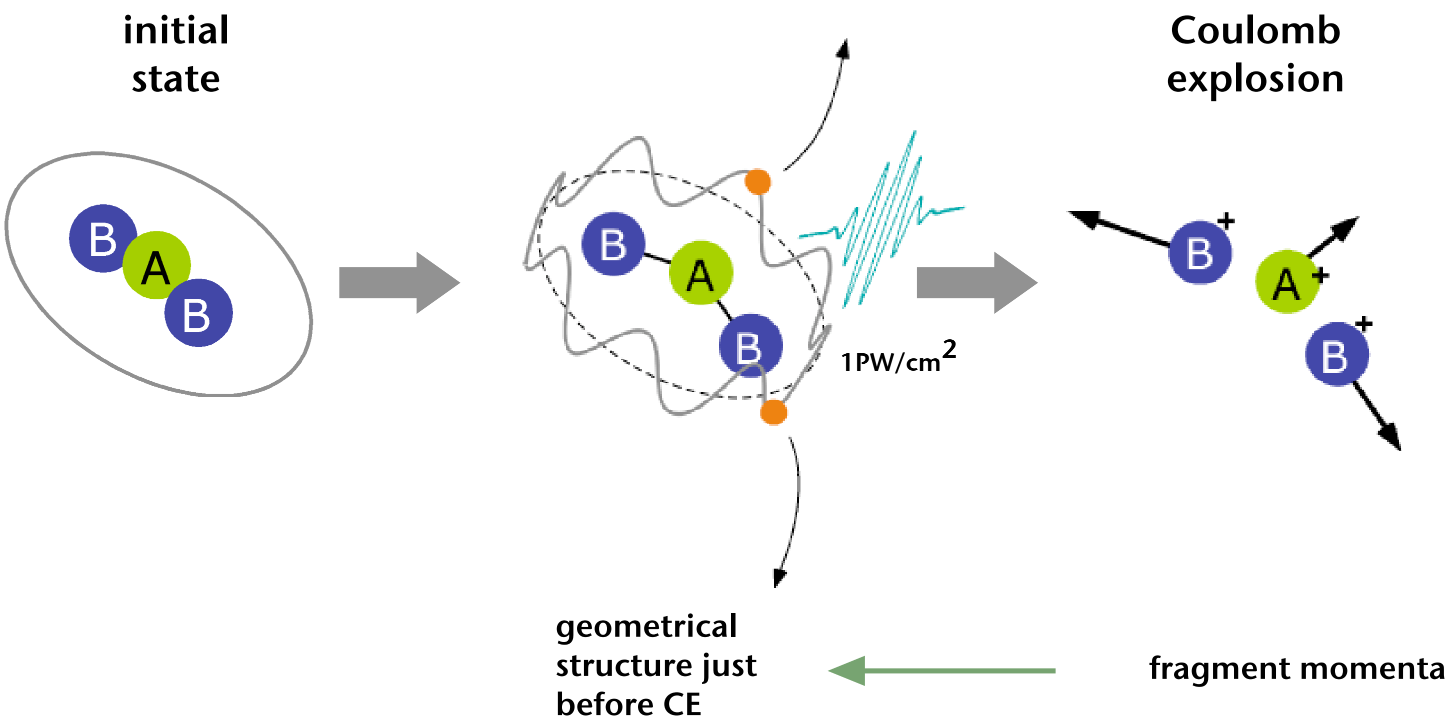
not observed in the perturbative regime of the light-molecule interaction





Coulomb explosion

in intense laser fields



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Okazaki Fireworks Festival

August 6th, 2010

20,000 fireworks
+ 0.5 M people

basic firework design

“a shell”

“stars” containing sparkler

multibreak shells

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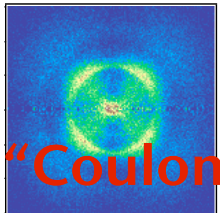
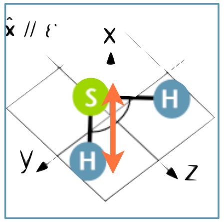
Research directions



Molecular dynamics in intense laser fields

- Dissociative ionization of NO in few cycle intense laser fields
- Electron-ion coincidence momentum imaging of CS_2 , H_2, etc

"Coulomb explosion imaging of molecules"



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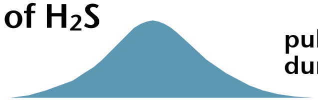
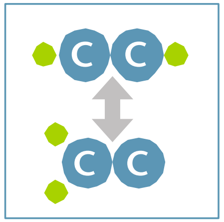


pulse duration ~ nuclear motion



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- Dissociation of CS_2^{4+}, "quantum clacker"
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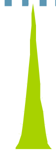

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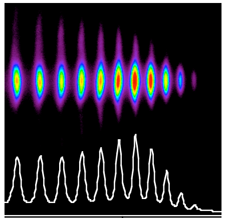
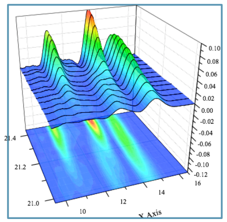


High-order harmonics: generation/application

- Characterization of high-order harmonics
- Construction of "Beam line"
- $Br_2 \longrightarrow Br+Br$



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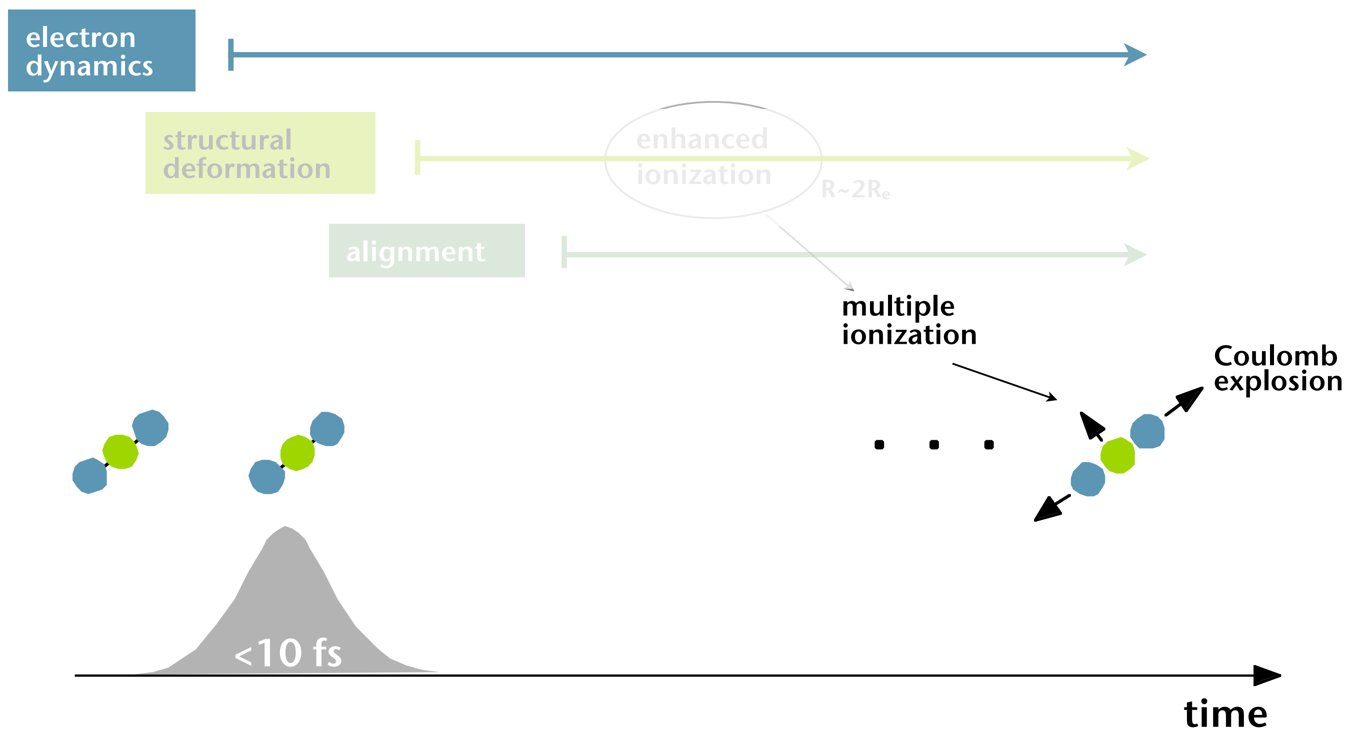
- Resonant/non-resonant pump-probe photoelectron spectroscopy

Molecular processes in intense laser fields



- beam foils
- highly charged ions

- Intense laser pulses (<10 fs)

F. Legare, et al., Phys. Rev. A 71, 013415 (2005), ibid 72, 052717 (2005).
E. Baldit, et al., Phys. Rev. A 71, 021403 (2005).
A. Matsuda, et al., J. Chem. Phys. 117, 114308 (2007).

Coincidence momentum imaging

Hasegawa, Hishikawa, Yamanouchi, Chem.Phys.Lett. 349(2001) 57

enables us...

to detect all the fragment ions in coincidence

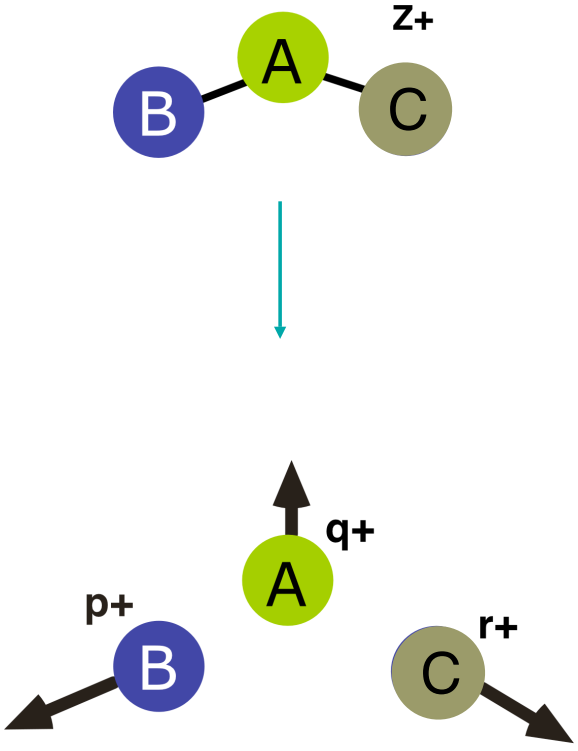
→ secure assignment of explosion pathway

(A^{p+}, B^{q+}, C^{r+})

to determine the momentum vector in lab frame

→ geometrical structures

nuclear motion in intense laser fields



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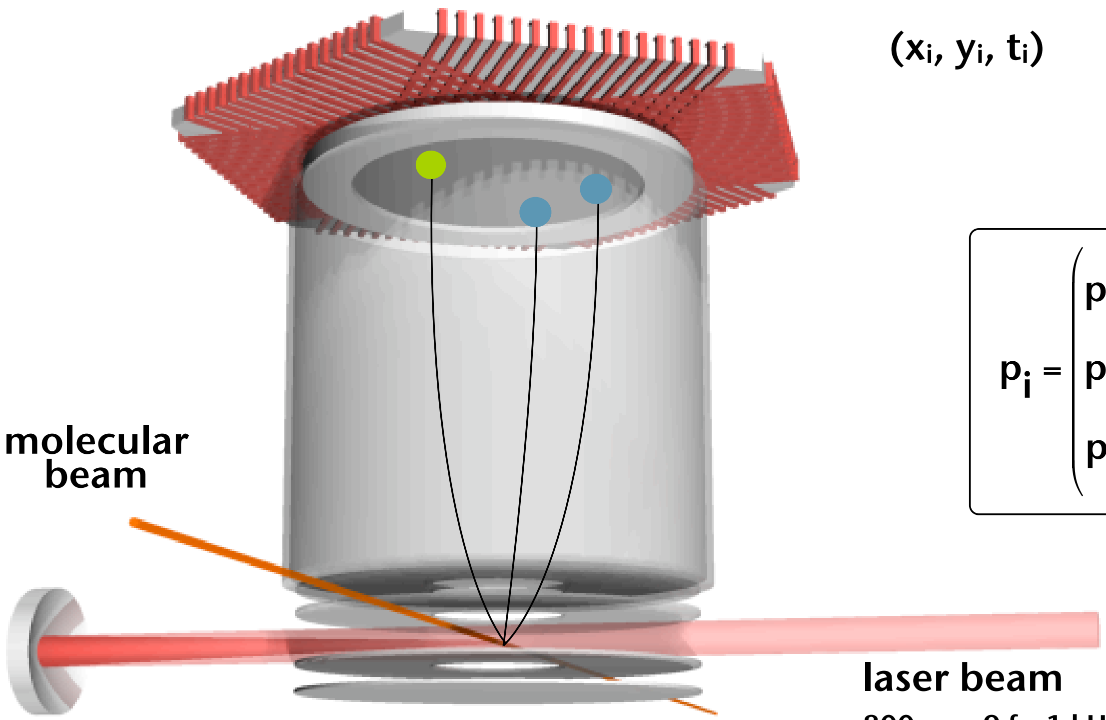
Experimental setup

coincidence momentum imaging



$$p_i = \begin{pmatrix} p_i^x \\ p_i^y \\ p_i^z \end{pmatrix} = \begin{pmatrix} m_i\, x_i\ / t_i \\ m_i\, y_i\ / t_i \\ q_i\, F(t_i - t_i^0) \end{pmatrix}$$

~1x10^{-8} Pa ⟶ <0.1 events/shot

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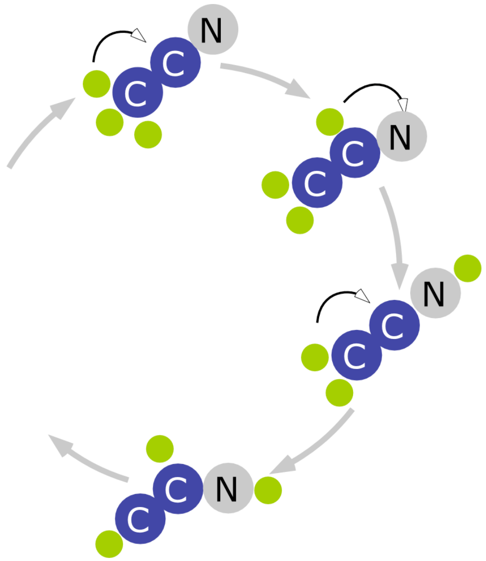
Visualizing hydrogen migration

hydrogen migration

in combustion, catalytic,
biosynthetic processes



large mobility of H atoms → main pathways of chemical reactions

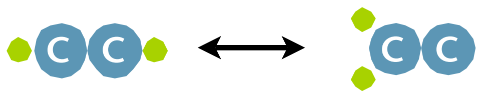
X-ray/electron diffraction

with pump-and probe scheme

e.g. H. Ihee et al., Science 291, 458 (2001)
Science 309, 1223 (2005)

► Ultrafast timescale

prototype of hydrogen migration



acetylene ⟷ vinylidene

T = 40 - 200 fs : C_2H_2

estimated spectroscopically

K. M. Ervin, J. Ho, W. C. Lineberger,
J. Chem. Phys. 91, 5974 (1989)

T < 60 fs : $C_2H_2^{2+}$

estimated from PAD

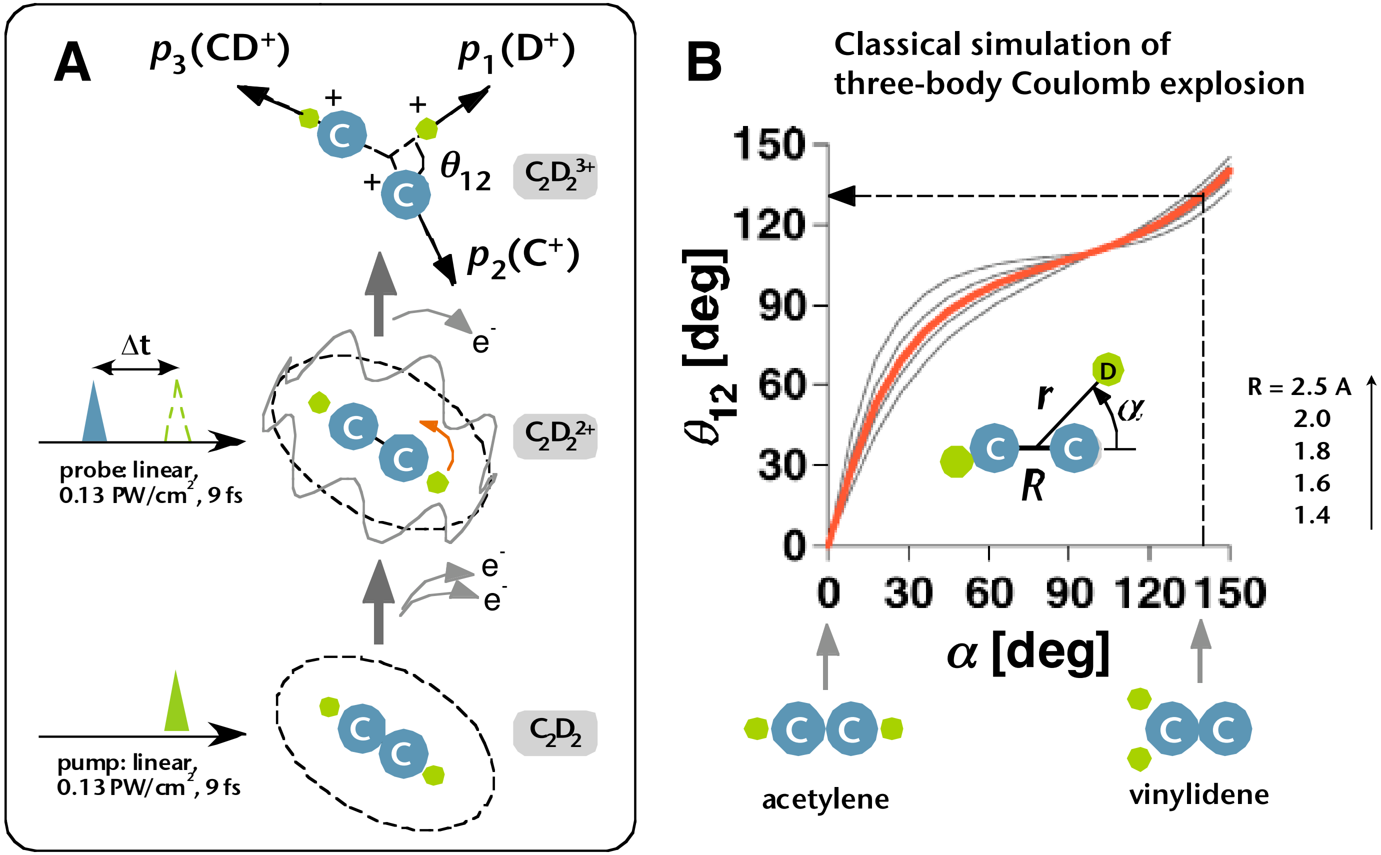
T. Osipov, et al.,
Phys. Rev. Lett. 90, 233002 (2003).

► Low diffraction intensity

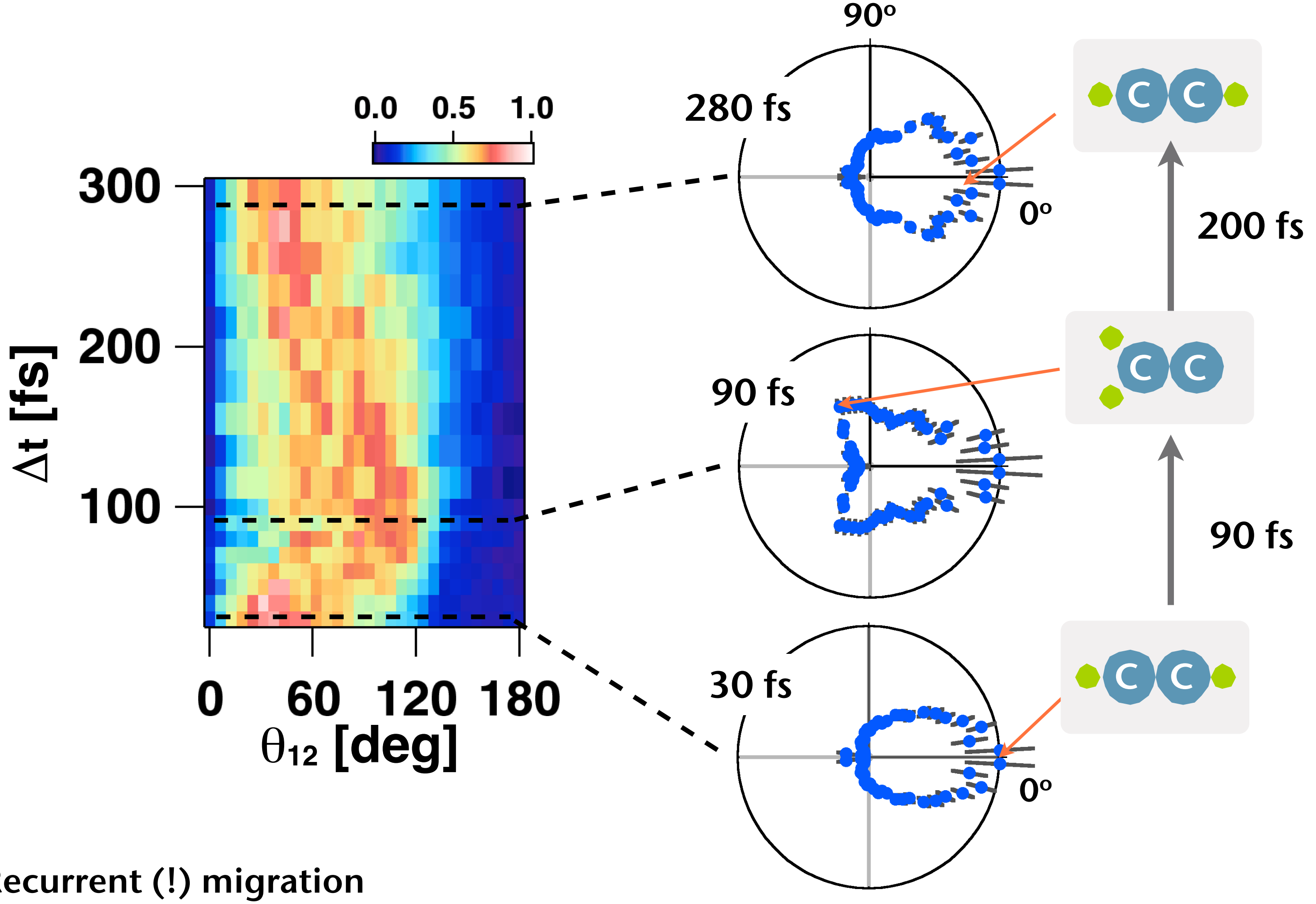
$$|F_g|^2 = |\Sigma\, f_i\, e^{-2\Pi i \gamma \cdot r}|$$

scattering factor $\propto Z^2$

Coulomb explosion imaging of ultrafast hydrogen migration : pump-probe



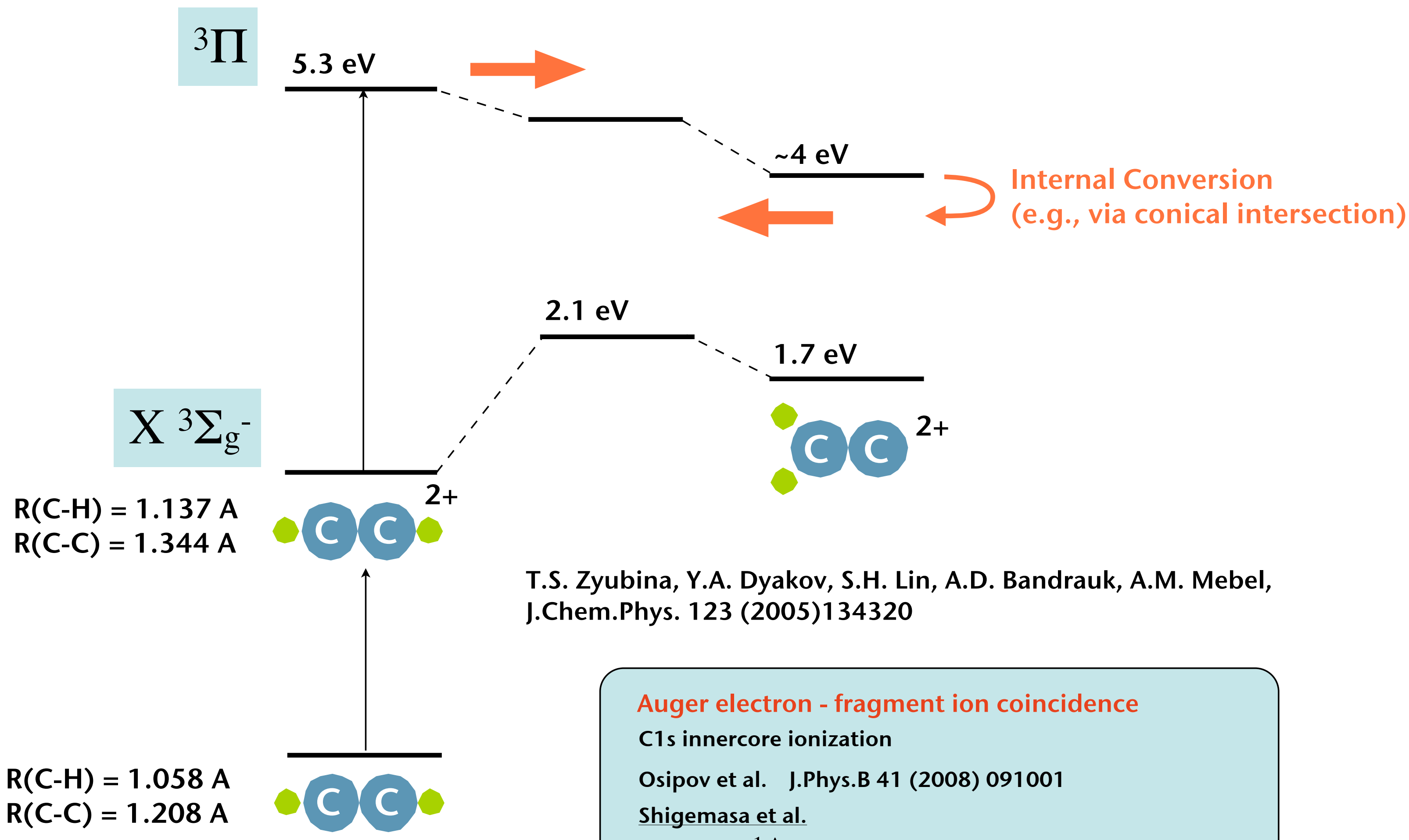
Ultrafast migration of hydrogen atoms



Recurrent (!) migration
visualized with sub-10fs intense laser pulses

A. Hishikawa, A. Matsuda, M. Fushitani, E. J. Takahashi, Phys. Rev. Lett. 99 (2007) 258301

Mechanism of recurrent migration



T.S. Zyubina, Y.A. Dyakov, S.H. Lin, A.D. Bandrauk, A.M. Mebel, J.Chem.Phys. 123 (2005)134320

Auger electron - fragment ion coincidence

C1s innercore ionization

Osipov et al. J.Phys.B 41 (2008) 091001

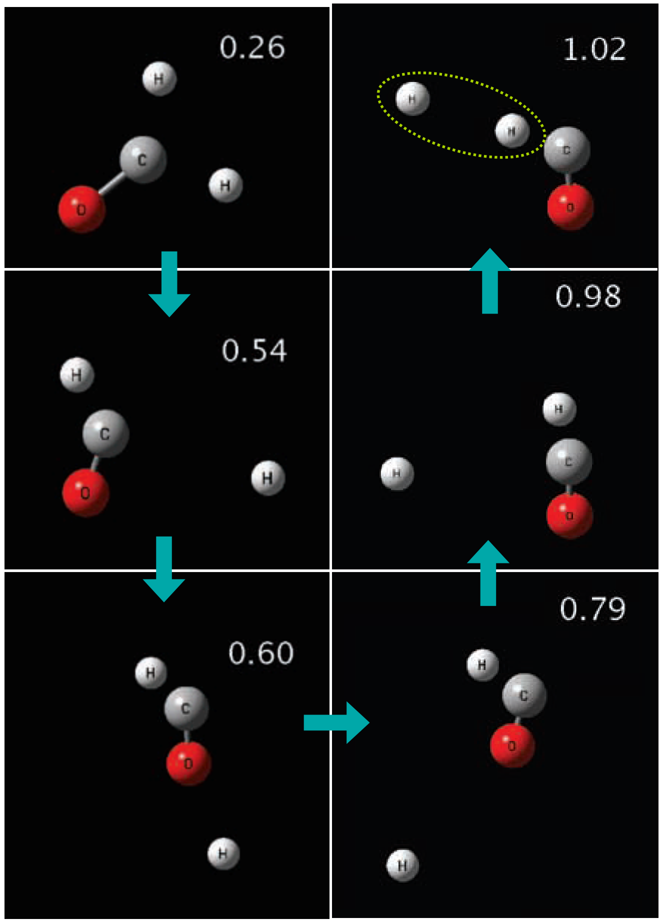
Shigemasa et al.

$a^1\Delta_g \longrightarrow C^+ + CD_2^+$

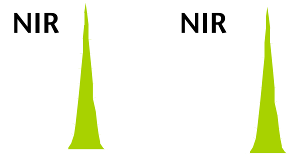
Future plans: roaming hydrogen

Townsend et al Science 306 (2004) 1158
Heazlewood et al PNAS 105 (2008) 12719 ⟵ high vibrational distribution of H_2

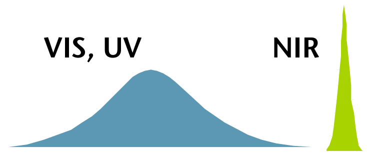
UV (λ~315 nm) photodissociation : $H_2CO \longrightarrow H_2 + CO$



► $C_2D_2^{2+}$ study : intense NIR x 2



► Real-time tracking of photochemical reactions
(perturbative regime) : UV + intense NIR



Coulomb explosion of H_2CO
7 and 35 fs intense laser fields

- feasibility of CEI in H_2CO?
- dynamics in intense laser fields ?

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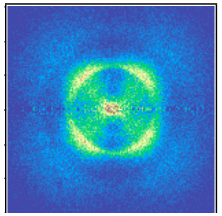
Research directions



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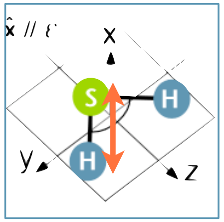

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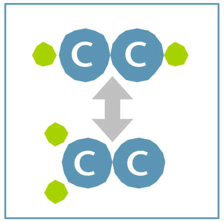

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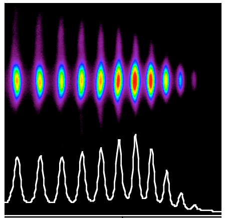
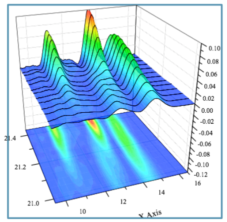


High-order harmonics: generation/application

- Generation and Characterization of high-order harmonics
- Construction of "Beam line"
- $Br_2 \longrightarrow Br+Br$,



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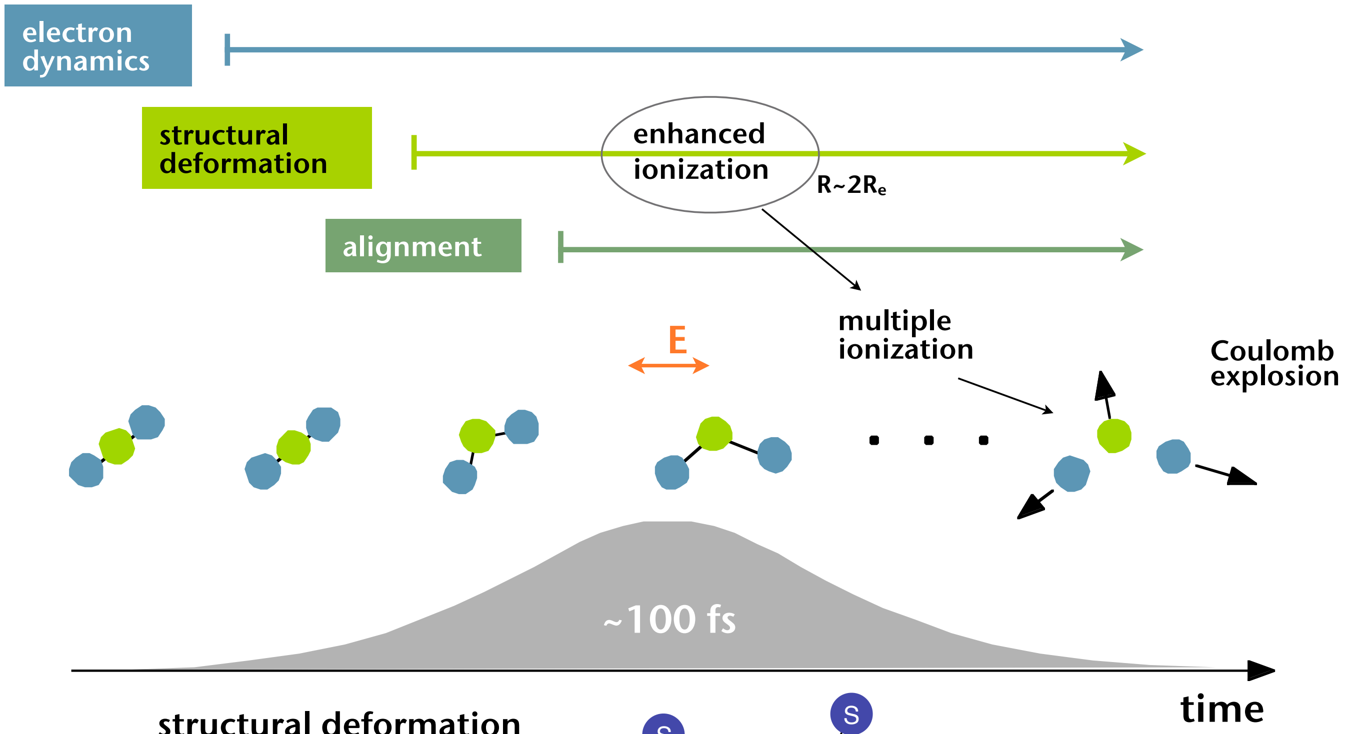
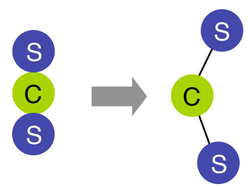
Molecular processes in intense laser fields



structural deformation
isomerization
hydrogen migration



@0.1PW/cm^2

cf. Hishikawa, Iwamae, Yamanouchi, Phys. Rev. Lett. 83 (1999) 1127.

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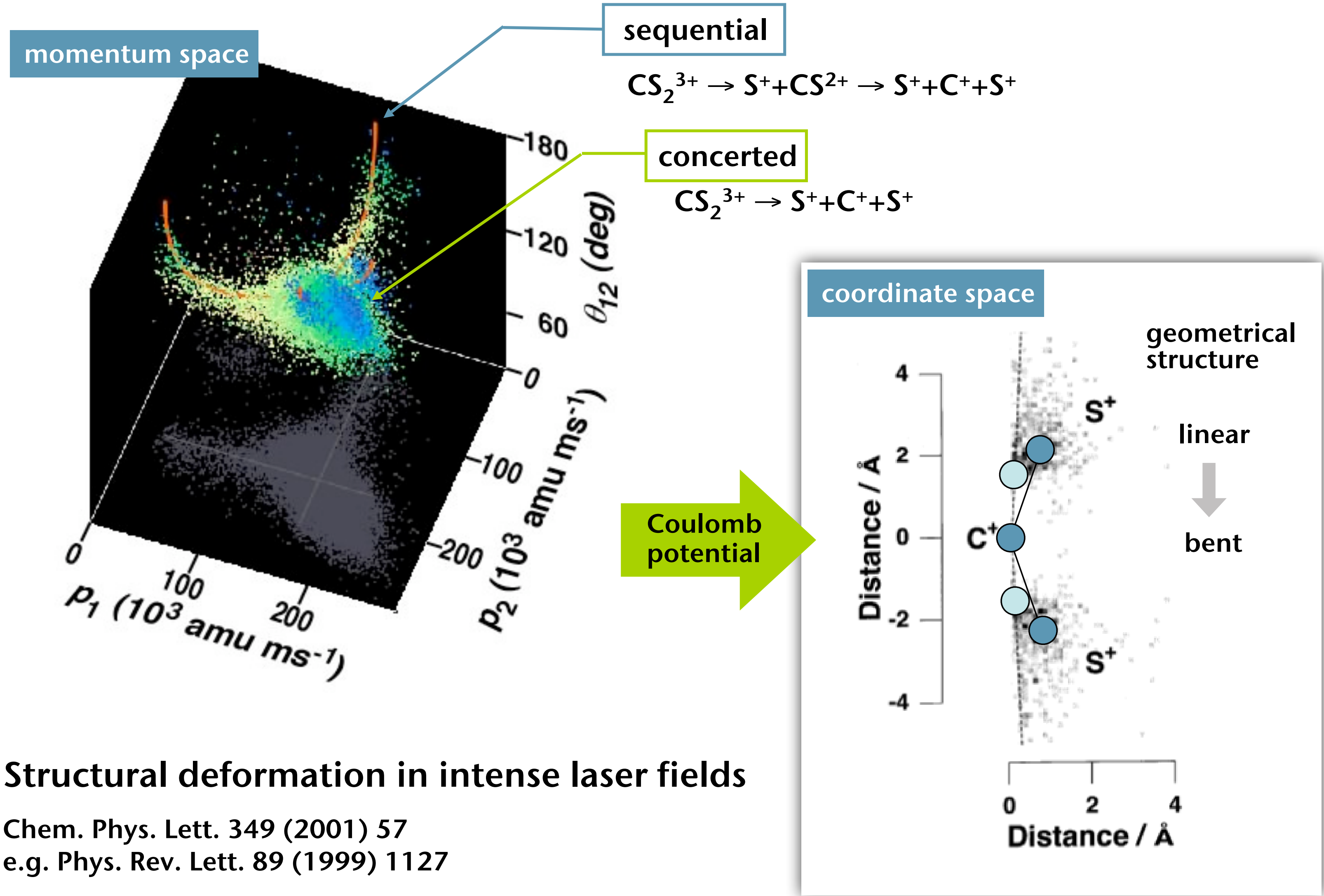
Coincidence momentum imaging of CS_2

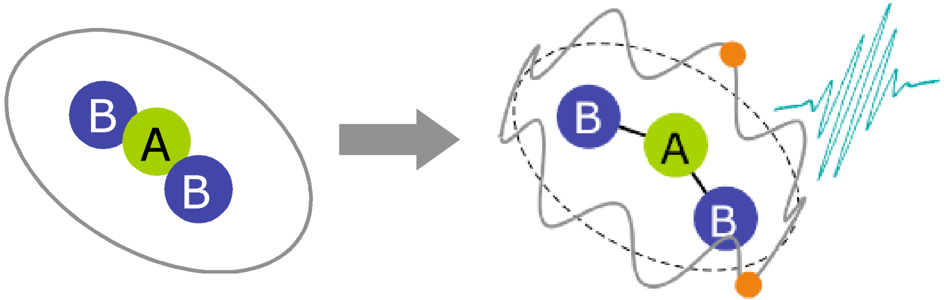
$CS_2^{3+} \rightarrow S^+ + C^+ + S^+$ in intense laser fields (60 fs, 0.2 PW/cm²)



Structural deformation in intense laser fields

Chem. Phys. Lett. 349 (2001) 57
e.g. Phys. Rev. Lett. 89 (1999) 1127

Reaction control using dressed molecules



Coulomb field

5×10^9 V/cm

~

Electric field

4×10^9 V/cm

light-dressed states

potential energy surface ---------- laser pulse shape

CONTROL

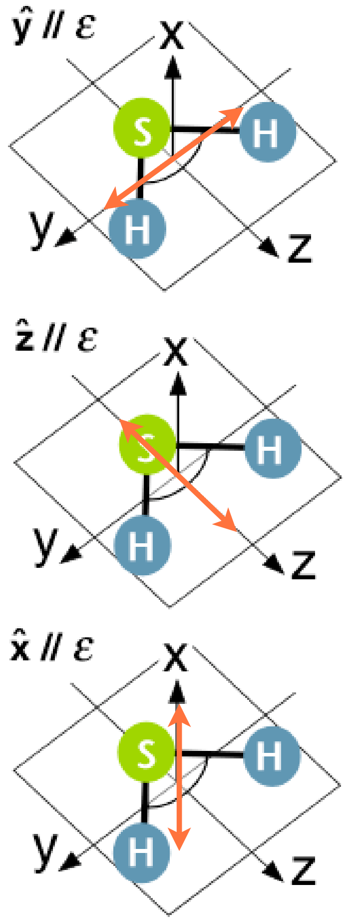
- structural deformation
- chemical reaction

Molecules in intense laser fields (1990 -)

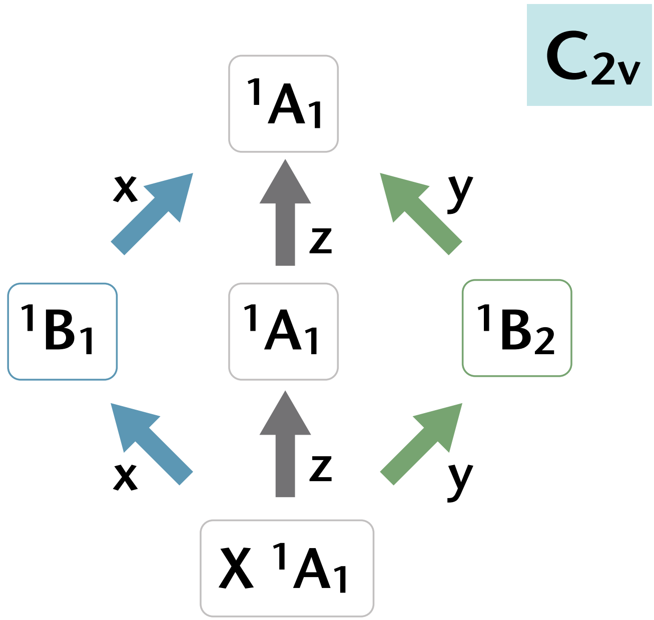
discussed with randomly oriented samples

Steering electrons in molecular frame

dependence on the direction of ε in molecular frame



Polyatomics have 3D molecular structures



electronic dipole interaction selection rule

↓

a set of electronic states coupled by the laser fields can be selected by the direction of ε

Molecular orientation from fragment momenta

three-body Coulomb explosion

$$\boxed{H_2S^{3+} \longrightarrow H^+ + S^+ + H^+}$$

- **number of available parameters** (single molecule)

  $3 \times 3 = 9$

- **translation momentum parameters = 3**

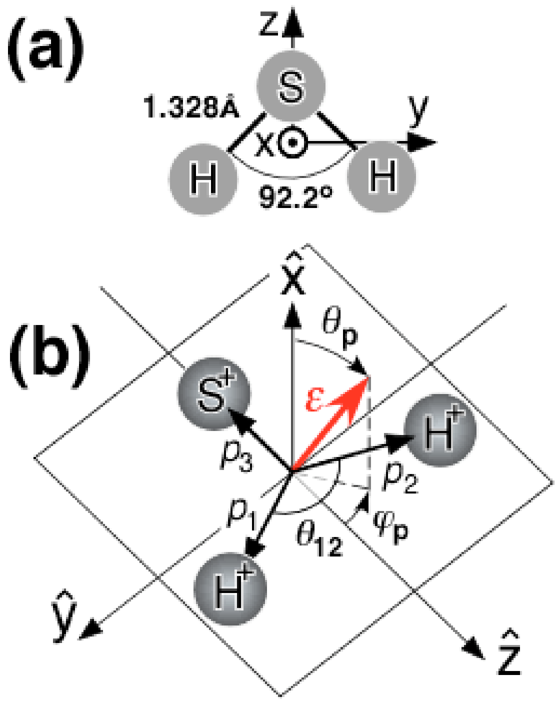
  (p_x^0, p_y^0, p_z^0)

- **structural parameters = 3**

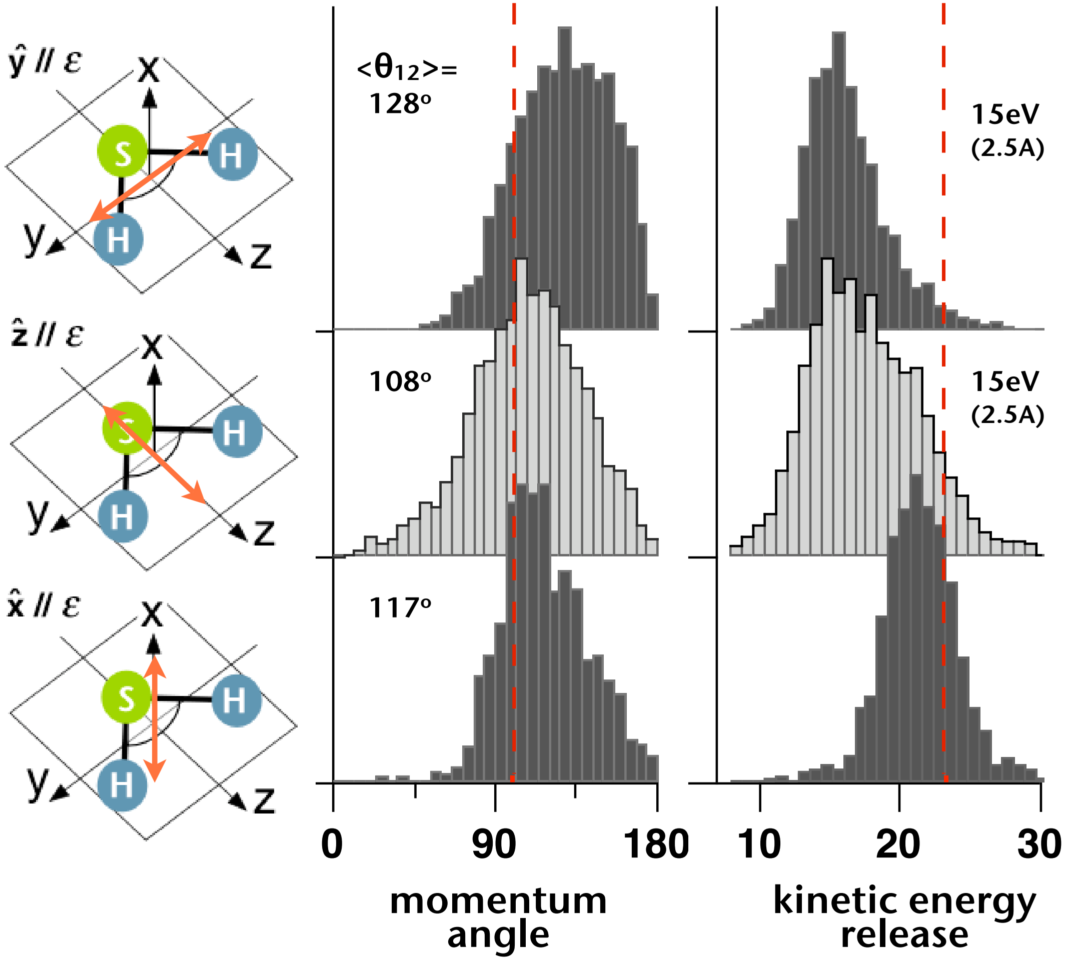
  $(\underbrace{E_{kin}}_{\text{symmetric stretching}}, \underbrace{\theta_{12}}_{\text{bending}}, \underbrace{\Delta p}_{\text{asymmetric stretching}})$, (p_1, p_2, θ_{12}), …

- **orientation parameters = 3**

  (x, y, z)



Reaction control by steering electrons in molecular frame



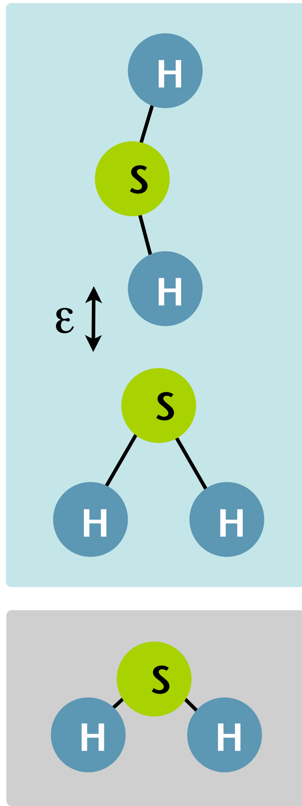
bond angle

∠H-S-H

bond length

R(S-H)

elongated structures along ε !

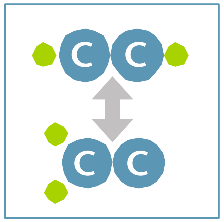


structure frozen prior to CE

Phys. Rev. Lett. 97 (2006) 243002

Summary

Development of atto & femto reaction imaging techniques



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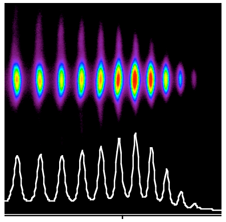
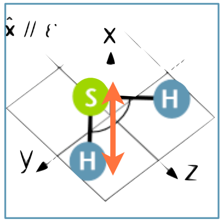


High-order harmonics: generation/application

- Characterization of high-order harmonics
- Construction of "Beam line"
- $Br_2 \longrightarrow Br+Br$, $I_2 \longrightarrow I+I$

→ discovery of new phenomena

Coherent control by laser reaction fields



Reaction control by steering electrons

- Orientation dependent Coulomb explosion of H_2S

→ new reaction scheme

→ Development of molecular sciences

Acknowledgements

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Mizuho Fushitani
Akitaka Matsuda
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Gustav Larsson (KTH)
Steven Hellingh (Stockholm Univ)
Hyeonho Choi (Seoul Nat. Univ)
Alexander Westerström (KTH)

high harmonics
pump-probe

multiple electron
coincidence
measurements

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fund from Japan Science and Technology Agency