Chiral Recognition in the Gas Phase investigated Using Femtosecond Photoelectron Circular Dichroism

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Attolab meeting 2018

Overview

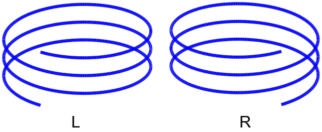
Overview

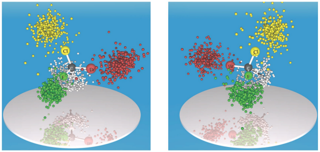
Chiral recognition

♠ **How to describe chirality?**

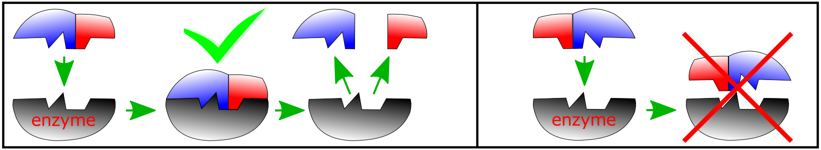
Lord Kelvin: " I call any geometrical figure, or group of points, chiral, and say that it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself."

Laurence D. Barron: Molecular light scattering and optical activity, Cambridge University Press

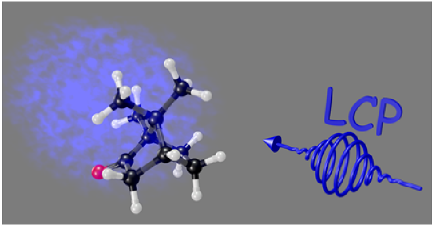




M.Pitzer et al.: Science 341, (2013)



Photoelectron Circular dichroism (PECD)



Differences in the differential photoelectron emission in the $\pm$ 10 % region (electric dipole interaction)

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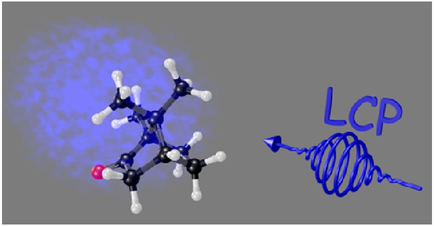
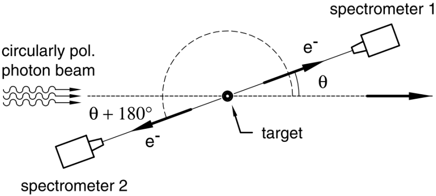


Differences in the differential photoelectron emission in the ± 10 % region (electric dipole interaction)

PECD survives averaging over different orientations of chiral molecules in space (measurement in laboratory frame possible)
B. Ritchie PRA 13, 1411 (1976), I. Powis JCP, 112, 1, (2000)

Demonstrated in Böwering et al., PRL 86, 1187 (2001)

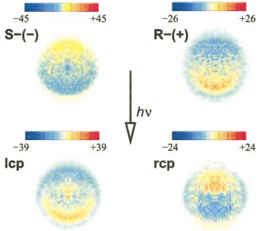


Photoelectron Circular dichroism (PECD)

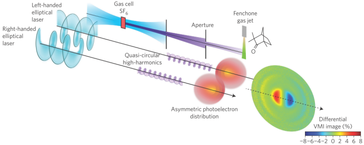
Single-photon ionization

Demonstrated using VMI

Garcia et al., JCP 119, 8781 (2003)



Determine polarization state of harmonics Mairesse et al., Nat. Phot. 314, (2014)



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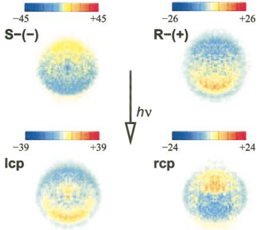

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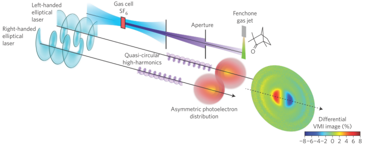
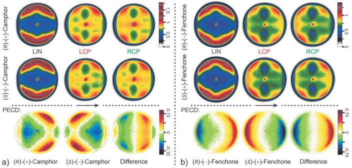


Multi-photon ionization

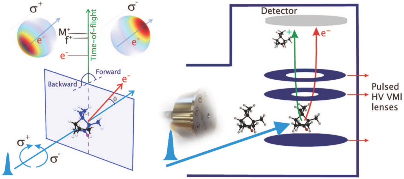
VMI

Lux et al., Angew. Chem. 51, (2012)



Mass-tagged PECD

Lehmann et al., J. Chem. Phys. 139, (2013)



Overview

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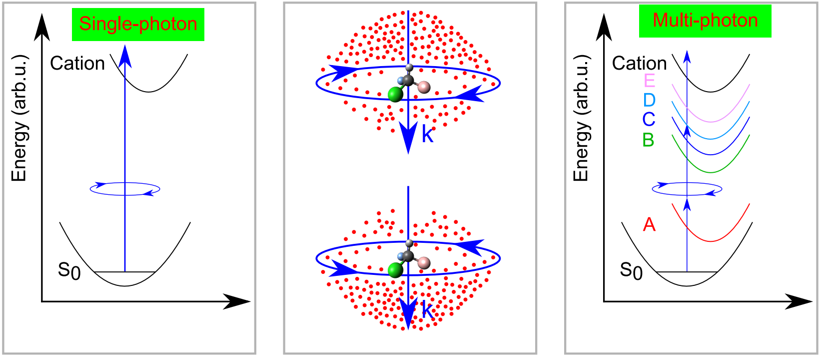
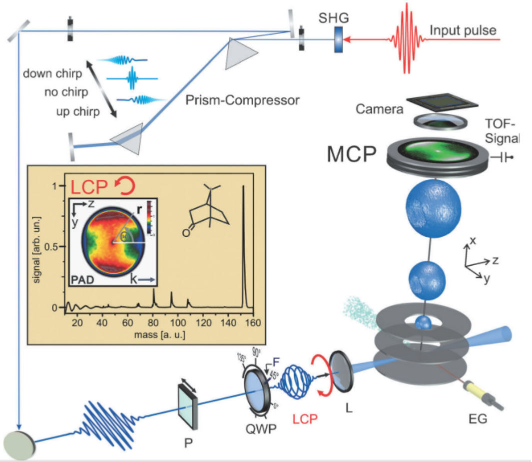
Excitation and ionization scheme



Overview

Experimental setup - femtosecond PECD



- Ti:Sa amplifier (25 fs, 0.8/1 mJ, 1/5 kHz)

C. Lux et al., ChemPhysChem, 16, 115-137, (2015)

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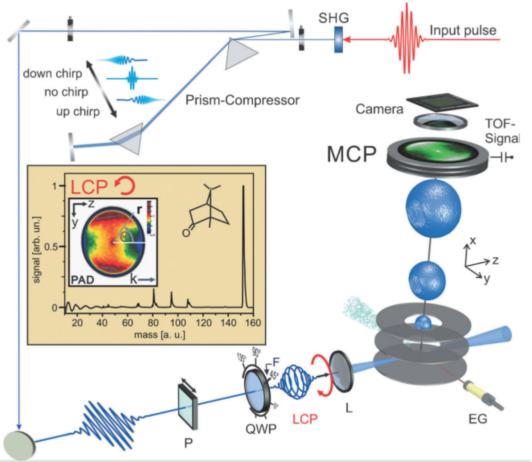

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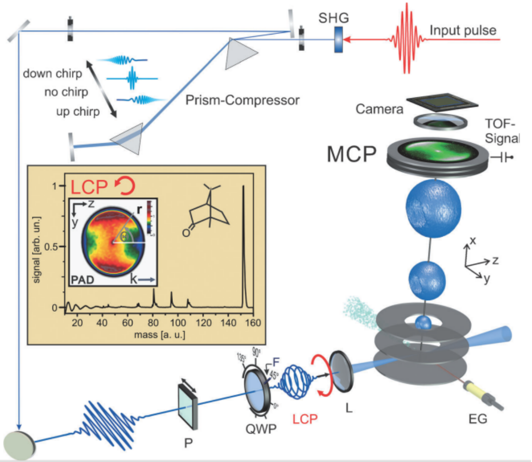

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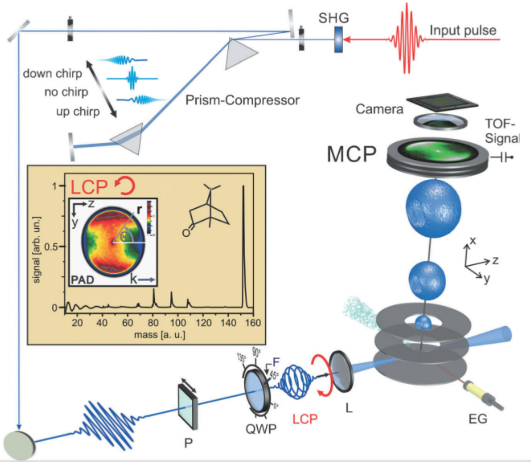

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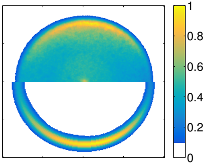
- Ti:Sa amplifier (25 fs, 0.8/1 mJ, 1/5 kHz)
- UV (~ 400 nm) $\rightarrow$ SHG/OPA (*TOPAS*)
- photoelectron momentum distributions measured by velocity map imaging (VMI)
- Reconstruction of 3D momentum distribution for LIN (detector plane) and CIRC possible

Overview

Data processing - Abel inverted (fenchone)

$\vec{k} \rightarrow$



LCP/RCP

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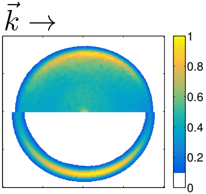

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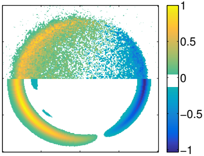

PECD

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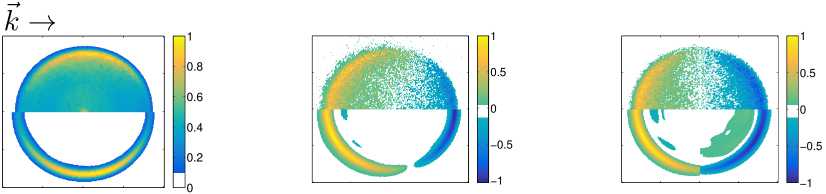

LCP/RCP

PECD

PECD Antisymm

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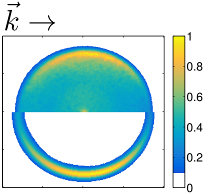

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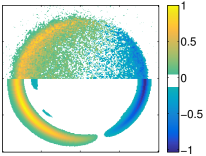
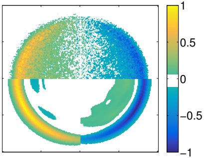


PECD

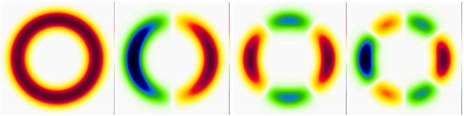


PECD Antisymm

Abel inversion via pBasex

Garcia et al., *Rev. Sci. Inst.*, 75, 11, (2004)

C. Lux et al., ChemPhysChem, 16, 115-137, (2015)



$$\text{PAD} = c_0 + c_1 + c_2 + c_3 + \ldots$$

Quantification: $\text{LPECD} = \frac{1}{c_0}\left(2c_1 - \frac{1}{2}c_3 + \frac{1}{4}c_5 - \frac{5}{32}c_7\right)$

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Origin of PECD

' Its [PECD] origin lies in quantum interference terms between outgoing waves developed, as the photoelectron is scattered off the chiral molecular potential.'

G. A. Garcia et al., Nature Communications, 4, 2132, (2013)

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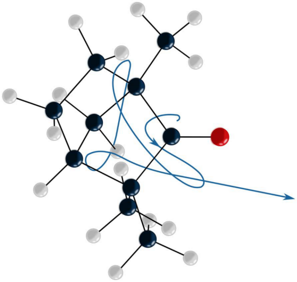

picture taken from S. Beaulieu et al., New J. Phys. 18, 102002G, (2016)

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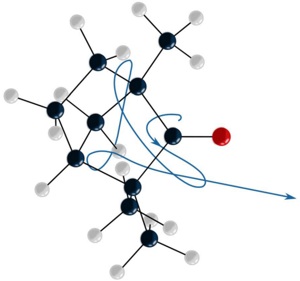

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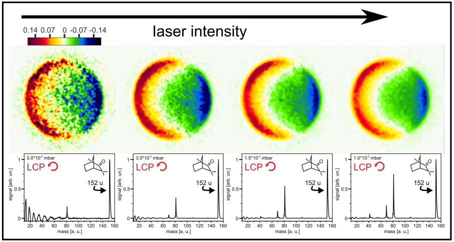
⇒ Ionization precedes fragmentation

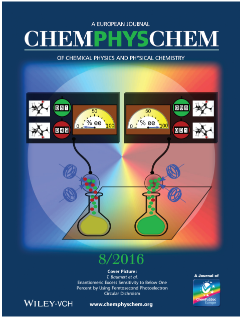


in agreement with coincidence findings (C. S. Lehmann et al., *J. Chem. Phys.*, 139, 234307 (2013), M. M. Rafiee Fanood et al., *J. Chem. Phys.*, 145, 124320 (2016))

Overview

Sensitivity of PECD

Enantiomeric excess (e.e.)



A.Kastner, et al., *ChemPhysChem* 17, 1119-1122, (2016)

→ sensitivity < 1 % e.e.

see also L.Nahon et al., *PCCP*, 18, 12696, (2016)

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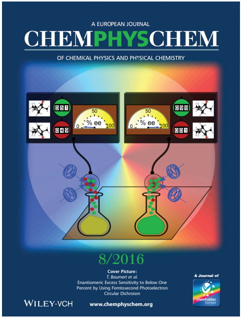

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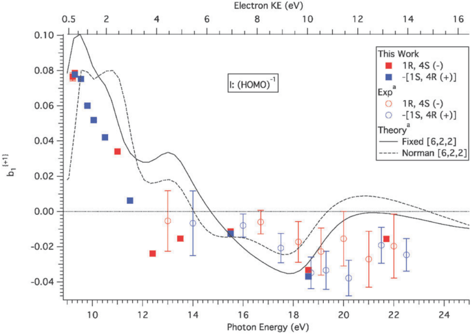
Photoelectron kinetic energy

→ well-known for single-photon studies

L. Nahon et al., J. El. Spec. Rel. Phen., 204, 322-334, (2015)

S. Turchini, J. Phys.: Condens. Matter, 29, 503001, (2017)



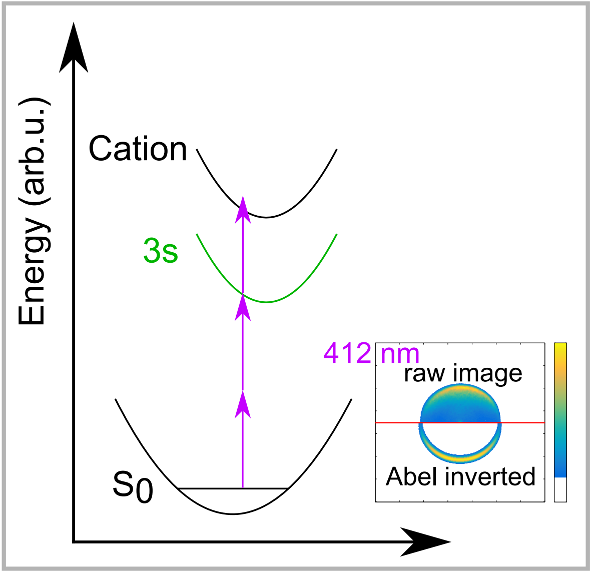
picture taken from L.Nahon et al., *PCCP*, 18, 12696, (2016)

→ fs-REMPI: changing λ

→ different intermediate states

Overview

Wavelength Scan - VMI PADs LIN (fenchone)



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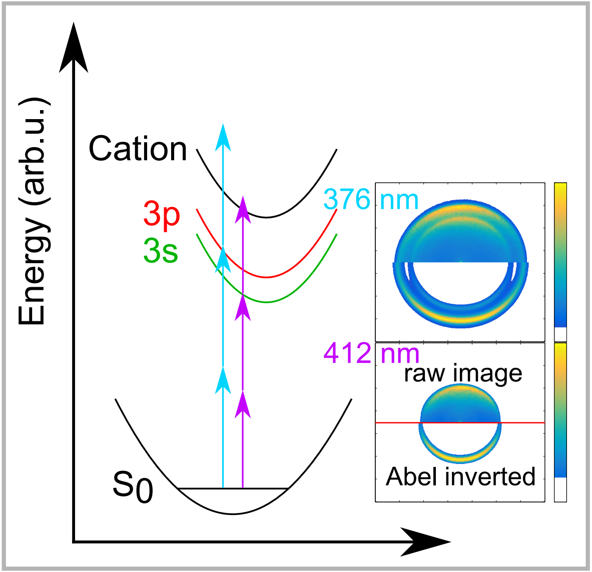

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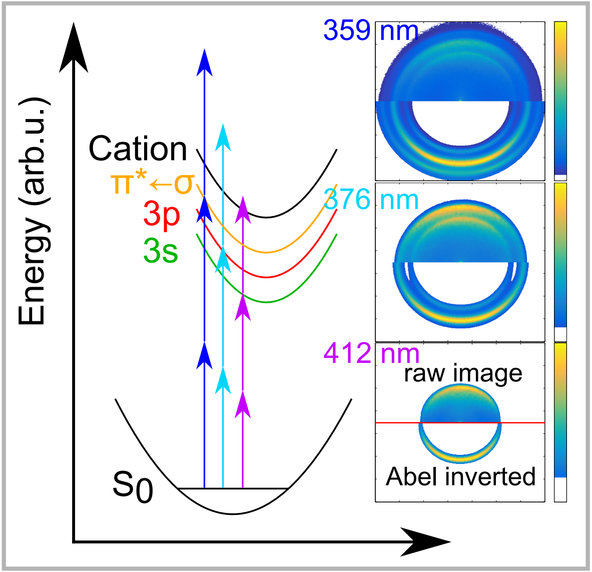

$E_{kin}^{e^-} \sim \hbar\omega \; (\Delta v = 0)$

$IP_a = (8.49 \pm 0.06)$ eV

$(IP_v = 8.6$ eV$)$

Wavelength Scan - PECD (fenchone)

How does the PECD depend on intermediate state and on photoelectron energy?

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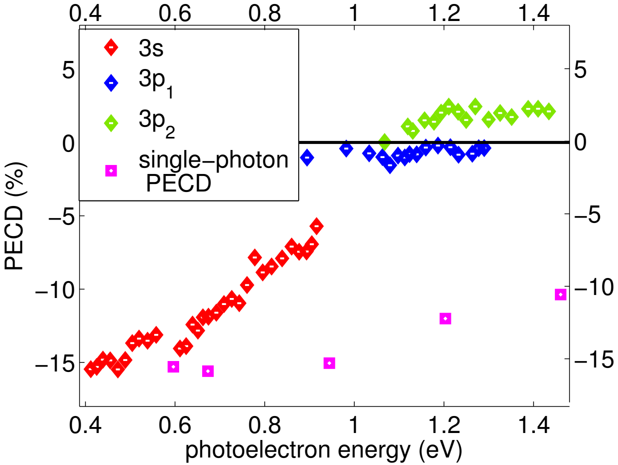

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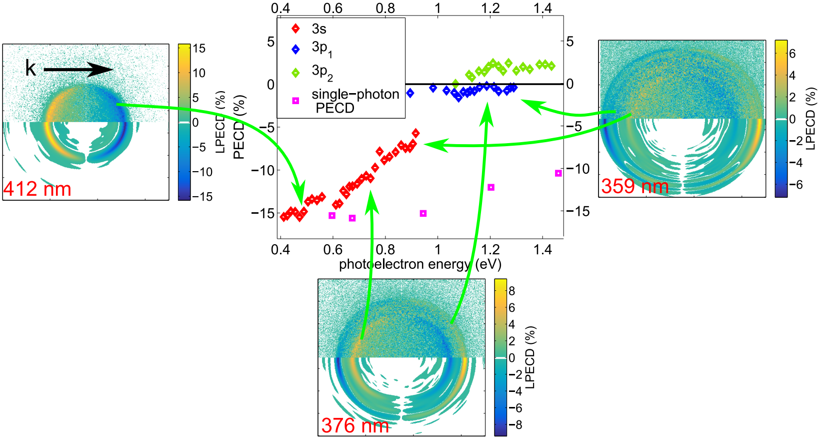
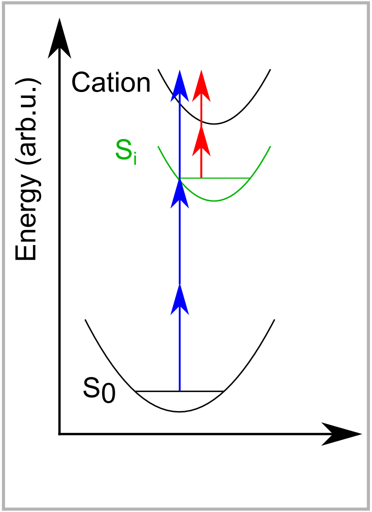


Overview

Bichromatic field ionization



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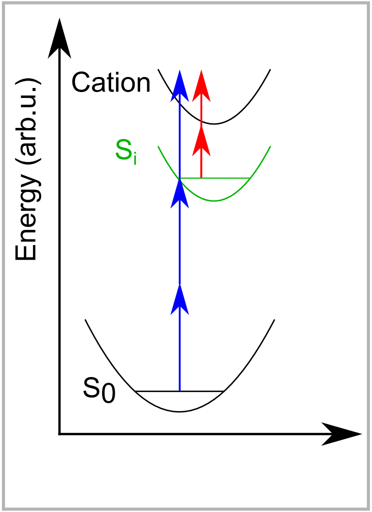

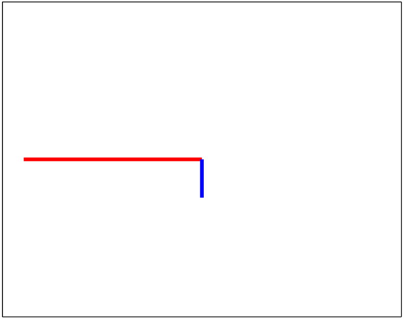

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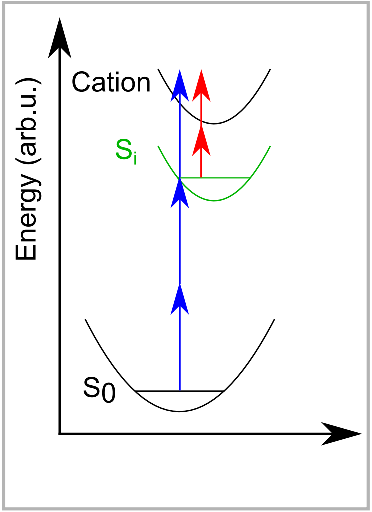
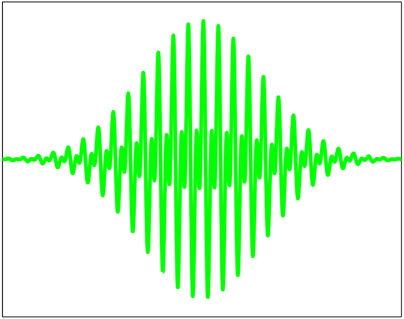
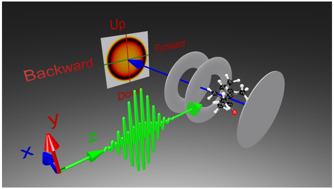
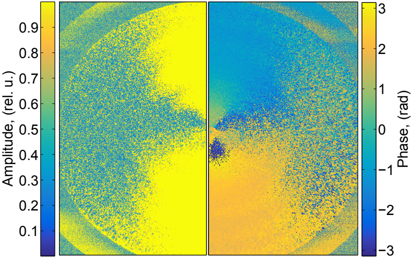




Exp. results (work in progress) for two-colors





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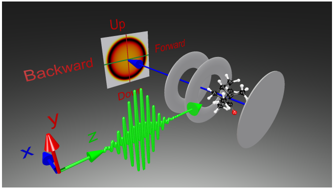
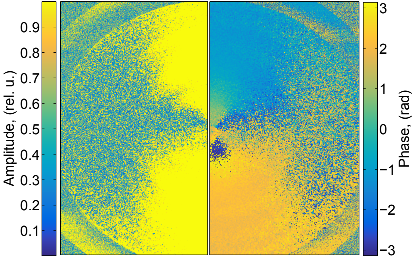
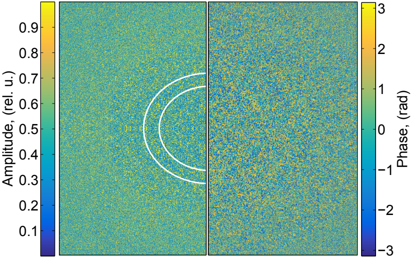
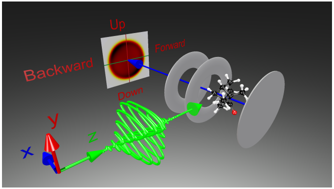
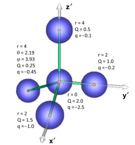




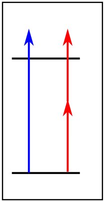


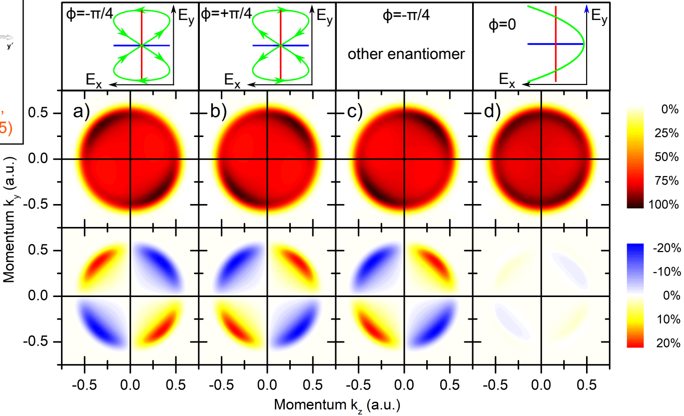


Theoretical results bichromatic field



Artemyev et al., JCP, 142, (2015)

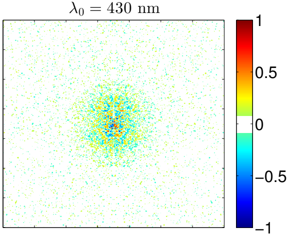


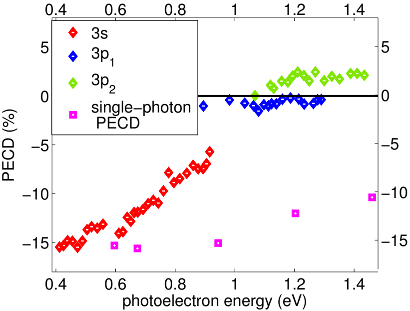


Overview

Summary and Outlook

Wavelength dependence





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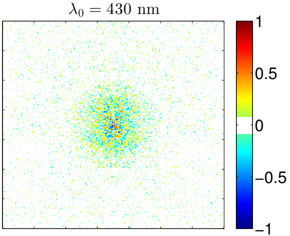
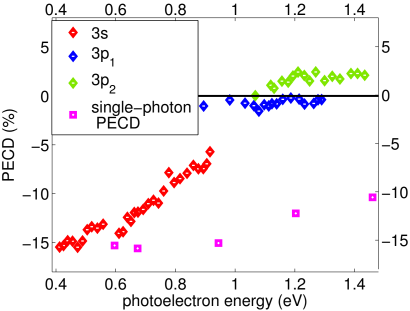
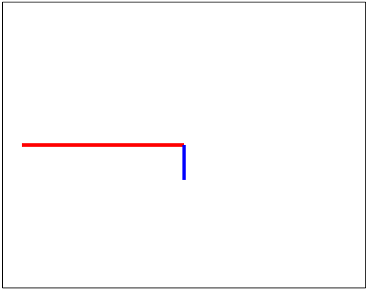
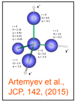
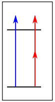


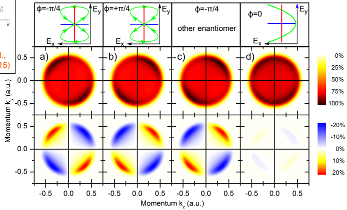


Bichromatic









Prof. T. Baumert
Dr. A. Senftleben
Dr. H. Braun
Dr. H. Lee
M. Adrian
T. Kalas
R. Savulea
C. Sarpe
T. Ring
S. Ranecky
A. Ungeheuer
S. Vasudevan
C. Witte
B. Zielinski

U Oldenburg
Prof. Dr. M. Wollenhaupt
Dr. T. Bayer
Dr. L. Englert
S. Kerbstadt

U Göttingen
B. C. Krüger
Dr. B. G. Park
Dr. T. Schäfer

Alumni
Dr. M. Krug
Dr. C. Lux

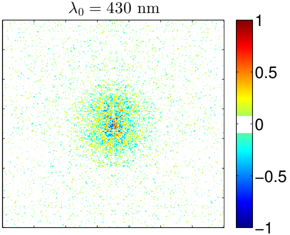
LOEWE
Exzellente Forschung für Hessens Zukunft

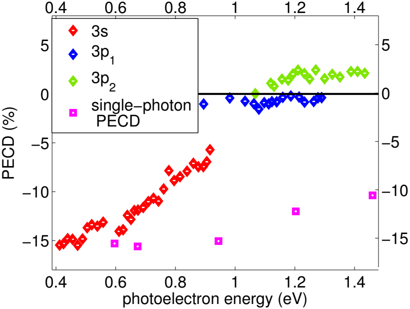
SFB 1319 ELCH

Deutsche Forschungsgemeinschaft
DFG

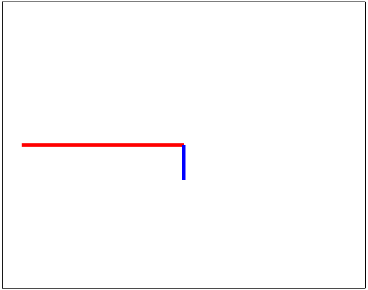
Summary and Outlook

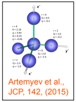
Wavelength dependence

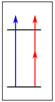


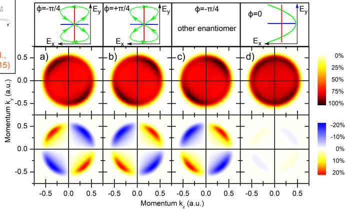


Bichromatic









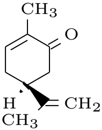
Chiral recognition in the gas phase

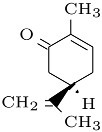
Terpenes

Amino acids and Sugars

Chiral recognition in the gas phase

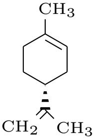
Terpenes

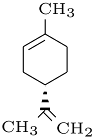




R-Carvone

S-Carvone





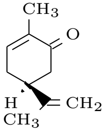
R-Limonene

S-Limonene

Amino acids and Sugars

Chiral recognition in the gas phase

Terpenes



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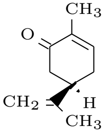
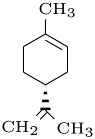
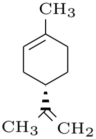


S-Carvone

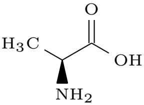


R-Limonene

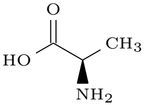


S-Limonene

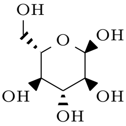
Amino acids and Sugars



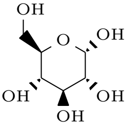
L-Alanine



D-Alanine



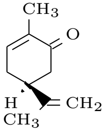
L-Glucose



D-Glucose

Chiral recognition in the gas phase

Terpenes



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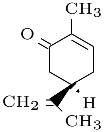
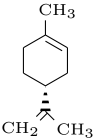
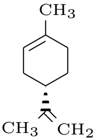


S-Carvone

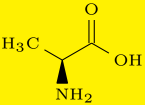


R-Limonene

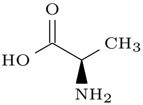


S-Limonene

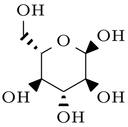
Amino acids and Sugars



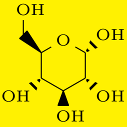
L-Alanine



D-Alanine



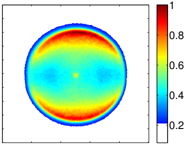
L-Glucose



D-Glucose

Data processing - VMI (fenchone)

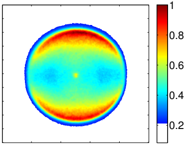
$\vec{k} \rightarrow$



LIN

Data processing - VMI (fenchone)

$\vec{k} \rightarrow$



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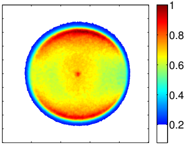
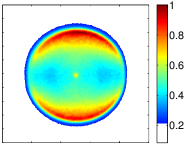


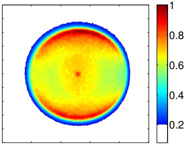
LCP

Data processing - VMI (fenchone)

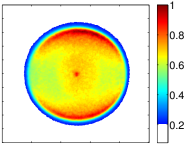
$\vec{k} \rightarrow$



LIN



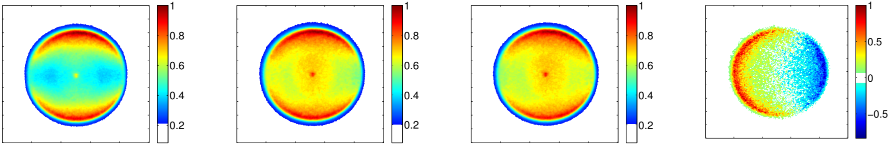
LCP



RCP

Data processing - VMI (fenchone)

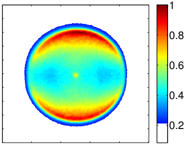
$\vec{k} \rightarrow$



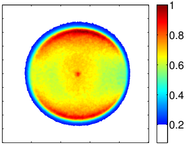
LIN LCP RCP LCP - RCP

Data processing - VMI (fenchone)

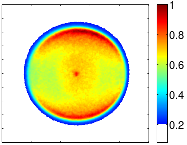
$\vec{k} \rightarrow$



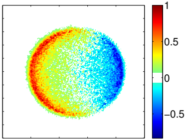
LIN



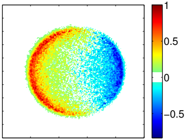
LCP



RCP



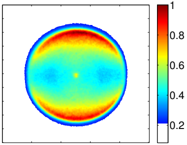
LCP - RCP



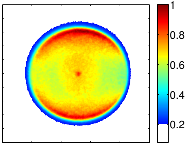
PECD =
LCP - RCP

Data processing - VMI (fenchone)

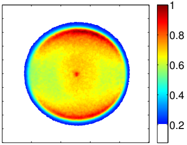
$\vec{k} \rightarrow$



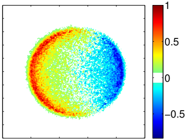
LIN



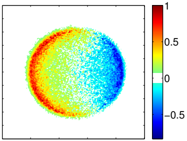
LCP



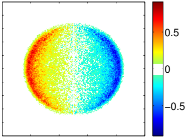
RCP



LCP - RCP



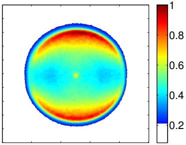
PECD $=$
LCP - RCP



PECD
Antisymmetric
Part

Data processing - VMI (fenchone)

$\vec{k} \rightarrow$



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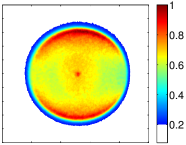
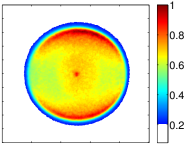
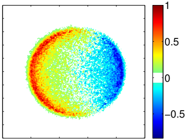


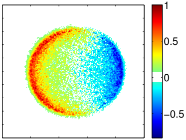
LCP



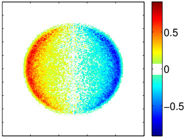
RCP



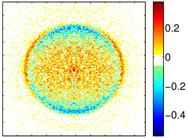
LCP - RCP



PECD =
LCP - RCP



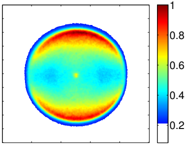
PECD
Antisymmetric Part



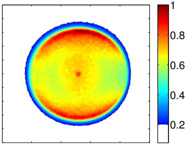
PECD
Symmetric Part

Data processing - VMI (fenchone)

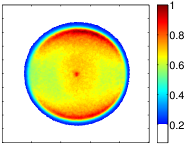
$\vec{k} \rightarrow$



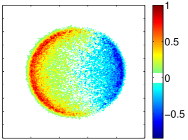
LIN



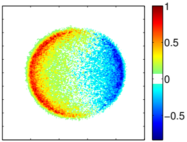
LCP



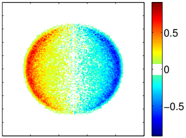
RCP



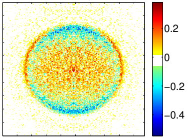
LCP - RCP



PECD = LCP - RCP



PECD Antisymmetric Part

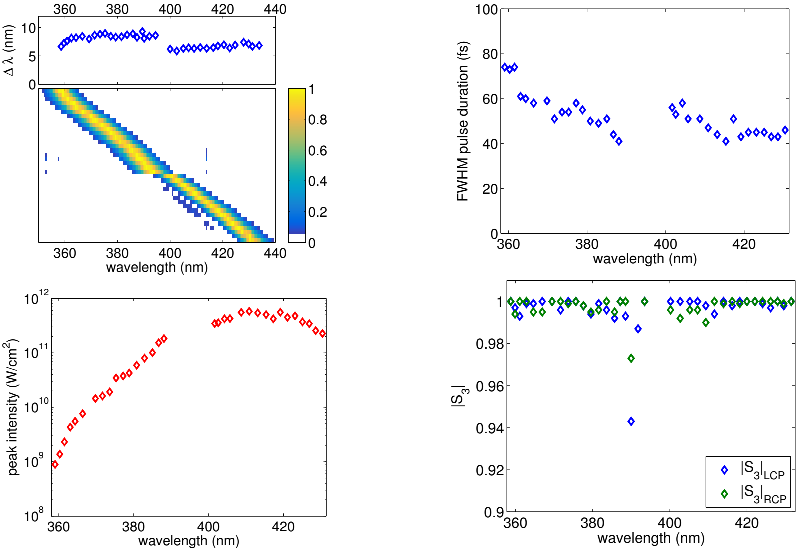


PECD Symmetric Part

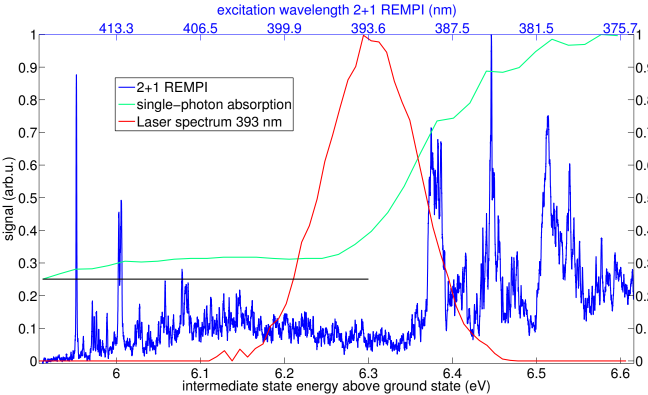
$$LPECD = \frac{2(F-B)}{T/2}$$

F: forward hemisphere
B: backward hemisphere
T: total signal

Wavelength Scan - laser pulse characterization



High-resolution 2+1 REMPI (T. Schäfer, U Göttingen)

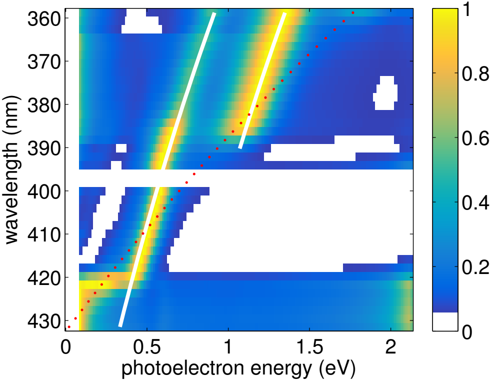


- wavelength dependent parent ion yield between 375–420 nm
- Excitation of B-band (3s←n, 5.95 eV) and of C-band (3p←n, 6.37 eV), energy separation 0.42 eV
- lifetime of 5.95 eV peak ~ 0.8 ps (3.3 ps in TR-PECD, S. Beaulieu et al., Far. Disc., 194, (2016), A. Comby et al., JPCL, 7, (2016))

Wavelength Scan - Photoelectron spectra (fenchone)

Scaling of photoelectron energy with excitation wavelength?

⇒ Consider Abel inverted photoelectron spectra

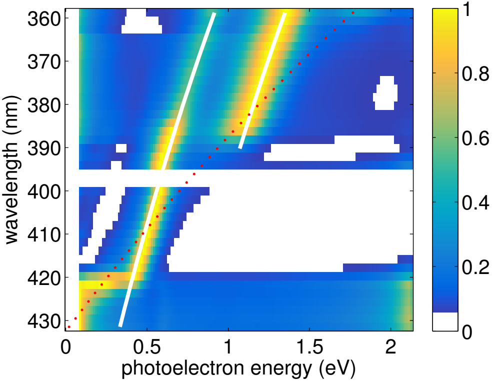


- 422–393 nm: 3s
- 393–363 nm: 3s & 3p
- 363–359 nm: 3s & 3p & $\pi^* \leftarrow \sigma$
- ~~$E_{kin}^{e^-} \sim 3\hbar\omega$?~~ NO! (see red dotted line...)
- $E_{kin}^{e^-} \sim \hbar\omega \; (\Delta v = 0)$ yielding adiabatic IP:

Wavelength Scan - Photoelectron spectra (fenchone)

Scaling of photoelectron energy with excitation wavelength?

$\Rightarrow$ Consider Abel inverted photoelectron spectra



- 422–393 nm: 3s
- 393–363 nm: 3s & 3p
- 363–359 nm: 3s & 3p & $\pi^* \leftarrow \sigma$
- ~~$E_{kin}^{e^-} \sim 3\hbar\omega$?~~ NO! (see red dotted line...)
- $E_{kin}^{e^-} \sim \hbar\omega$ $(\Delta v = 0)$ yielding adiabatic IP:

$$3\frac{hc}{\lambda} - IP_a^{Fen} = E_{kin}^{e^-}$$

$$IP_a^{Fen} = (8.49 \pm 0.06) \text{ eV}$$

$$(IP_v^{Fen} = 8.6 \text{ eV})$$