Lundbeck Foundation
Theoretical
Center for
Quantum
System Research

Polar molecules in femto- and attosecond pulses

Lars Bojer Madsen

2010

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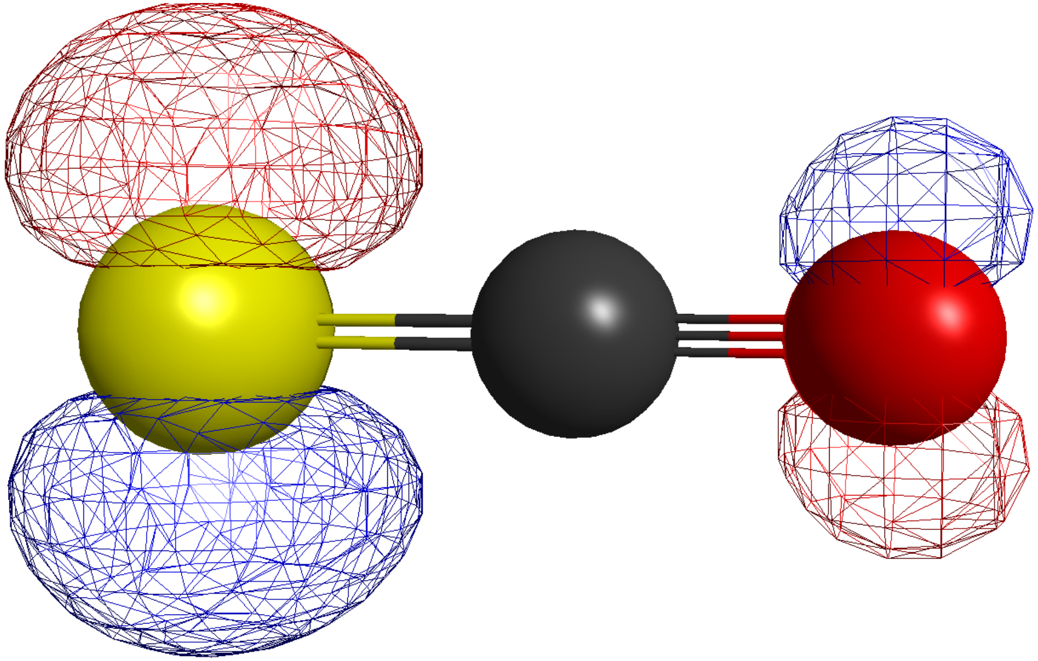
Outline

- Characteristics of polar systems
- Photoelectron angular distributions
- High-order harmonic generation
- Nuclear motion
- Summary and outlook

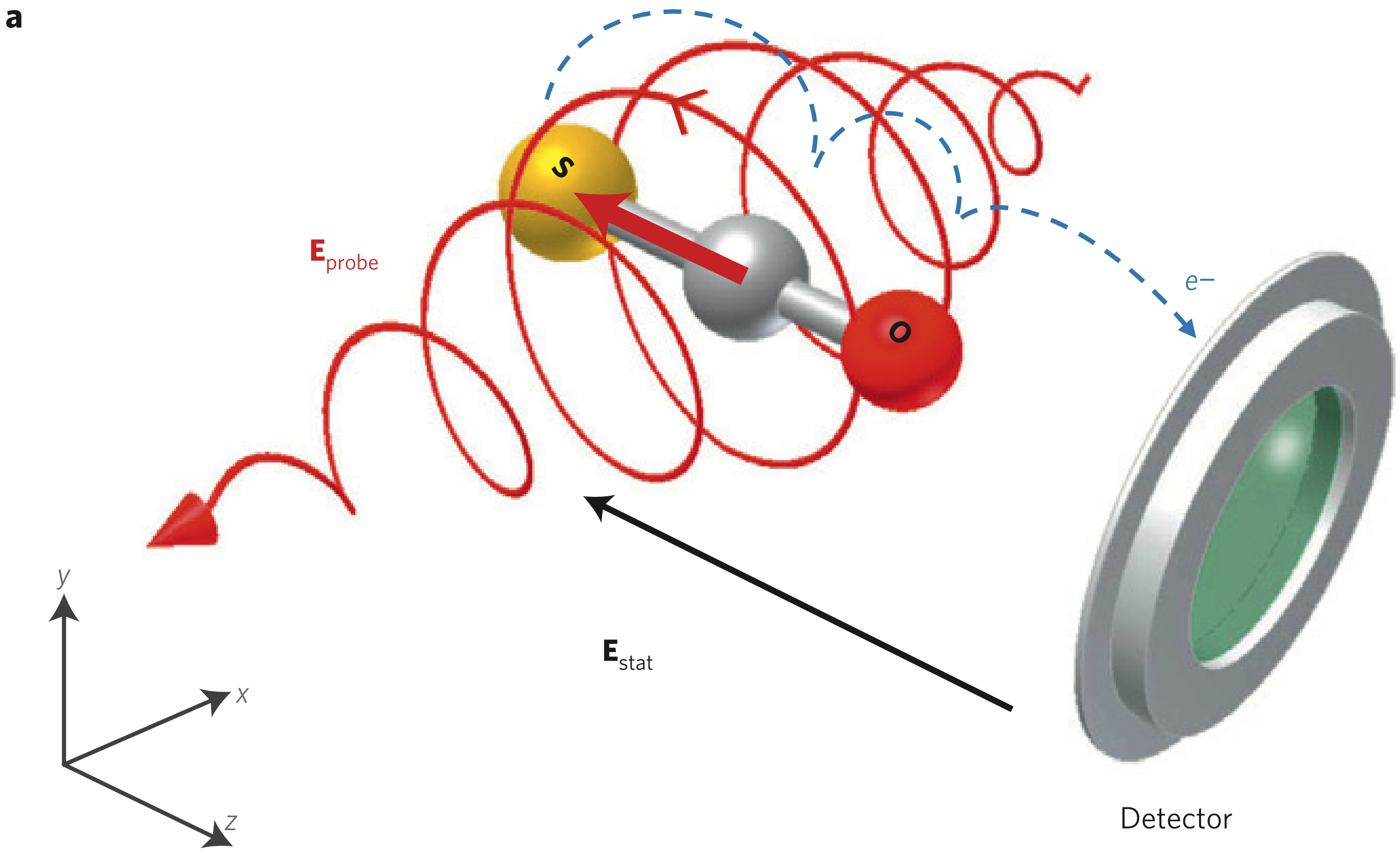
Characteristics

- Asymmetric charge distribution. Permanent dipole moment.



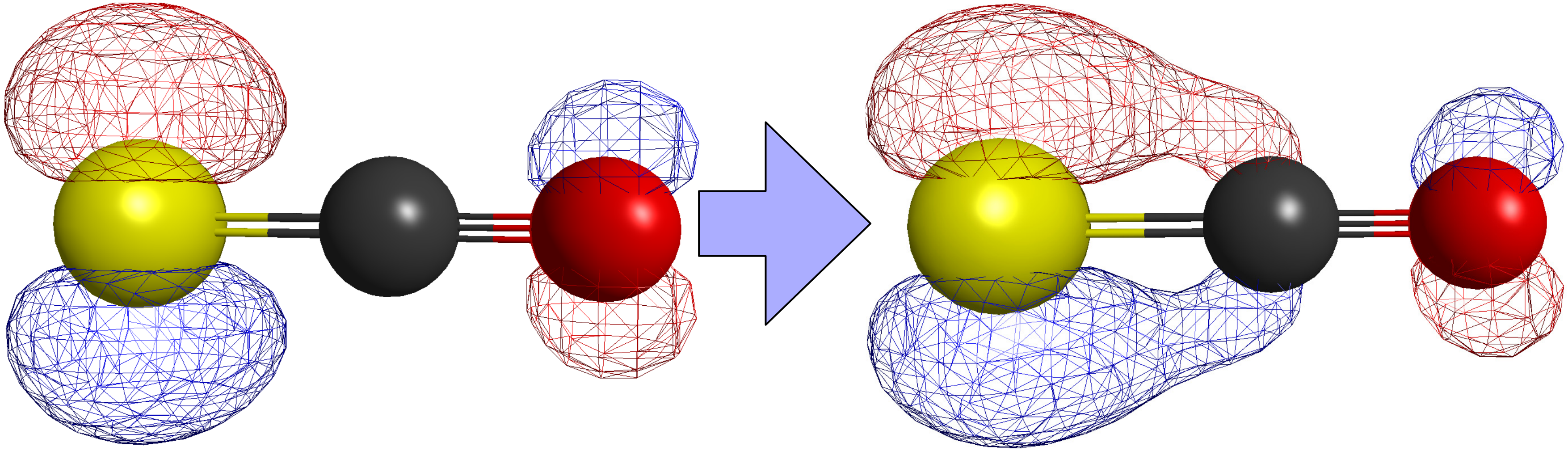
Characteristics

- Unique targets: Can be oriented and fixed in space due to dipole and polarizabilities



Characteristics

- Energy shifts (Stark shifts)



$$\epsilon = \epsilon_0 \cdot \begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix}^{\mathrm{T}} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \cdot \frac{1}{2} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}^{\mathrm{T}} \begin{pmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix} \cdot \cdots$$

Characteristics

- Dipole of the molecular potential $\boldsymbol{\mu}_p$
- Role of the dipole of the unrelaxed cation

$$V(\boldsymbol{r})|_{r\to\infty} = -1/r + \boldsymbol{\mu}_p \cdot \hat{\boldsymbol{r}}/\boldsymbol{r}^2 + \cdots$$

Characteristics

- Dipole moment of molecule
  - Control of external orientation
- Dipole moment of orbital (HOMO)
  - Ionization step. Ionization potential
- Dipole of unrelaxed cation (multipole)
  - Ionization step. Propagation step

$$V(\boldsymbol{r})|_{r\to\infty} = -1/r + \boldsymbol{\mu}_p \cdot \hat{\boldsymbol{r}}/\boldsymbol{r}^2 + \cdots$$

Key question

- How do these different dipoles affect the dynamics? Can their effects be separated out?

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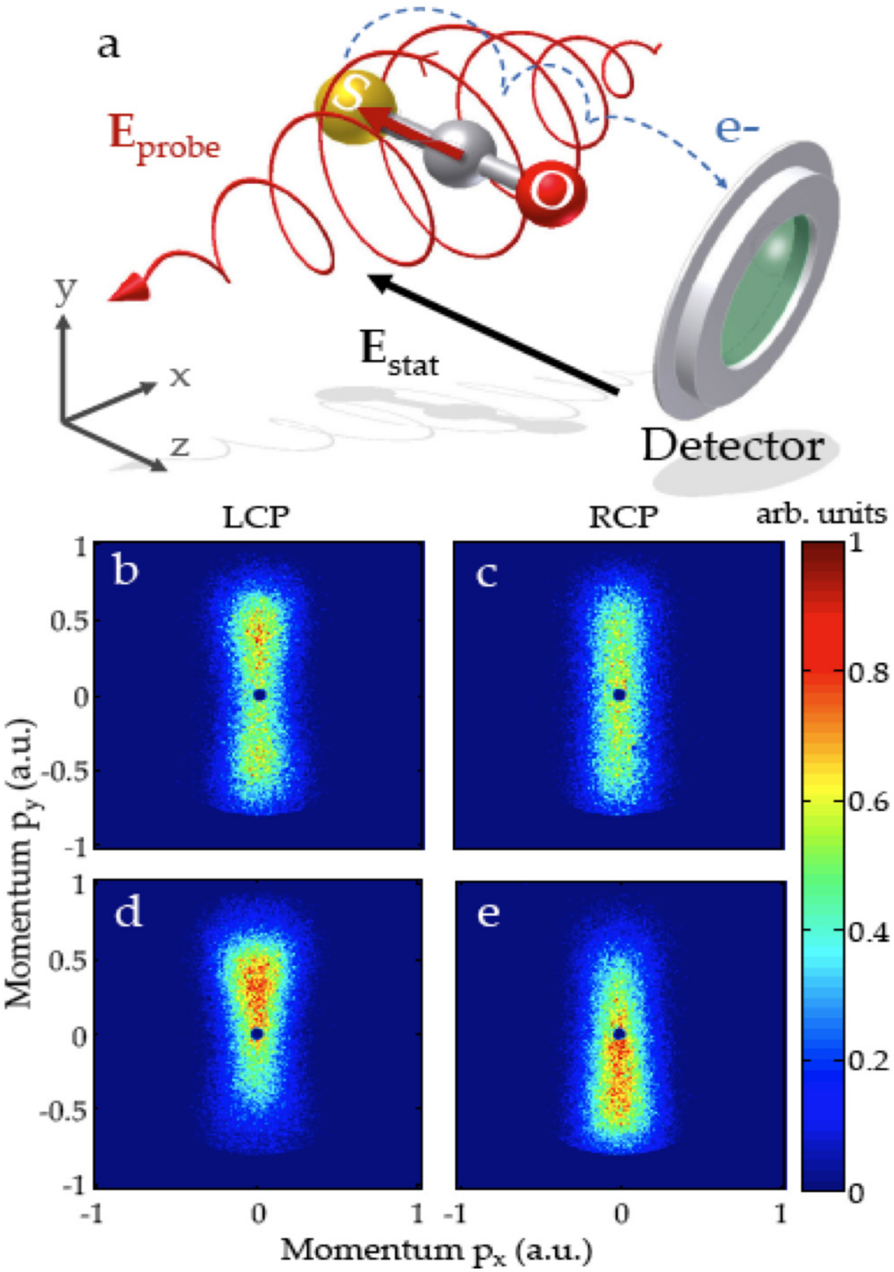


Holmegaard *et al*.,
Nat. Phys. **6**, 428 (2010).

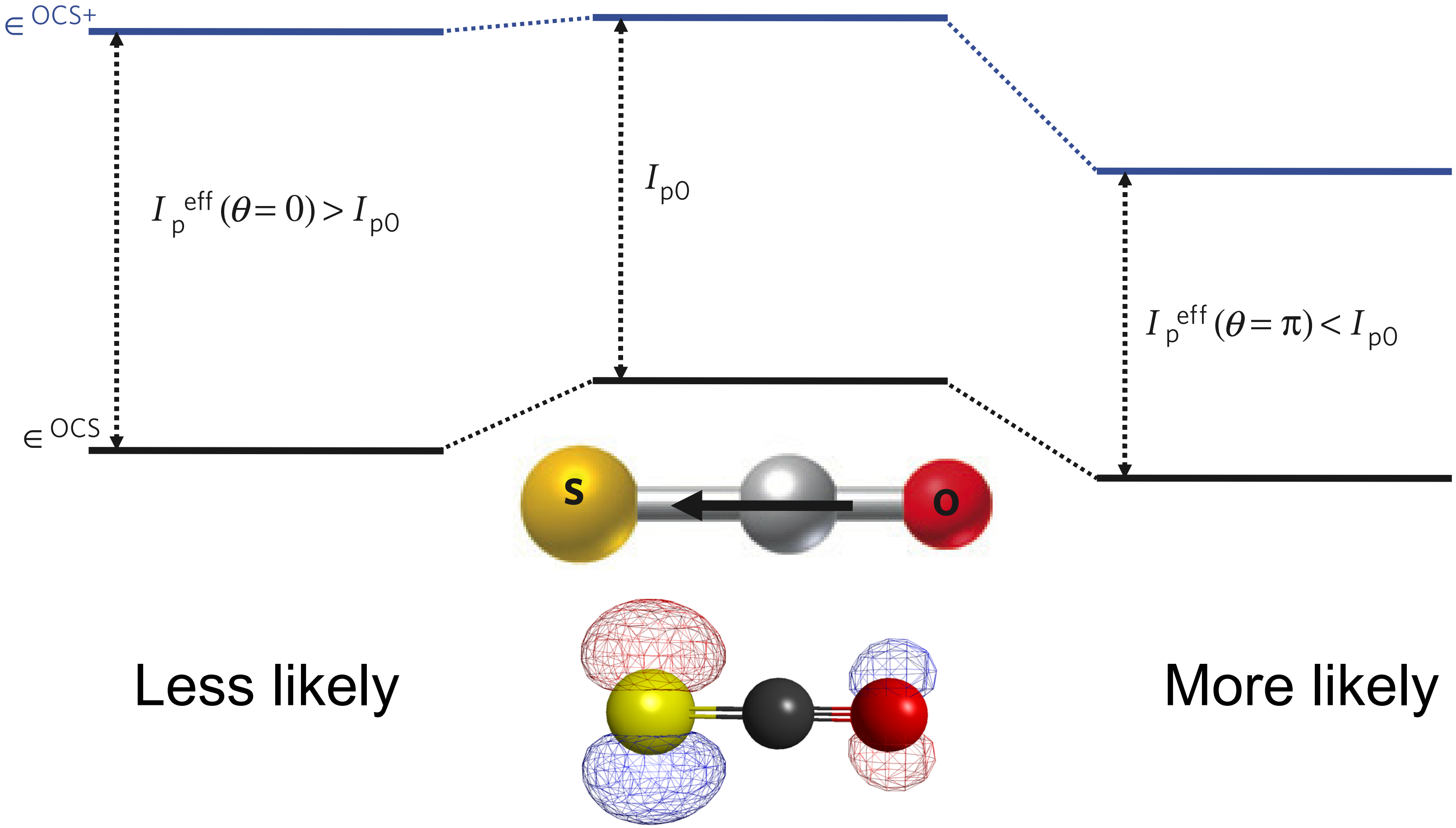
1. Can we understand the up-down asymmetry?
2. What does it tell us about the molecule?

3. Experiment is in the tunneling regime
4. The electron adiabatically adjust to the instantaneous magnitude and direction of the field

$$w(\theta) = \frac{1}{2\kappa(\theta)^{\frac{2}{\kappa)\kappa)}-1}} \left(\frac{2\kappa(\theta)^3}{E}\right)^{\frac{2}{\kappa)\kappa)}-1} \exp\left(-\frac{2\kappa(\theta)^3}{3E}\right) \exp\left(-6\left(\frac{2}{\kappa(\theta)^2}\right)\left(\frac{E}{\kappa(\theta)^3}\right)\right),$$

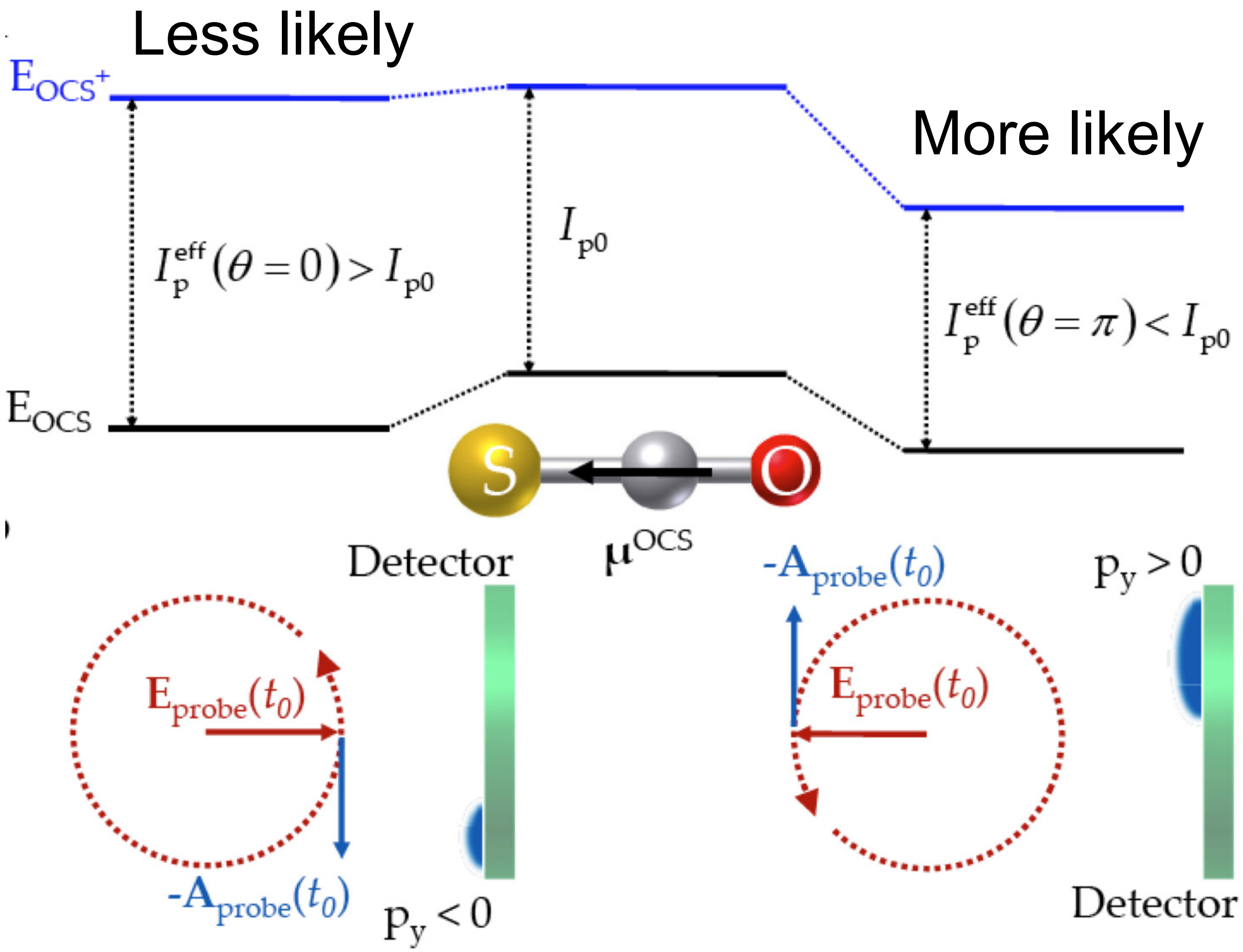
$$\kappa(\theta) = \sqrt{2I_p(\theta)}$$

$$\begin{aligned} I_{\mathrm{p}}^{\mathrm{eff}}(\theta) = {} & I_{\mathrm{p0}} + (\mu^{\mathrm{OCS}^+} - \mu^{\mathrm{OCS}}) E_{\mathrm{probe}} \cos\theta \\ & + \frac{1}{2} E_{\mathrm{probe}}^{2} [\{(\alpha_{\parallel}{}^{\mathrm{OCS}} - \alpha_{\parallel}{}^{\mathrm{OCS}^+}) - (\alpha_{\perp}{}^{\mathrm{OCS}} - \alpha_{\perp}{}^{\mathrm{OCS}^+})\} \cos^2\theta \\ & + (\alpha_{\perp}{}^{\mathrm{OCS}} - \alpha_{\perp}{}^{\mathrm{OCS}^+})] \qquad (1) \end{aligned}$$



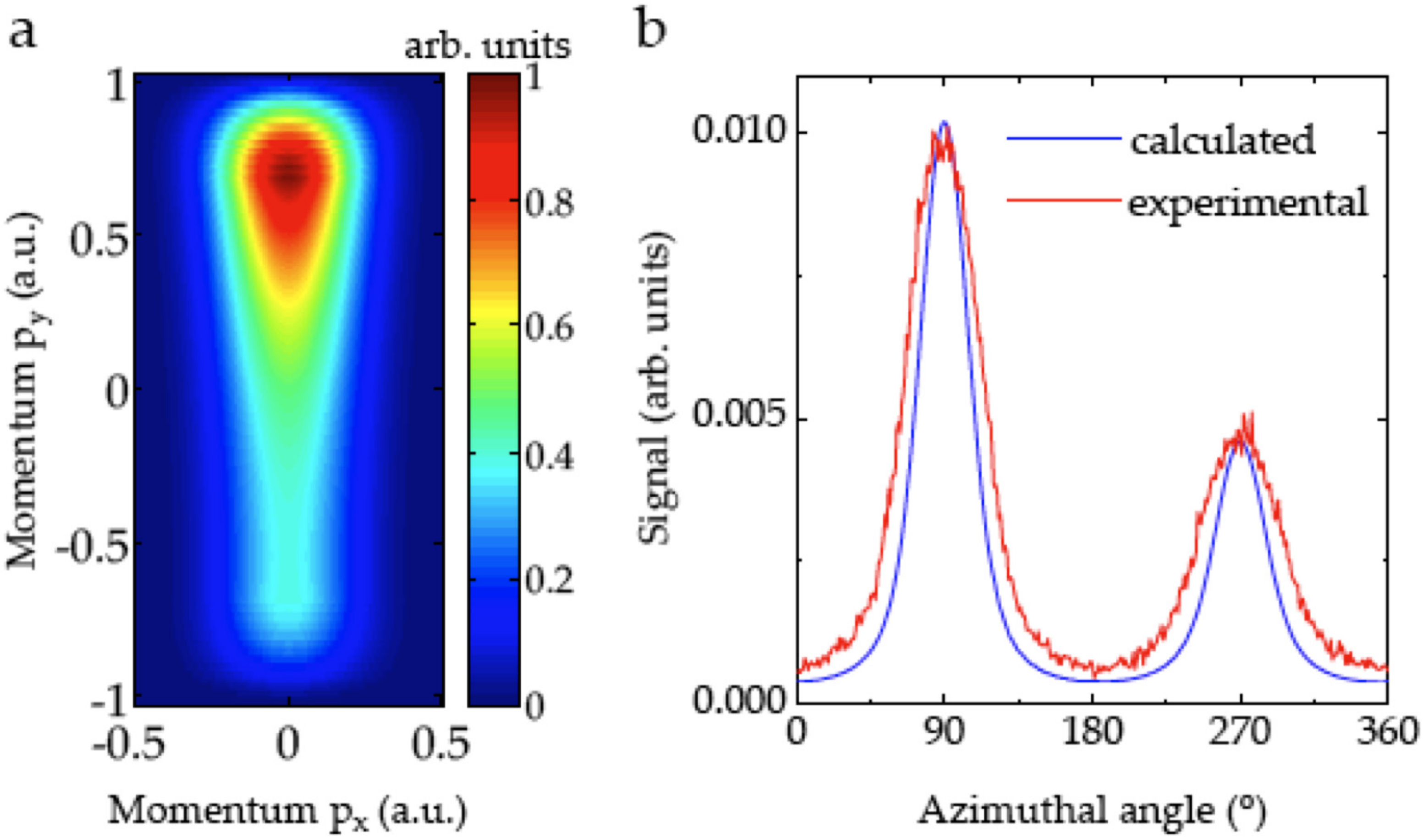
Less likely

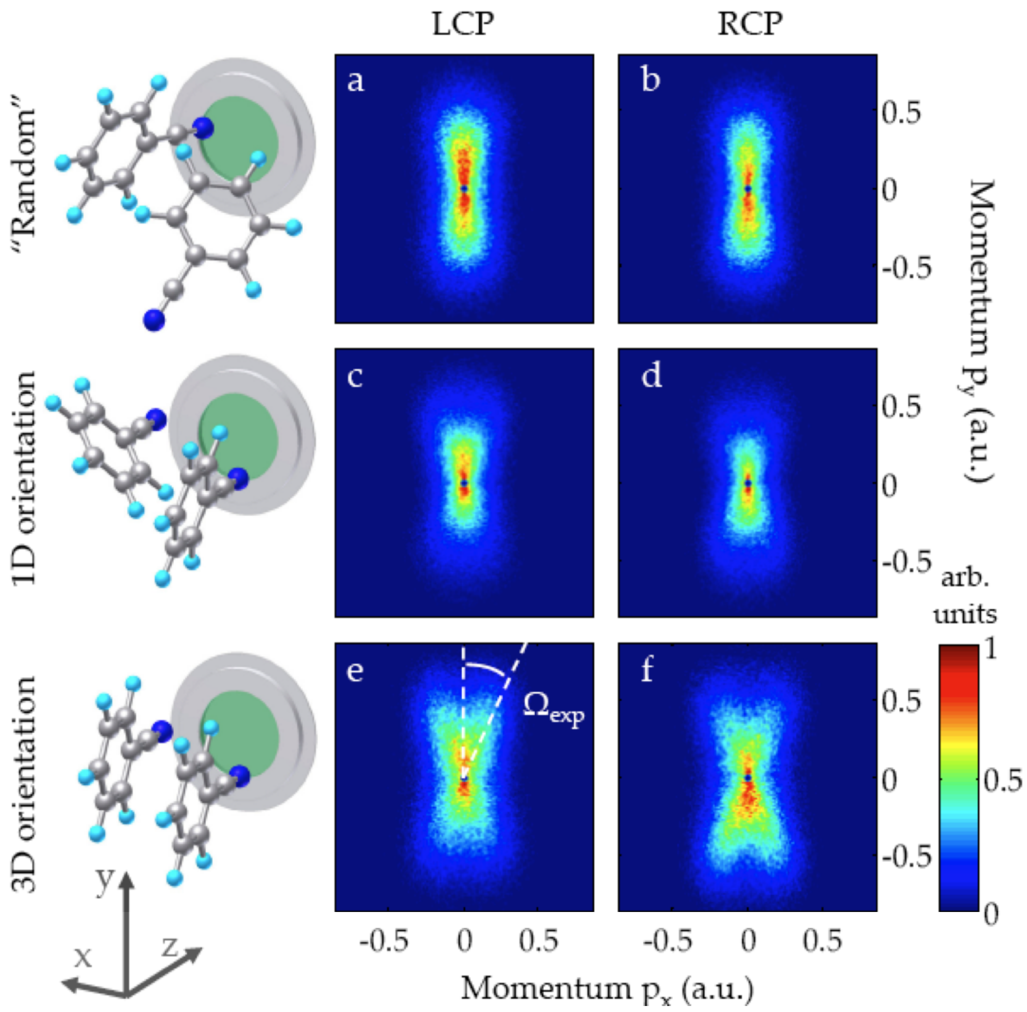
More likely



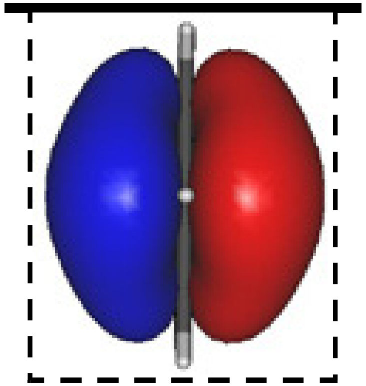
$$\mathbf{E}(t) = E_0\left(\sin(\omega t)\hat{\mathbf{e}}_y + \cos(\omega t)\hat{\mathbf{e}}_z\right)$$

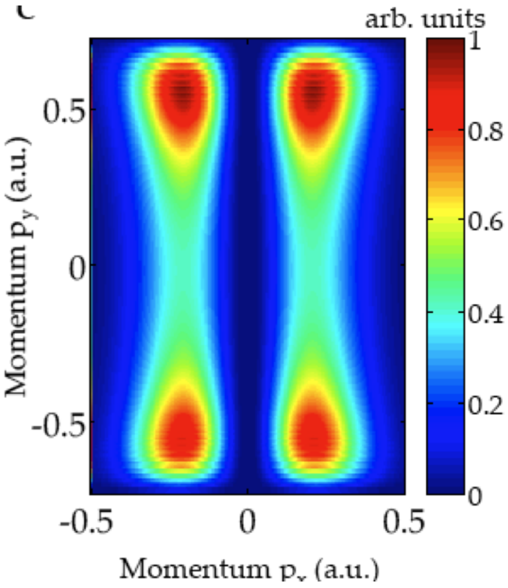
$$p_y = -A_y(\theta) = -\frac{E_0}{\omega}\cos(\theta); \quad p_z = -A_z(\theta) = \frac{E_0}{\omega}\sin(\theta), \quad \theta = \omega t_0$$


a
arb. units
1
0.8
0.6
0.4
0.2
0
1
0.5
0
-0.5
-1
-0.5
0
0.5
Momentum p_y (a.u.)
Momentum p_x (a.u.)
b
calculated
experimental
0.010
0.005
0.000
0
90
180
270
360
Signal (arb. units)
Azimuthal angle (°)



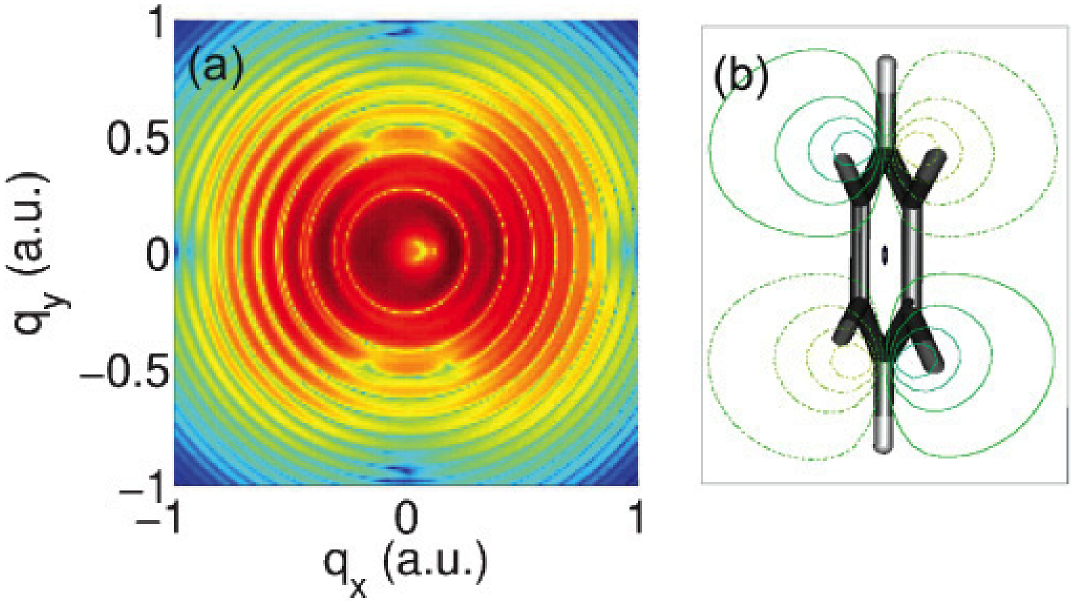
$$\Omega_{\text{exp}} = 18^\circ \pm 1^\circ$$





$$\Omega_{\text{theo}} = \arctan\left(\frac{2\omega}{\sqrt{\pi F_0 \kappa}}\right) \simeq 18.8^\circ$$

Imprints of angular nodes on 2D momentum distributions



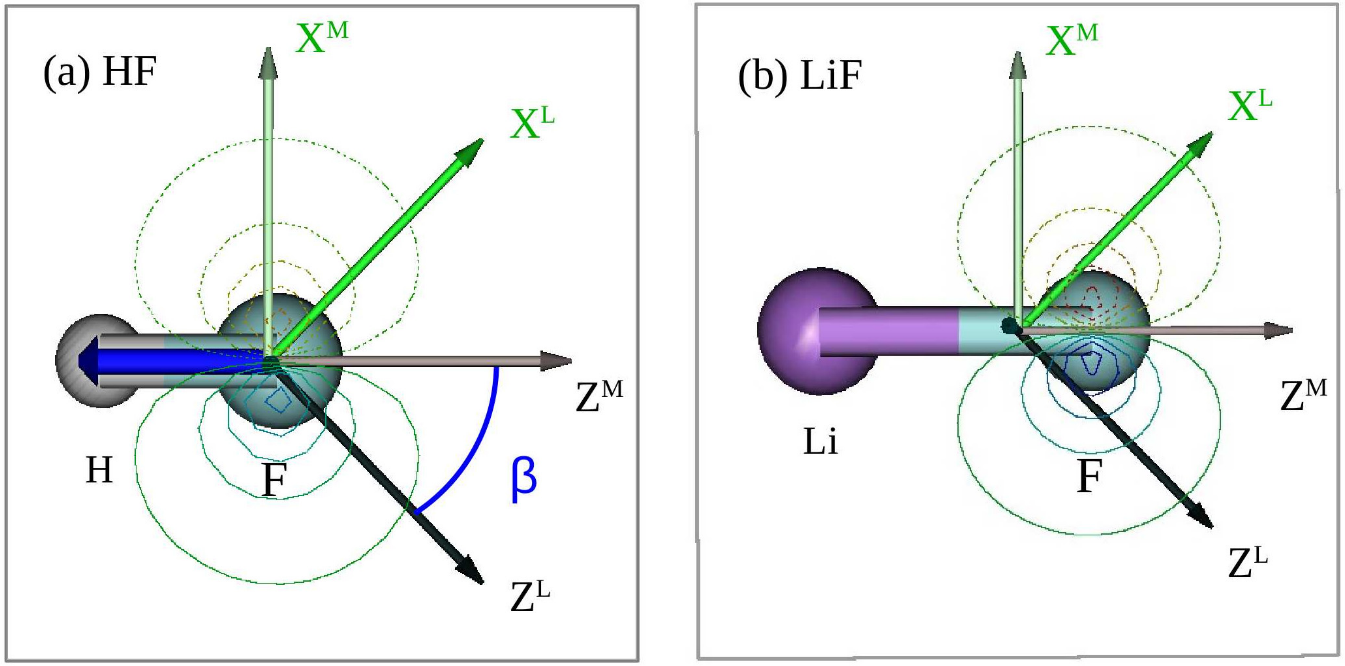
Martiny et al, PRA 2010

Which dipole was at play?

- Dipole of the HOMO for OCS in circularly polarized fields
- Experiments explained without taking the dipole of the molecular potential into account

MFPADs with the TDSE

Linearly polarized field

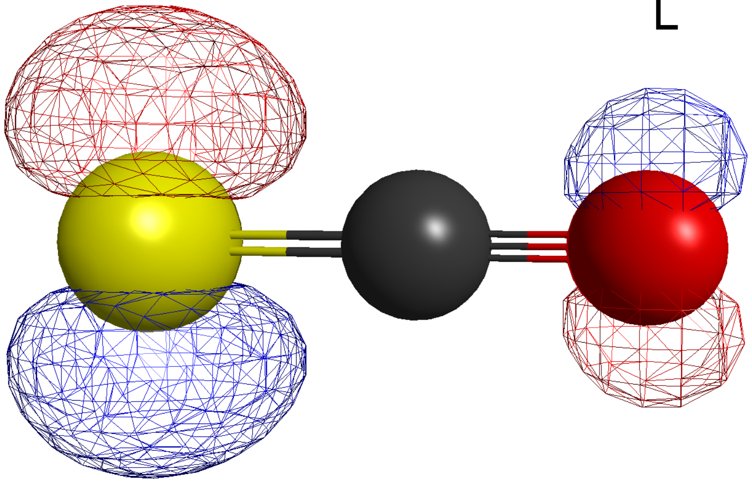


MFPADs with the TDSE

- No asymmetry in the case of one-photon ionization in the high-energy limit

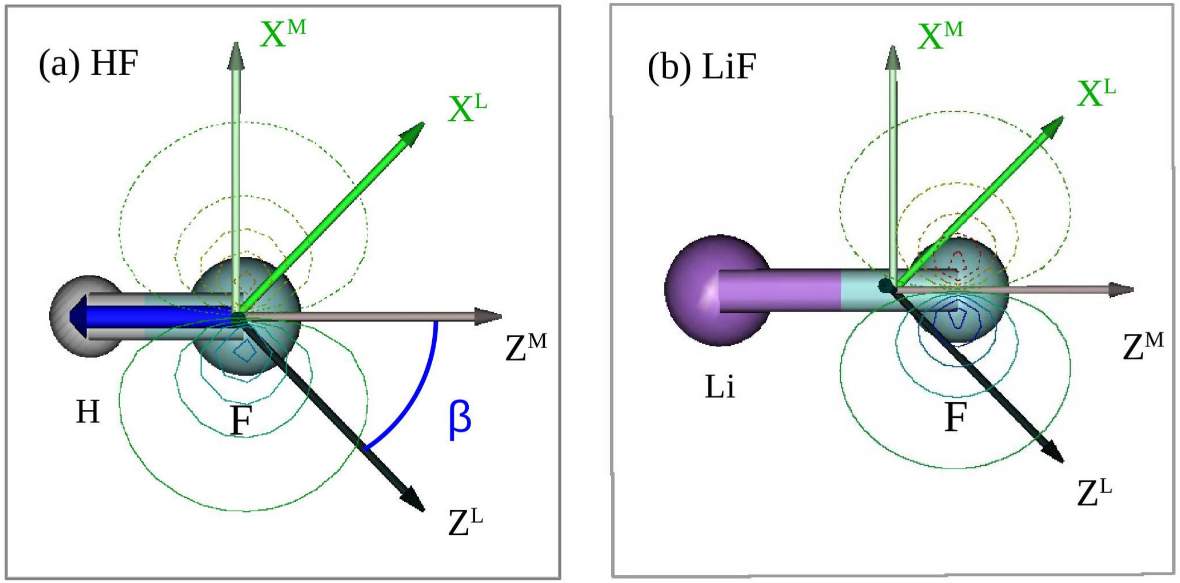
$$M_{fi}(\vec{k}) = \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} \vec{\epsilon}\cdot\vec{r}\phi_0$$

$$M_{fi}(-\vec{k}) = \int d\vec{r} e^{i\vec{k}\cdot\vec{r}} \vec{\epsilon}\cdot\vec{r}\phi_0 = \left[M_{fi}(\vec{k})\right]^{\star}$$



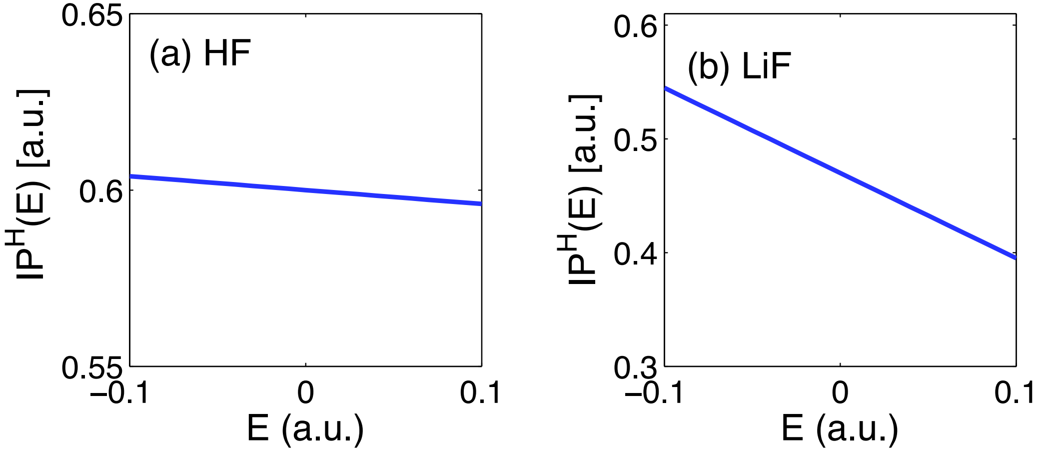
MFPADs with the TDSE

- Asymmetries are due to the difference between a plane wave and an exact scattering state, i.e., phase shifts induced by the asymmetric molecular potential
- Such potential effects may be enhanced in a linearly polarized field due to multiple re-scatterings off the core
- Effects beyond first-Born-like approaches (Strong-field-approx.)



Asymmetry due to orbital dipole

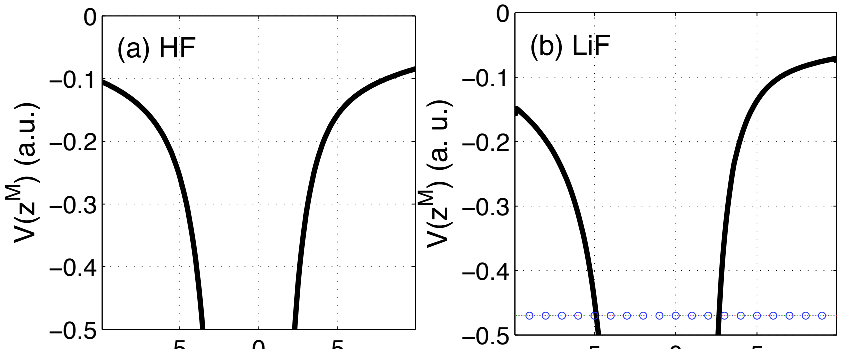
0.1D



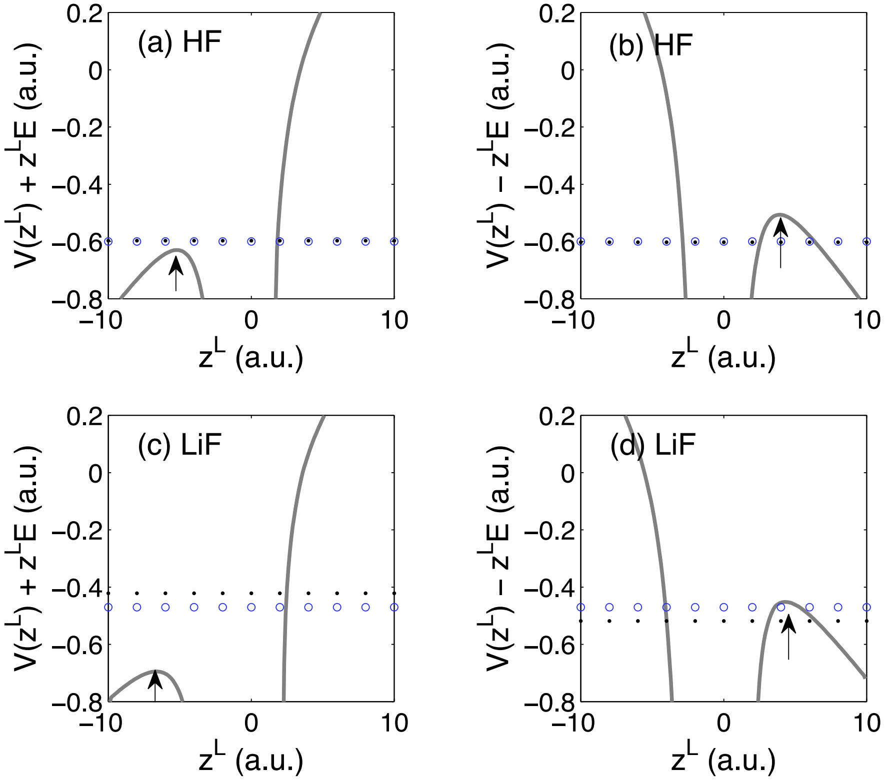
1.9D

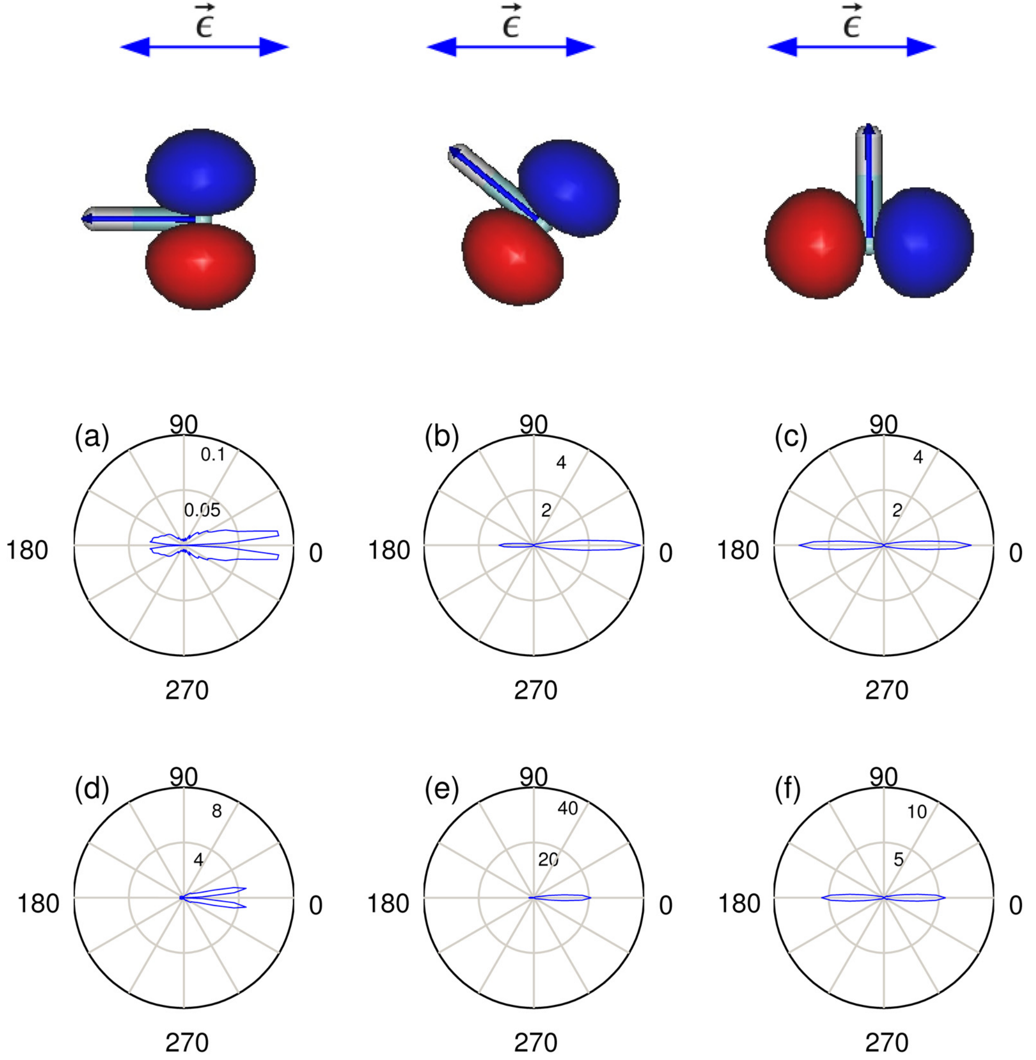
Asymmetry due to dipole from the potential

1.8 D



4.8 D

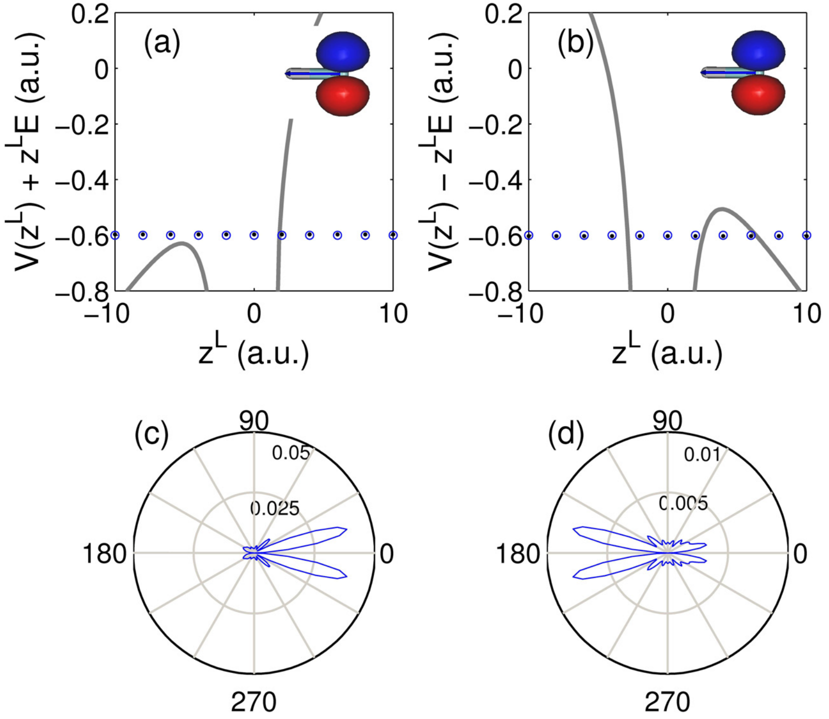



$\vec{\epsilon}$
$\vec{\epsilon}$
$\vec{\epsilon}$
(a)
90
0.1
0.05
180
0
270
(b)
90
4
2
180
0
270
(c)
90
4
2
180
0
270
(d)
90
8
4
180
0
270
(e)
90
40
20
180
0
270
(f)
90
10
5
180
0
270

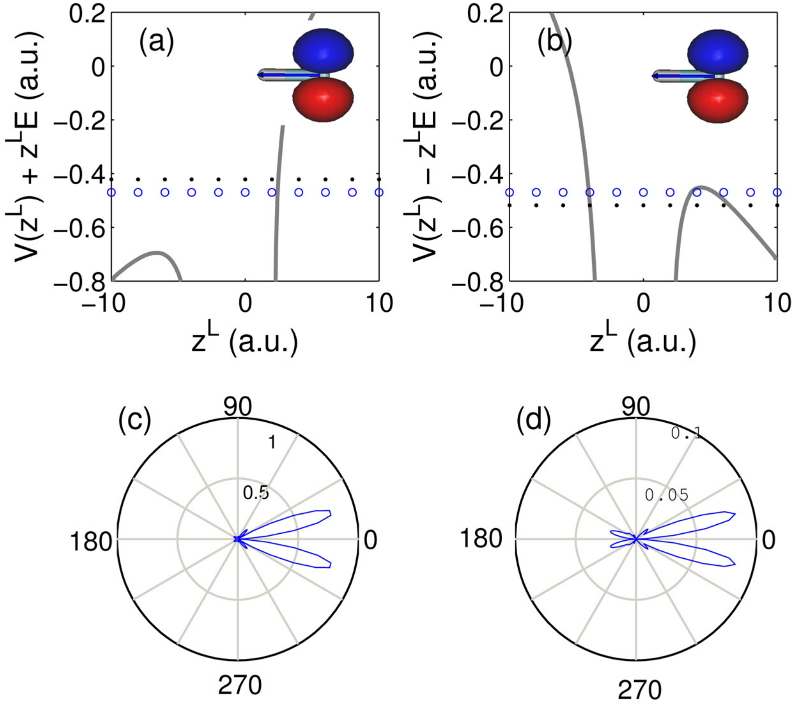
HF

LiF

HF


(a)
V(z^L) + z^L E (a.u.)
z^L (a.u.)
0.2
0
−0.2
−0.4
−0.6
−0.8
−10
0
10
(b)
V(z^L) − z^L E (a.u.)
z^L (a.u.)
(c)
90
180
0
270
0.05
0.025
(d)
90
180
0
270
0.01
0.005

LiF


(a)
V(z^L) + z^L E (a.u.)
z^L (a.u.)
0.2
0
−0.2
−0.4
−0.6
−0.8
−10
0
10
(b)
V(z^L) − z^L E (a.u.)
z^L (a.u.)
(c)
90
180
0
270
1
0.5
(d)
90
180
0
270
0.1
0.05

Conclusion on MFPADs

- MFPADs can be obtained for a broad range of species
- Time-dependent phenomena. Sensitive to valence electrons. Charge migration
- Strong-field ionization by circularly polarized fields minimizes rescattering and reflect the orbital
- Strong asymmetries in the photoelectron angular distributions with linearly polarized fields highlighting the role of the dipole term of the molecular potential, and the dipole of the orbital.

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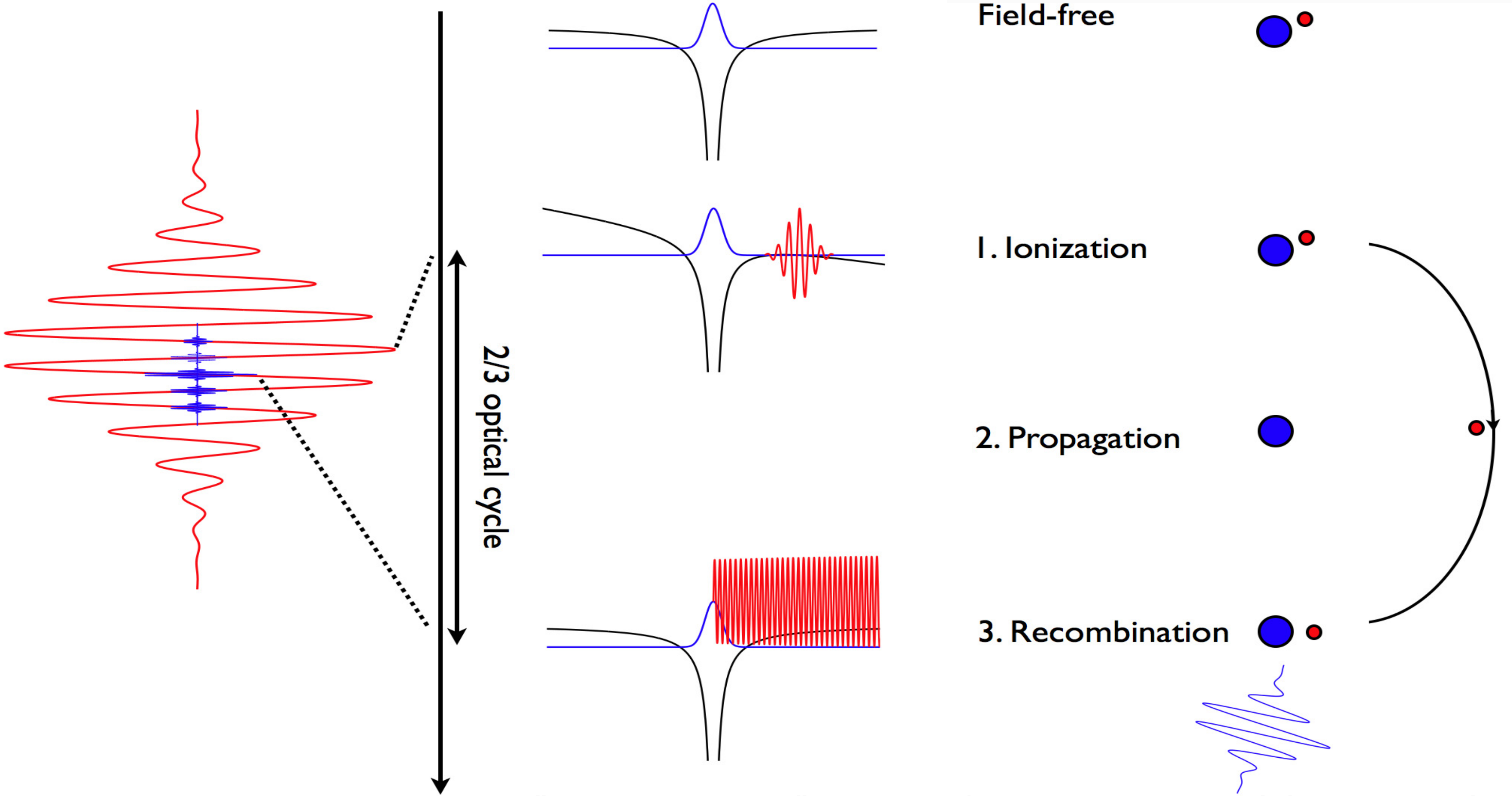
High-order harmonic generation

HHG with the three-step model

PRL **71**, 1994 (1993)



"Atomic Antenna". M.Yu.Kuchiev. JETP Lett. **45**(7), 404-406 (1987)

$$S_{\mathbf{n}}(\omega) = \left| \mathbf{n} \cdot \int \mathrm{e}^{\mathrm{i}\omega t} \frac{\mathrm{d}}{\mathrm{d}t} \langle \mathbf{v}_{\mathrm{dip}}(t) \rangle \, \mathrm{d}t \right|^2$$

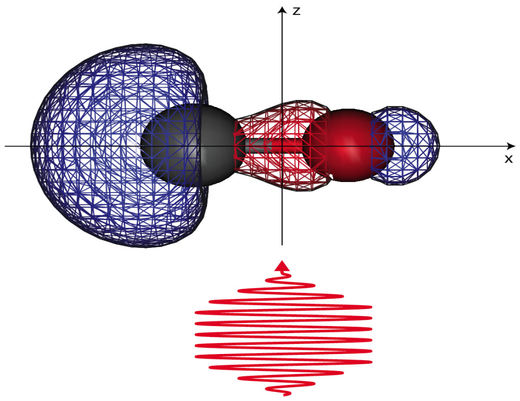
$$\begin{aligned} \langle \mathbf{v}_{\lambda}(\mathcal{R}, t) \rangle \; &= \mathrm{i} \int_0^t \mathrm{d}\tau \int \mathrm{d}\mathbf{k} \, \mathbf{v}^*_{\mathrm{rec},\lambda}(\mathcal{R}, \mathbf{k}, t) \mathrm{e}^{-\mathrm{i}S_{\lambda}(\mathbf{k},t,t-\tau)} \\ &\times \mathbf{F}(t-\tau) \cdot \mathbf{d}_{\mathrm{ion},\lambda}(\mathcal{R}, \mathbf{k}, t-\tau) \\ &+ \mathrm{c.c.}, \end{aligned}$$

$$S_{\lambda}(\mathbf{k}, t, t-\tau) = \int_{t-\tau}^{t} \left(\frac{1}{2} \left[\mathbf{k} + \mathbf{A}(t'') \right]^2 - E_{\lambda} \right) \mathrm{d}t''$$

$$S_{\mathbf{n}}(\omega) = \left| \mathbf{n} \cdot \int \mathrm{e}^{\mathrm{i}\omega t} \frac{\mathrm{d}}{\mathrm{d}t} \langle \mathbf{v}_{\mathrm{dip}}(t) \rangle \, \mathrm{d}t \right|^2$$

$$\begin{aligned} \langle \mathbf{v}_\lambda(\mathcal{R}, t) \rangle \; &= \mathrm{i} \int_0^t \mathrm{d}\tau \int \mathrm{d}\mathbf{k} \, \mathbf{v}^*_{\mathrm{rec},\lambda}(\mathcal{R}, \mathbf{k}, t) \mathrm{e}^{-\mathrm{i}S_\lambda(\mathbf{k},t,t-\tau)} \\ &\times \mathbf{F}(t-\tau) \cdot \mathbf{d}_{\mathrm{ion},\lambda}(\mathcal{R}, \mathbf{k}, t-\tau) \\ &+ \mathrm{c.c.}, \end{aligned}$$

$$S_\lambda(\mathbf{k}, t, t-\tau) = \int_{t-\tau}^{t} \left(\frac{1}{2} \left[\mathbf{k} + \mathbf{A}(t'') \right]^2 - E_\lambda \right) \mathrm{d}t''$$



$$S_{\mathbf{n}}(\omega) = \left| \mathbf{n} \cdot \int \mathrm{e}^{\mathrm{i}\omega t} \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \mathbf{v}_{\mathrm{dip}}(t) \right\rangle \mathrm{d}t \right|^2$$

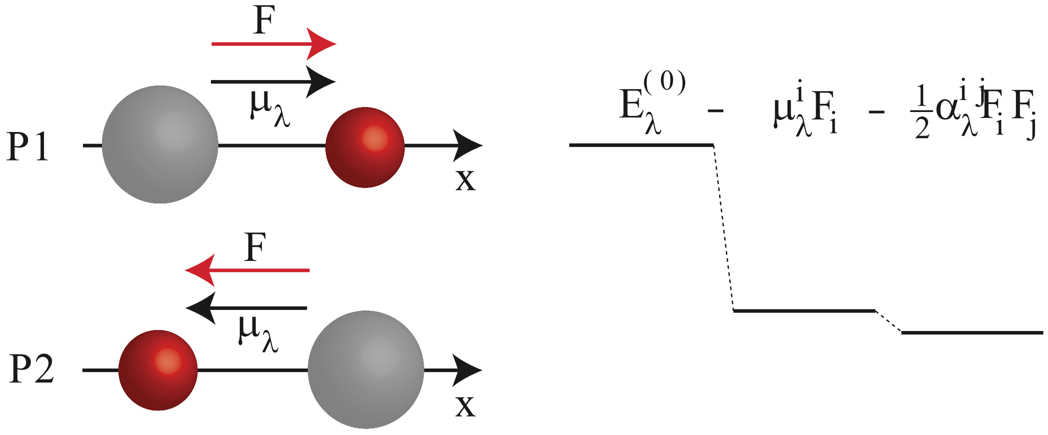
$$\begin{aligned} \langle \mathbf{v}_\lambda(\mathcal{R}, t) \rangle \; &= \mathrm{i} \int_0^t \mathrm{d}\tau \int \mathrm{d}\mathbf{k}\, \mathbf{v}^*_{\mathrm{rec},\lambda}(\mathcal{R}, \mathbf{k}, t) \mathrm{e}^{-\mathrm{i}S_\lambda(\mathbf{k},t,t-\tau)} \\ &\times \mathbf{F}(t-\tau) \cdot \mathbf{d}_{\mathrm{ion},\lambda}(\mathcal{R}, \mathbf{k}, t-\tau) \\ &+ \mathrm{c.c.}, \end{aligned}$$

$$S_\lambda(\mathbf{k}, t, t-\tau) = \int_{t-\tau}^{t} \left(\frac{1}{2} \left[\mathbf{k} + \mathbf{A}(t'') \right]^2 - E_\lambda \right) \mathrm{d}t''$$

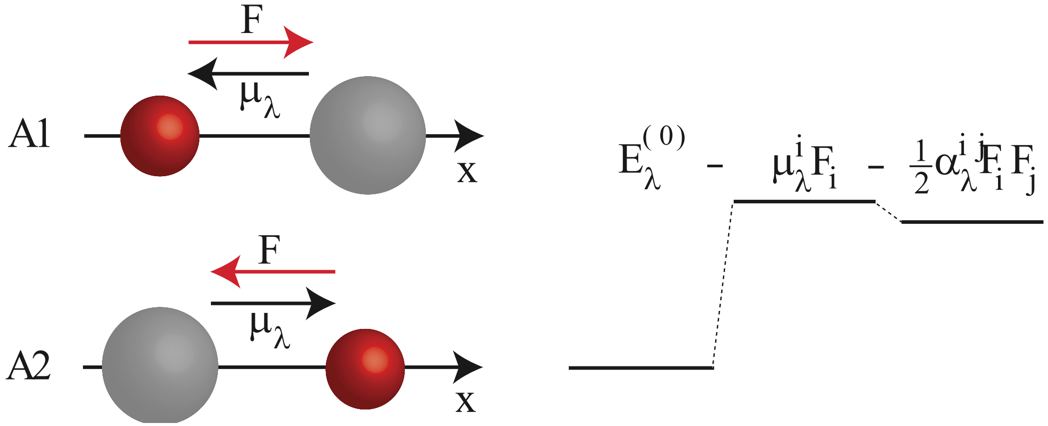
For a polar molecule

$$E_\lambda = E_\lambda^{(0)} - \mu_\lambda^i F_i - \frac{1}{2} \alpha_\lambda^{ij} F_i F_j$$

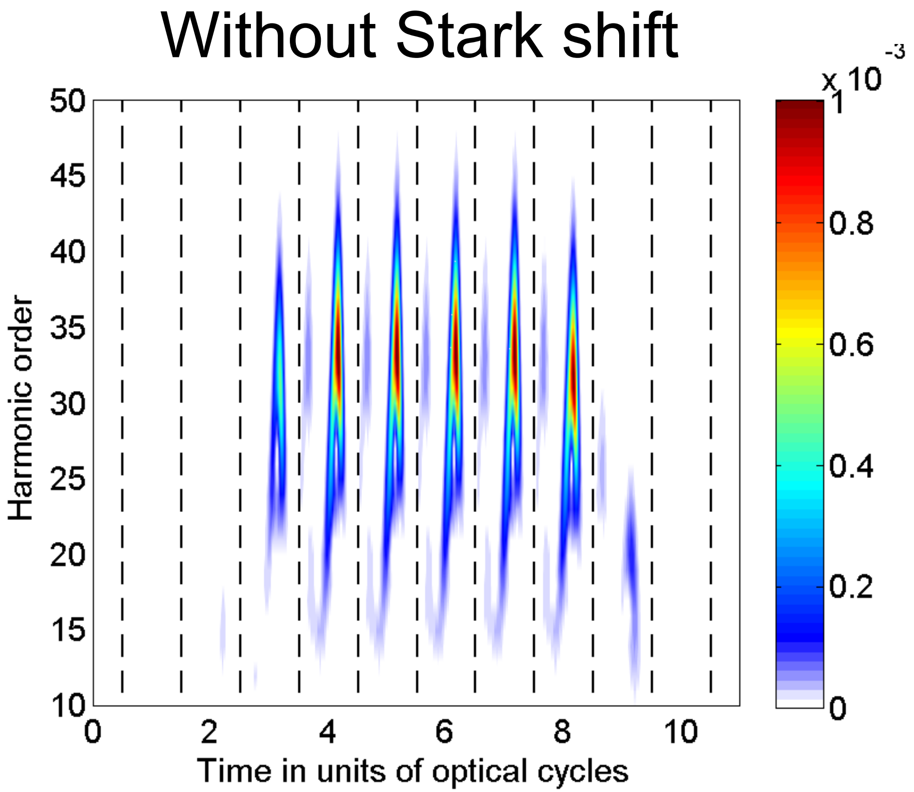
(a) Parallel geometry

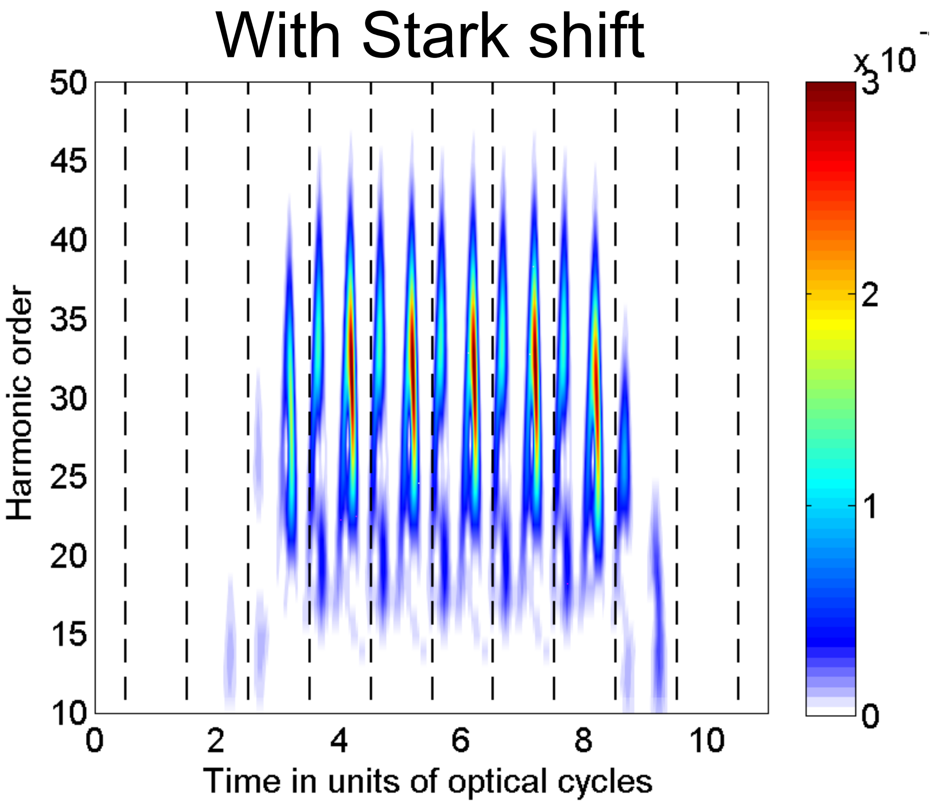


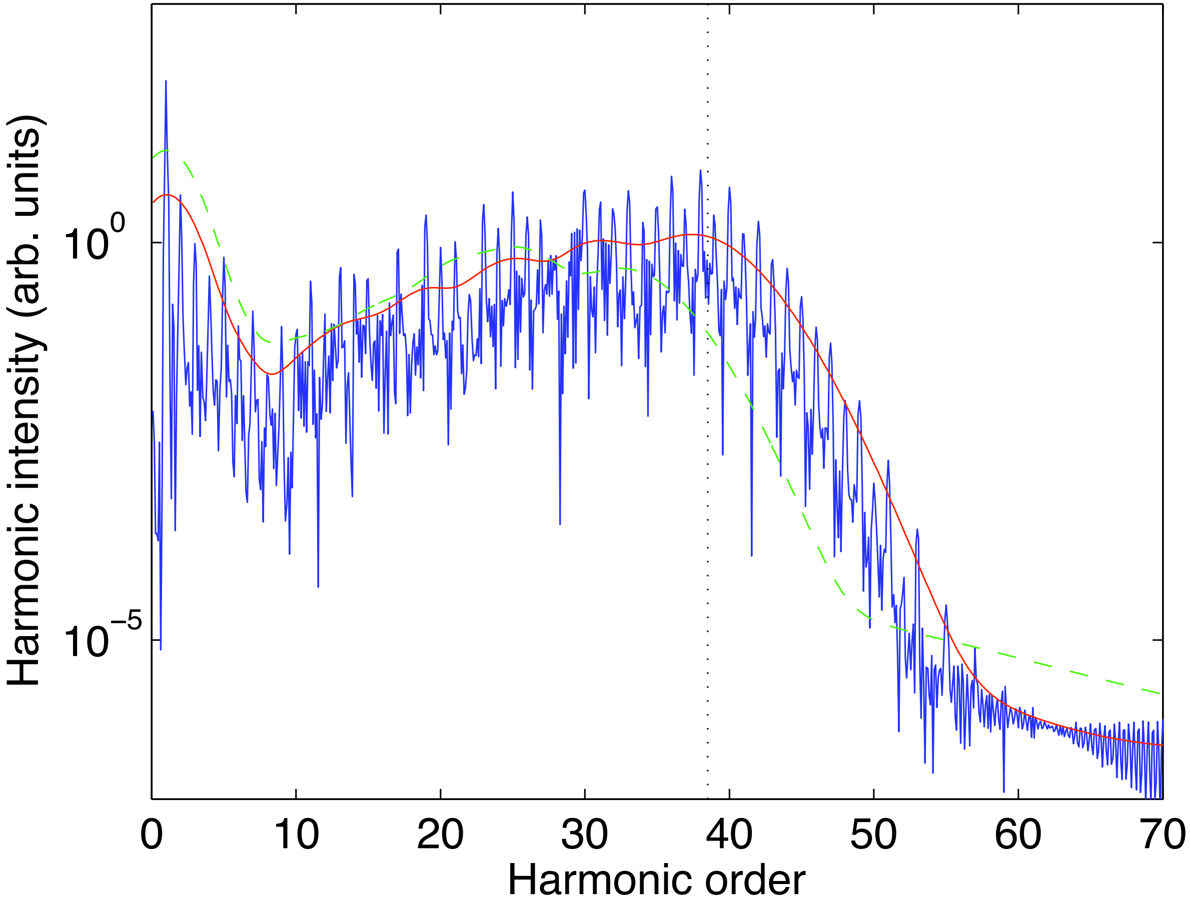
(b) Antiparallel geometry



System-induced gating


Without Stark shift


With Stark shift



Etches and LBM, JPB (2010)

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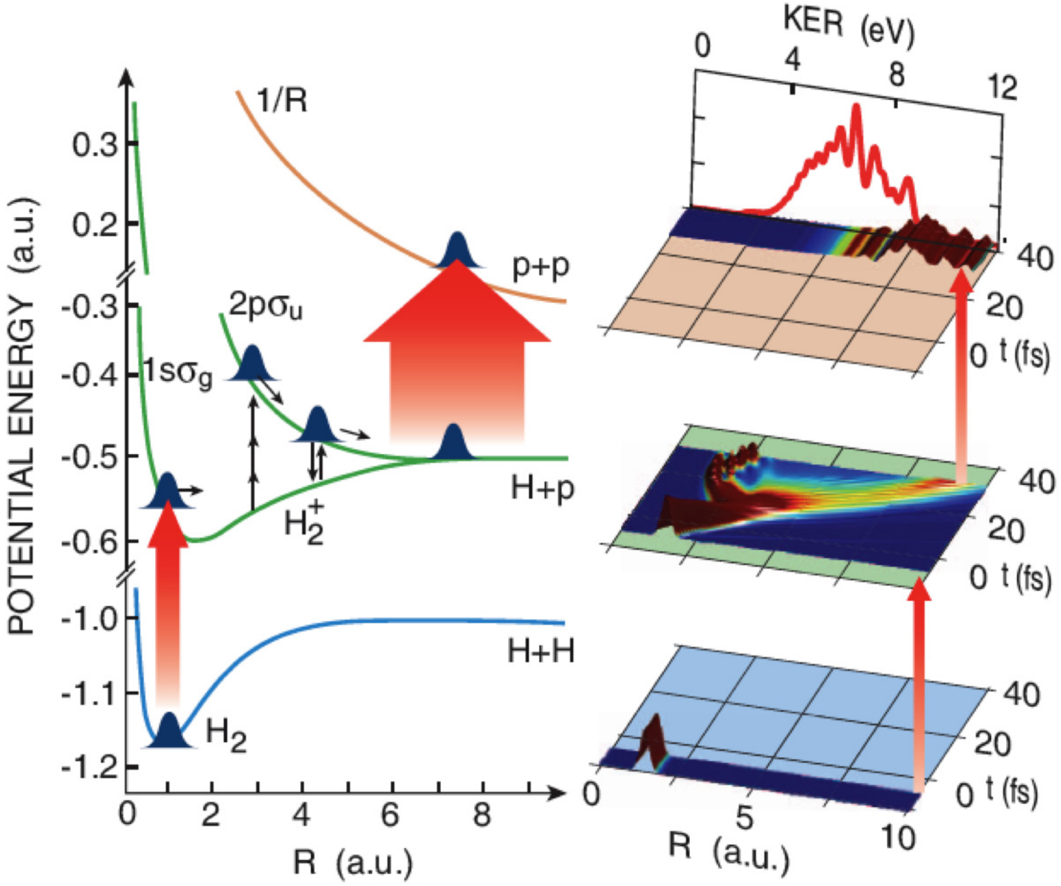
Nuclear motion: Dissociative ionization

- Theoretical frame-work that treats both electrons and nuclei when the pulse lengths are such that the nuclei move during the pulse (Example FLASH 10 fs - 50 fs)

Dissociative double ionization

- Full problem not understood
    - ☐ Nuclei: ”Exact” on electronic bound state curves
    - ☐ Electrons: ”Exact” for frozen nuclei
- Born-Oppenheimer and existing electronic rates in a single theoretical framework.

Dissociative double ionization



$$H = H_s - \frac{i}{2}\sum_m C_m^\dagger C_m$$

Monte Carlo Wave Packet

- Describes open quantum systems
- Non-hermitian evolution of wave functions
- Equivalent to the master equation
- Stochastic jumps between states (Hilbert spaces)

Dissociative double ionization

Theory

- Wave function in a basis of electronic states

$$|\Psi\rangle = \sum_a \int d\vec{R}\; X_a(\vec{R},t)|\phi_{Ra}\rangle \otimes |\vec{R}\rangle$$

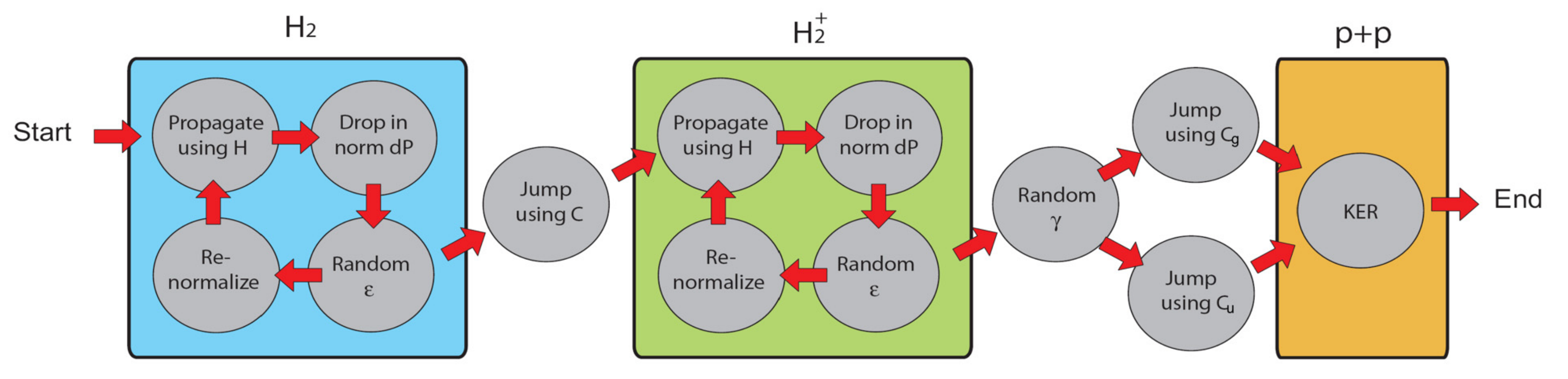
- Rates are R-dependent

$$C_u = \int d\vec{R}\sqrt{\Gamma_u(\vec{R})}|\phi_{R,c}\rangle\langle\phi_{R,u}| \otimes |\vec{R}\rangle\langle\vec{R}|$$

$$H = H_s - \frac{i}{2}\sum_m C_m^\dagger C_m$$

Input

- Electronic BO curves
- Ionization rates as a function of *R* and intensity
- Dipole moment functions within a given system (charge state)



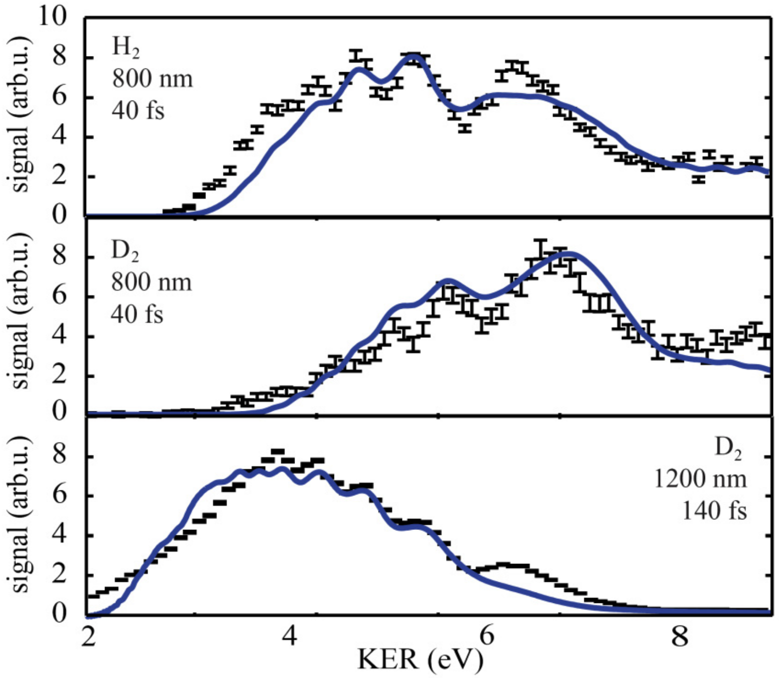
Results

Final result

- Averaged over many runs and focal-volume
- Includes many different instants of ionization

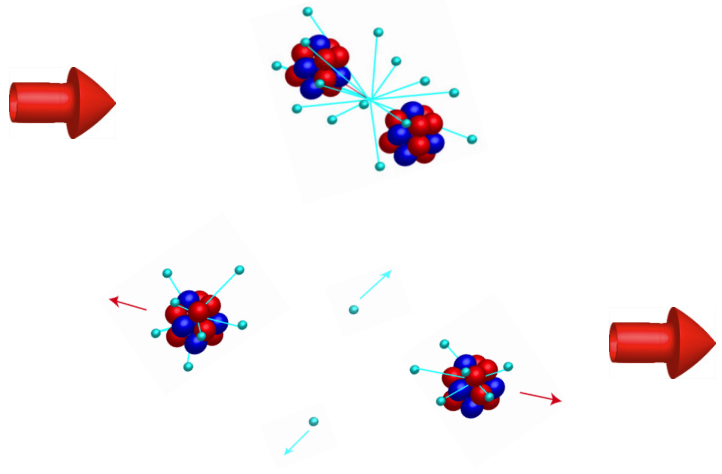
Experiment

- Staudte et al., Phys. Rev. Lett **98**, 073003 (2007)

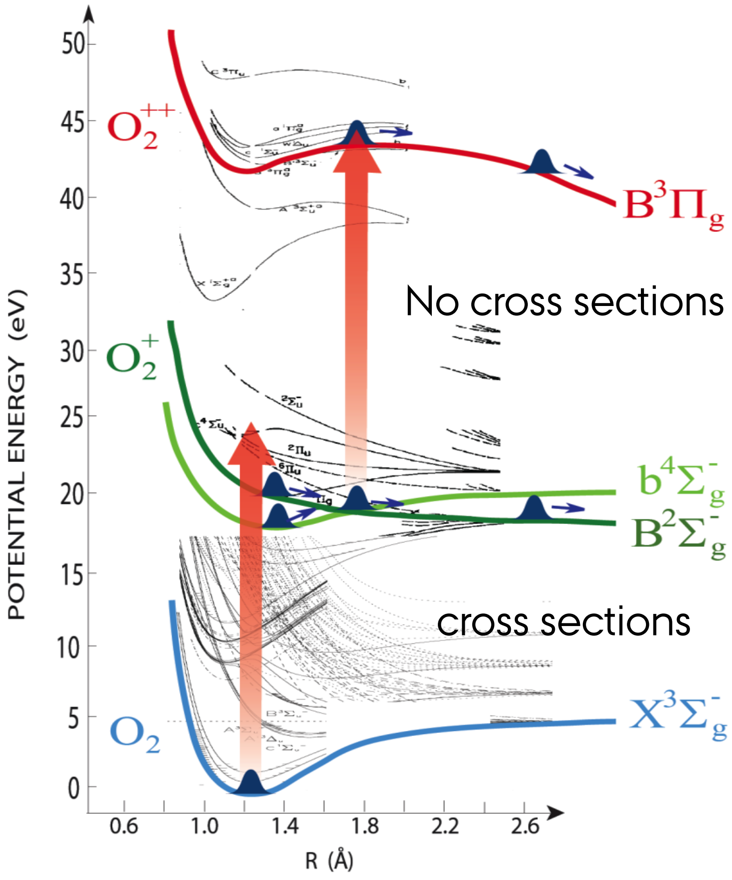


Oxygen in FEL

Ionization of Oxygen



Born Oppenheimer



No cross sections

cross sections

Conclusion: Dissociative ionization

- Methodology seems promising
- Room for improvements: Include more electronic state, improved rates,…
- Other systems than H_2
- Heteronuclear systems

- Leth, LBM, Mølmer, PRL (2009), PRAs (2010).

Summary and outlook

- Polar molecules in femto- and attosecond pulses
- Dipole of the HOMO (MFPADs and HHG)
- Dipole of the molecular potential (TDSE: ionization and HHG). SFA?
- Dipole of the active orbital in"Attosecond streaking photoelectron spectroscopy", Baggesen, LBM, PRL (2010)
- Nuclear motion