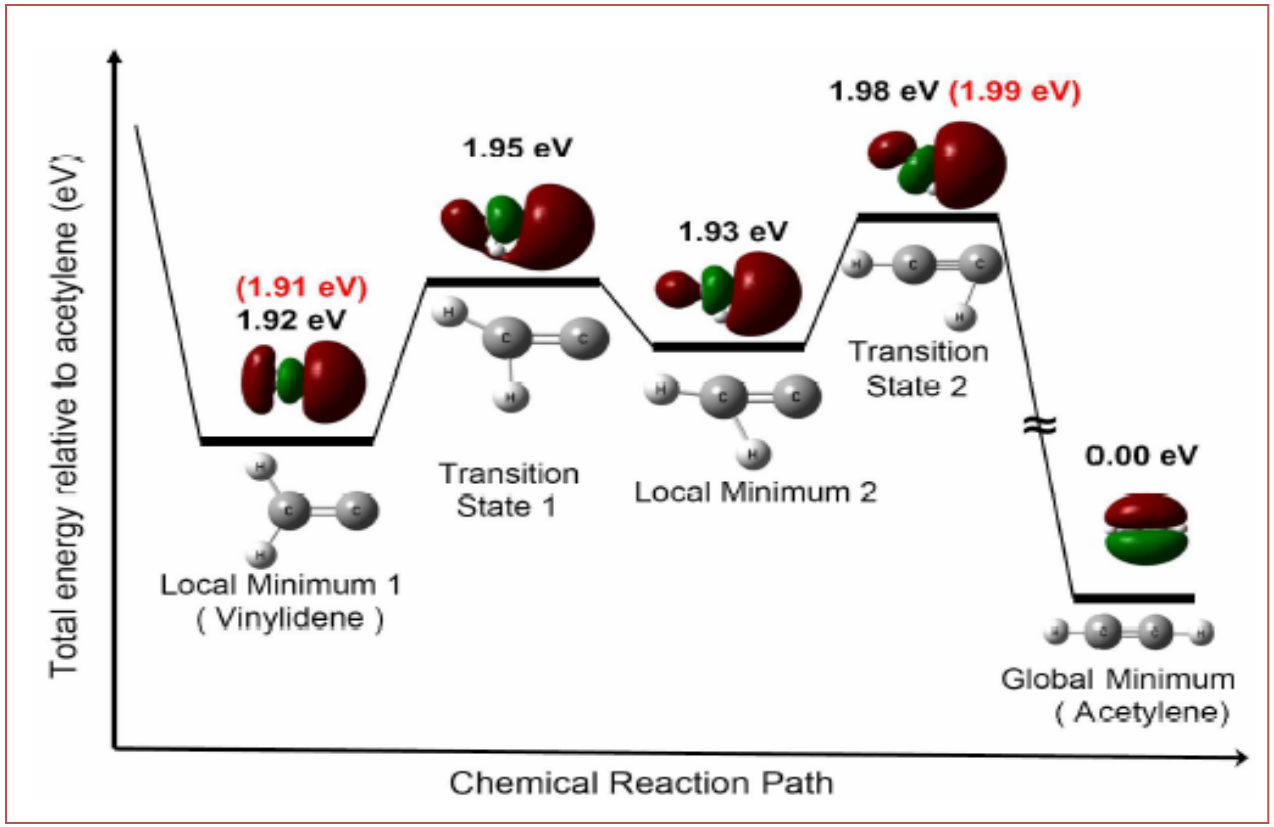
Dynamic Imaging of molecules using laser-induced High-order harmonics and High-energy photoelectrons

Goal: probing **time-dependent** structural changes

Example: Isomerization of C_2H_2

C. D. Lin
Kansas State U.



For **Spatial imaging**

X-ray diffraction

Electron diffraction (100 keV)

For temporal resolution

Tens of picoseconds resolution

New tools:

Free-electron X-ray lasers ($$$ $$$ $$$); others;
Diffraction concept

This proposal:

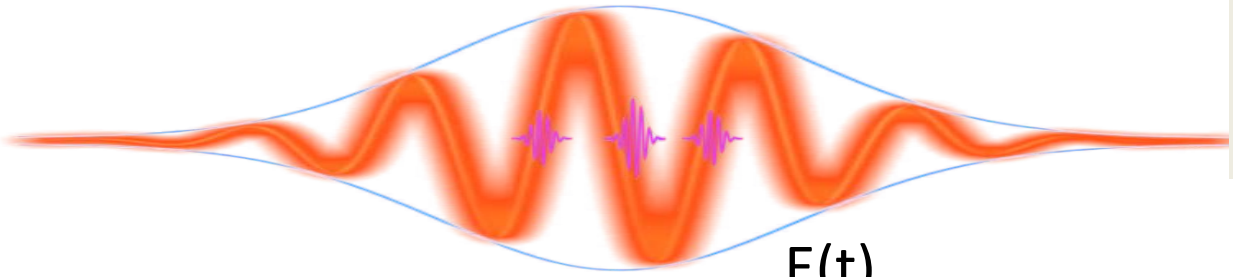
Use ***Infrared laser pulses***

Few femtoseconds are already available

But λ >> atomic dimensions,

Can it provide needed spatial resolution?

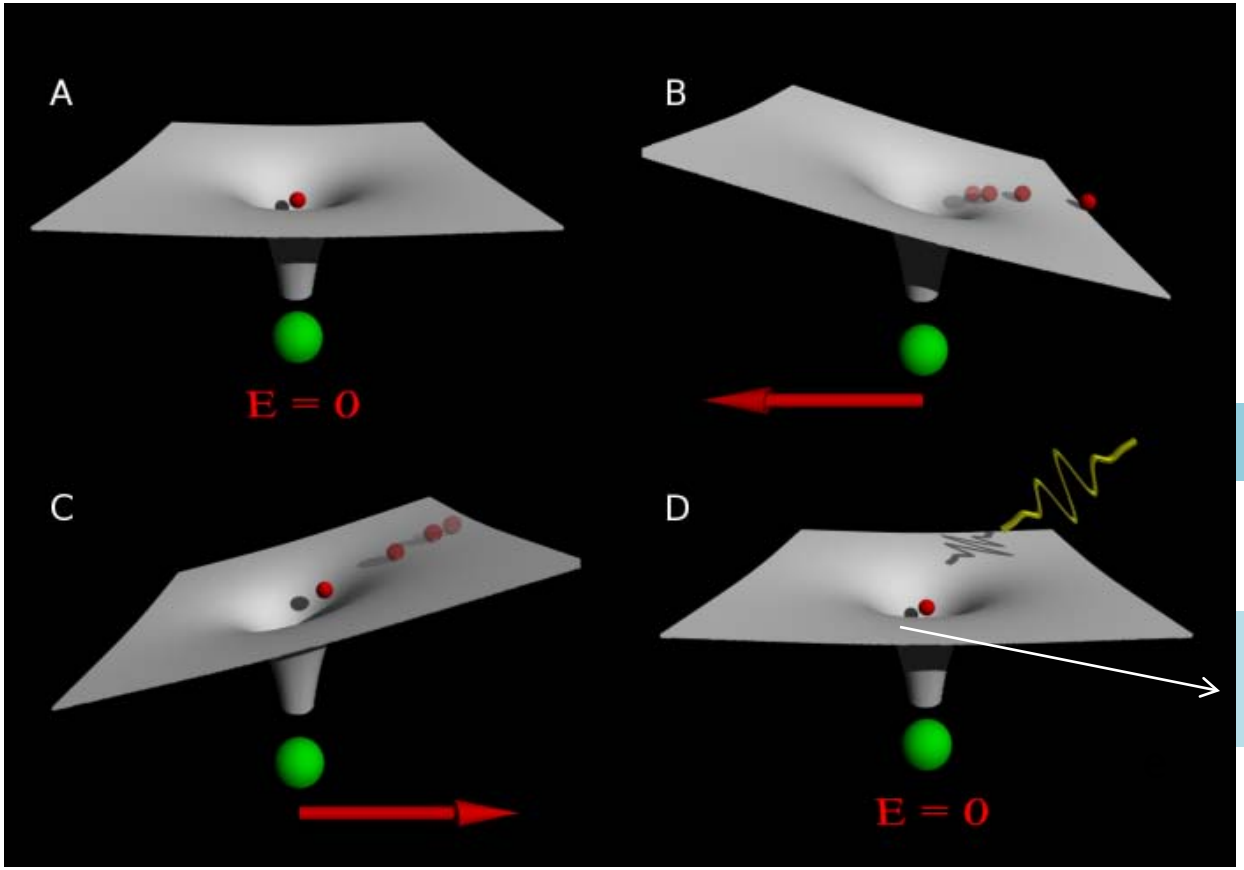
Relies on Rescattering concept



E(t)

Rescattering Model (RS)

Krause, Schafer, Kulander
Corkum 1993



Quantitative RS
QRS
2009

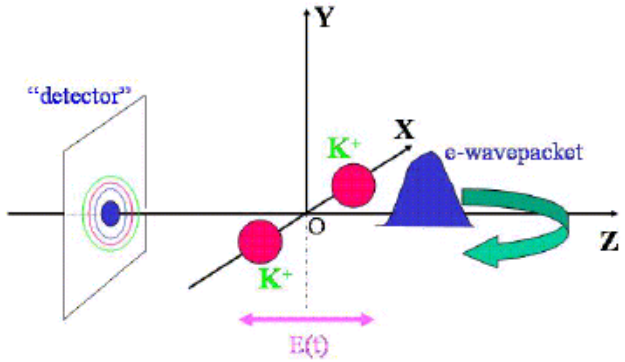
High-harmonic generation

High-energy photoelectrons

Electrons revisit the target ion-> structure info

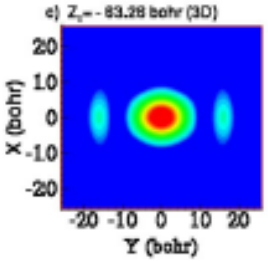
Adopted from: http://www.nat.vu.nl/~kjeld/x-ray.html

Electron Self-diffraction -- History



Previous work/TDSE

- Zuo et al **1996** (R=20)
2. Lein et al 2002
3. Spanner et al 2004 (R=4)
4. Yurchenko et al 2004 (R=6)
5. Hu and Collins 2005 (R=15)



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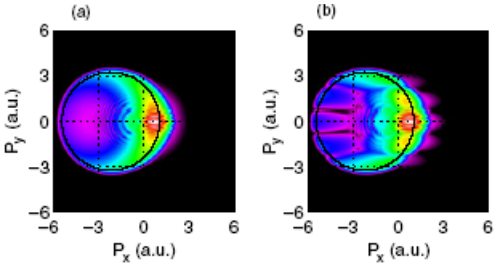

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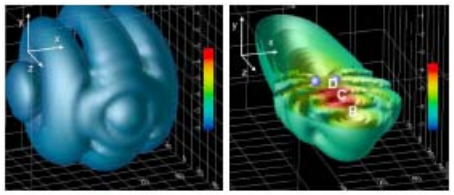

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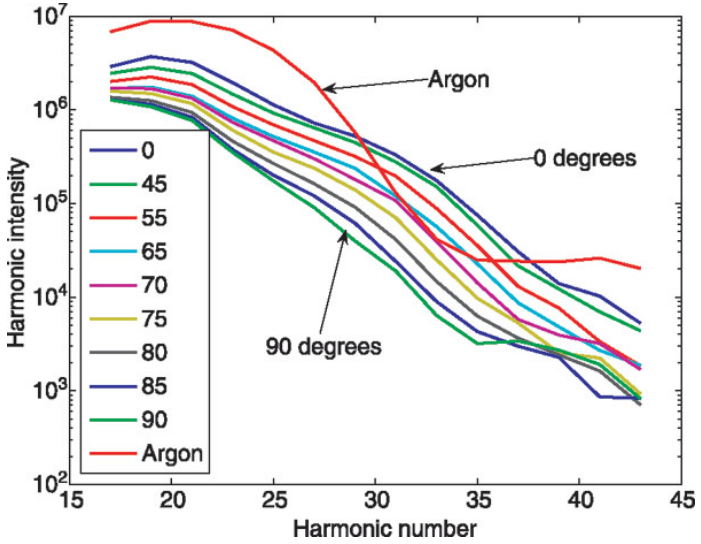
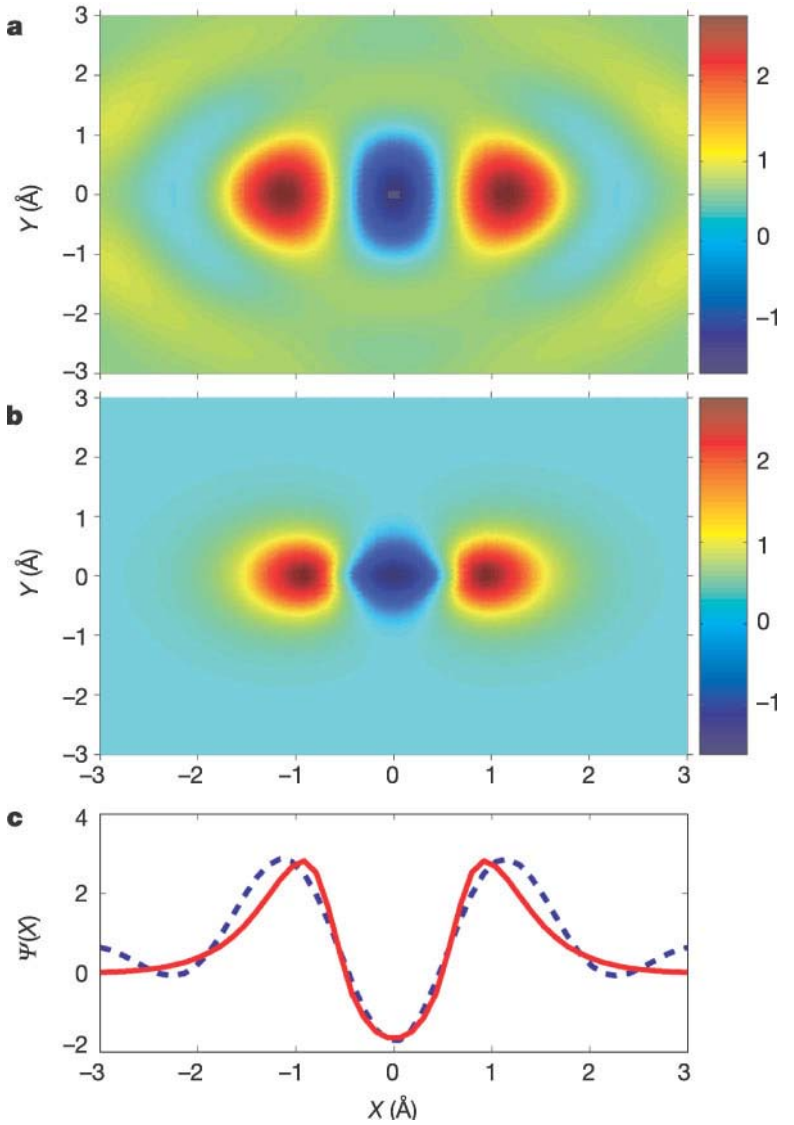
Interferences from diffraction and from laser

Itatani et al, Nature 2004 "
Tomographic imaging of molecular orbitals"

Based on plane waves for continuum electrons





Problems of tomograpy examined in Le 2007, PRA.

Tomography: Neat, plausible but wrong – N2 is the ONLY example

QRS: Quantitative Rescattering Theory

Starace's talk earlier

HHG: **HHG= (wave packet) x (photoionization crs)**

Laser-Free Cross sections
A&M theory last 60 years

HATI spectra: **Electron momentum spectra= (wave packet) x (elastic DCS)**

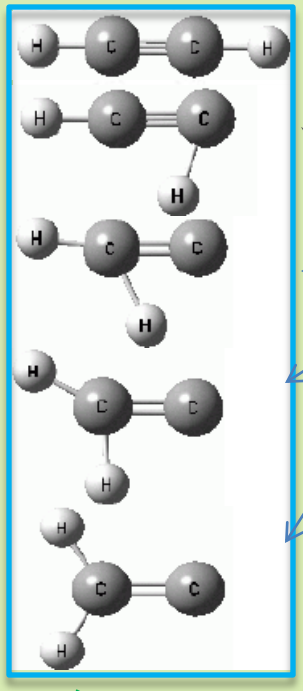
Laser parameters

Structure Retrieval

Used to retrieve Laser's pulse duration, intensity and CEP from experimental data

Collaborators: A. T. Le, Z. J. Chen, JL Xu, C. Jin, S. Micheau
Toru Morishita (UEC, Japan)
H. L. Zhou (Georgia State)
Robert Lucchese (Texas A&M)

Scheme of Dynamic Chemical Imaging



retrieval

retrieval

MFPAD

DCS

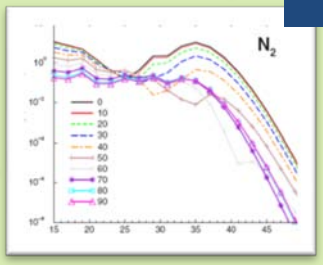
HHG

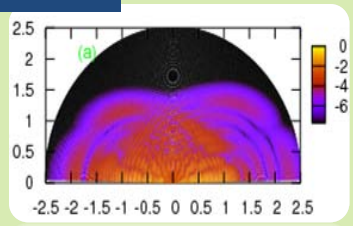
Macroscopic effect

HATI

QRS

QRS





Ingredients of dynamic chemical imaging theory:

Forward direction– (from known structure →HHG and HATI)

- **Need accurate Theory of HATI and HHG from molecular targets**
- **Computationally be efficient**
- **Target structure info insensitive to (or independent of) lasers**

The QRS fulfills all these requirements → DCS / Photoionization

Backward direction -- (DCS/PICS--> structure)

Spatial information: use Inverse scattering theory or algorithm to retrieve structure of the target from DCS and PICS

Temporal resolution: provided by the probe laser pulse duration

Testing the QRS for HATI: use simple targets

1. Solving the time-dependent Schrödinger Equation numerically

("EXACT")

TDSE

$$H = H_{atom} + H_i(t)$$

$$H\Psi(\vec{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t)$$

$$I(p_v,\theta_v) = W(p_r)\sigma(p_r,\theta_r)$$

Limited to one-electron model atomic systems

2. Second-order strong field approximation

(Simple)

SFA2

$$f_2(\vec{k}) = -\int_{-\infty}^{\infty} dt \int_{t}^{\infty} dt' \int d\vec{p} \left\langle \chi_{\vec{k}}(t') \middle| V \middle| \chi_{\vec{p}}(t') \right\rangle \left\langle \chi_{\vec{p}}(t) \middle| H_i(t) \middle| \Psi_0(t) \right\rangle$$

$$I_{SFA}(p_v,\theta_v) = W_{SFA}(p_r)\sigma_{B1}(p_r,\theta_r)$$

3. Electron scattering (for HATI) DCS

$$\left[-\frac{\nabla^2}{2}+V(r)-\frac{k^2}{2}\right]\Psi_{\boldsymbol{k}}^{-}(\boldsymbol{r})=0,$$

$$f(\theta)=f_c(\theta)+\hat{f}(\theta),$$

$$\hat{f}(\theta)=\sum_{l=0}^{\infty}\frac{2l+1}{k}\exp(2i\sigma_l)\exp(i\delta_l)\sin\,\delta_l P_l(\cos\,\theta),$$

$$f_c(\theta)=-\,\eta\exp(2i\sigma_0)\frac{\exp\{-i\eta\,\ln[\sin^2(\theta/2)]\}}{2k\,\sin^2(\theta/2)}.$$

Well developed tools in the last 50 years

Electron scattering
Photoionization

4. Photo-recombination (for HHG)—molecular target

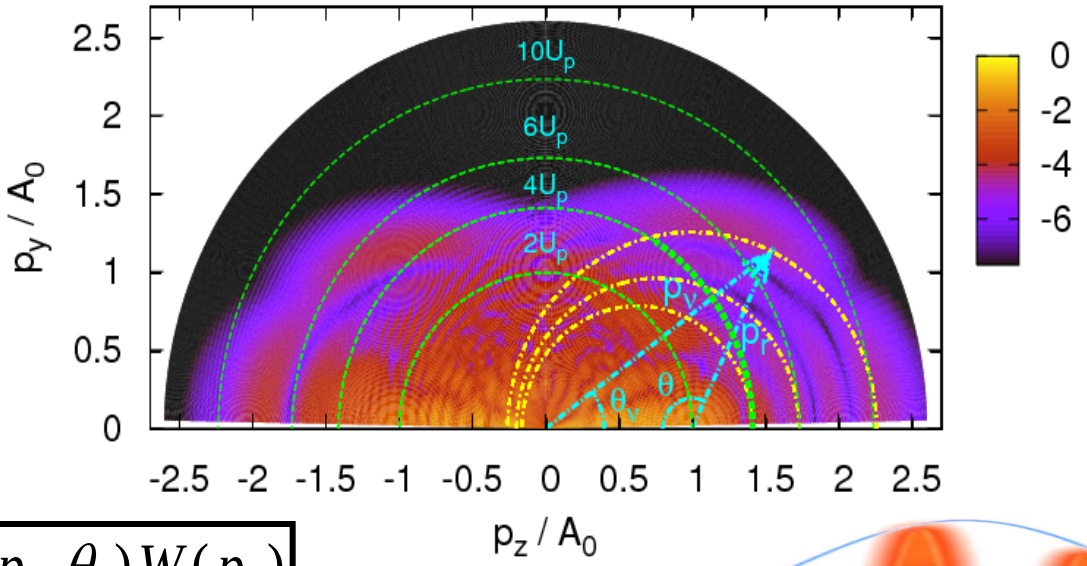
$$\Psi_{\boldsymbol{k}}^{-}(\boldsymbol{r})\;=\;\frac{1}{\sqrt{k}}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}i^l\exp[-i(\sigma_l+\delta_l)]R_{El}(r)Y_{lm}(\Omega_{\boldsymbol{r}})Y_{lm}^{*}(\Omega_{\boldsymbol{k}}).$$

$$\frac{d^2\sigma^R}{d\Omega_{\boldsymbol{n}}d\Omega_{\boldsymbol{k}}}=\frac{4\pi^2\omega^3}{ck}\left|\langle\Psi_i|\boldsymbol{r}\cdot\boldsymbol{n}|\Psi_{\boldsymbol{k}}^{+}\rangle\right|^2.$$

Also: R-matrix method, close-coupling, coupled cluster, ….

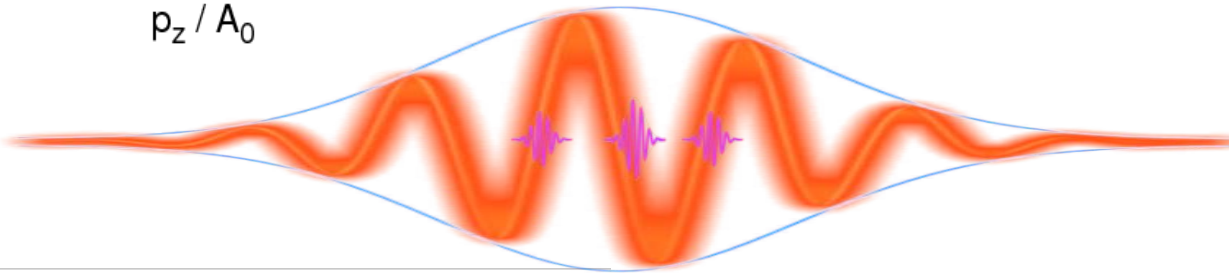
Testing the QRS model from atoms

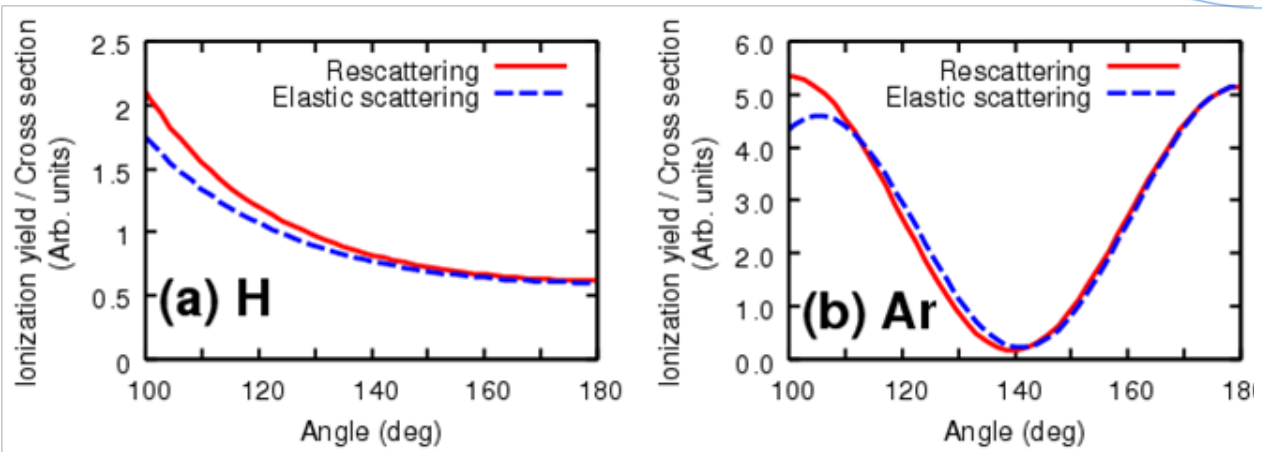
From TDSE



$$I(\mathbf{p}_v) = \sigma(p_r, \theta_r) W(p_r)$$

$$\mathbf{p}_v = -\mathbf{A}_r + \mathbf{p}_r$$





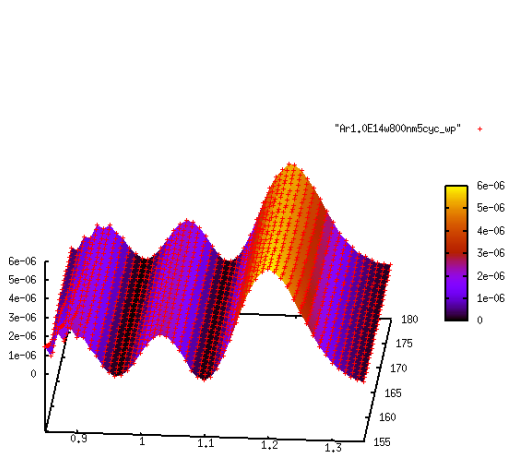
Wave Packets

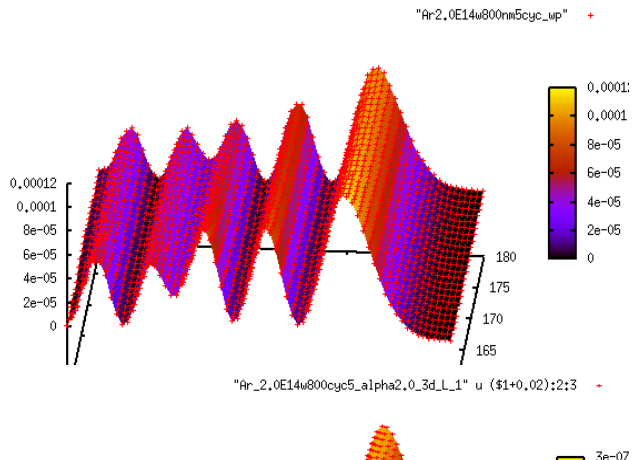
Th

Nearly identical from TDSE and SFA2

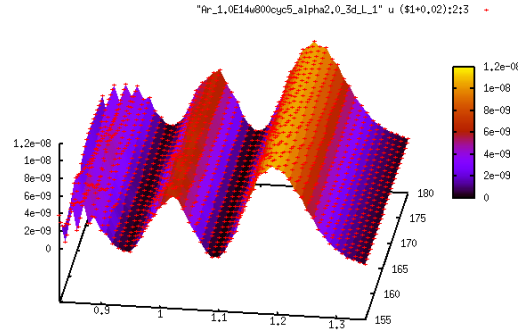
$I_0 = 1 \times 10^{14}$ W/cm^2

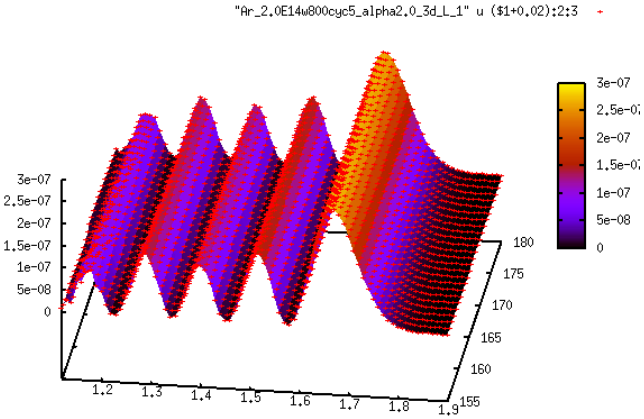
$I_0 = 2 \times 10^{14}$ W/cm^2





TDSE





SFA2

Argon: λ=800 nm, FWHM=5 fs

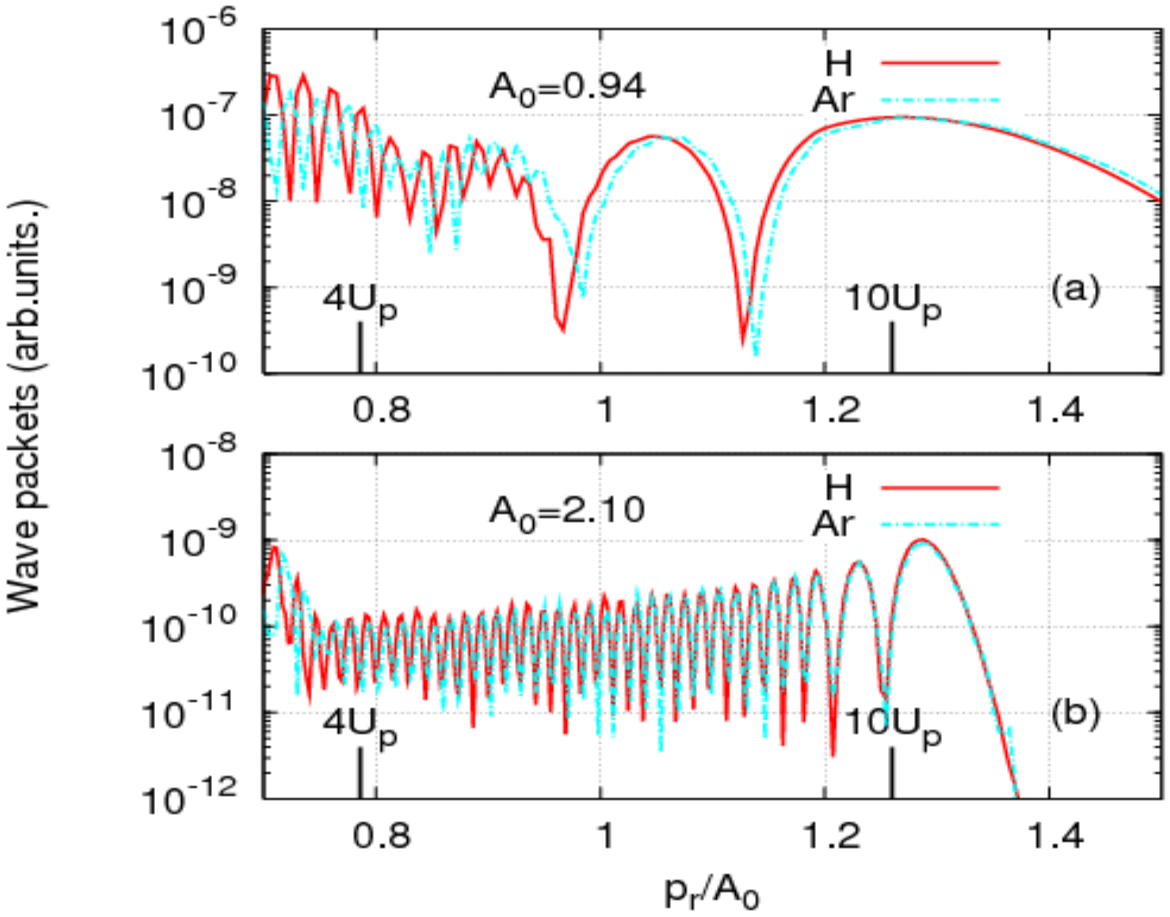
$$I(\mathbf{p}_v)/\sigma(p_r,\theta_r) = W(p_r,\theta_r)$$

Wave Packet

TDSE

Depends on lasers only—target independent

$I_0=1.0\times10^{14}$ W/cm^2 , λ=800 nm, FWHM=5 fs

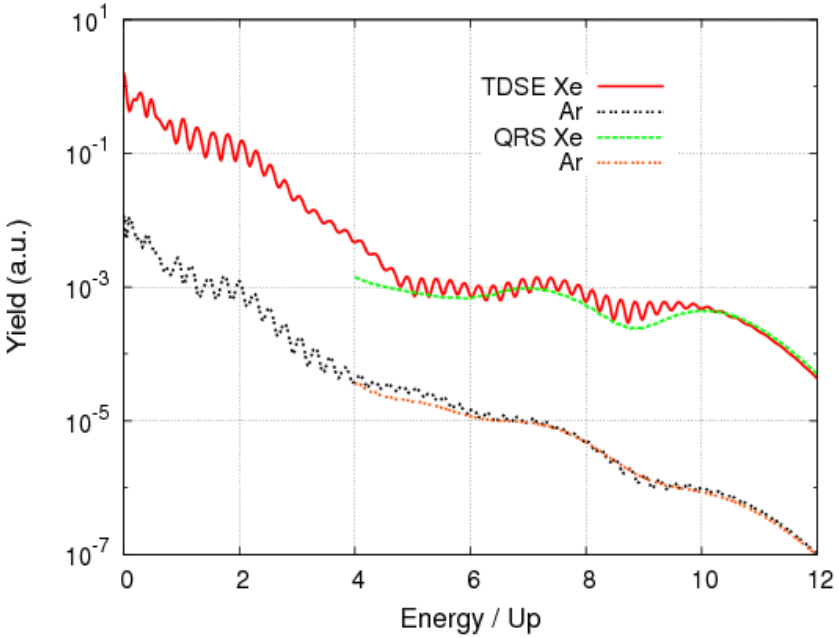


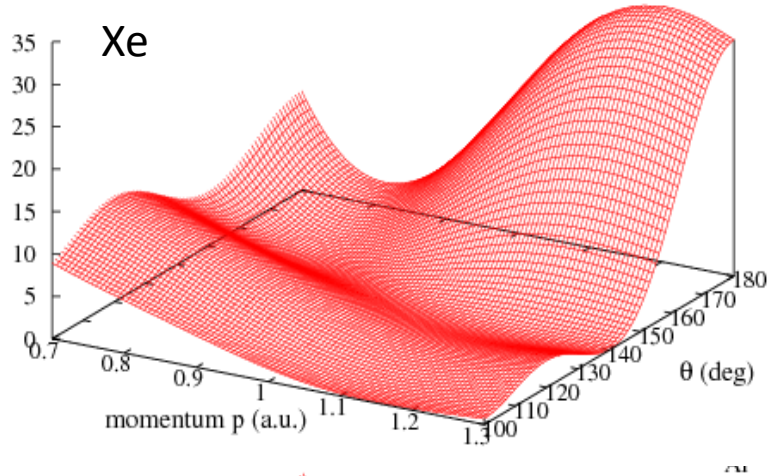
$I_0=0.8\times10^{14}$ W/cm^2 , λ=2000 nm, FWHM=5 fs

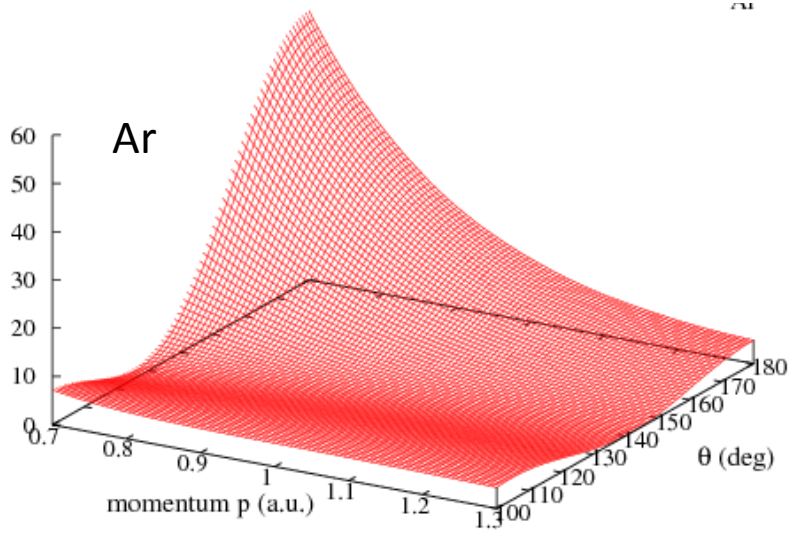
target dependence of HATI --DCS

Single intensity

$$I(\mathbf{p}_v) = \sigma(p_r, \theta_r) W_{SFA}(p_r)$$







$I_0 = 1.0 \times 10^{14}$ W/cm^2 , λ=800 nm, FWHM=5 fs

Simplicity and significance of the QRS:

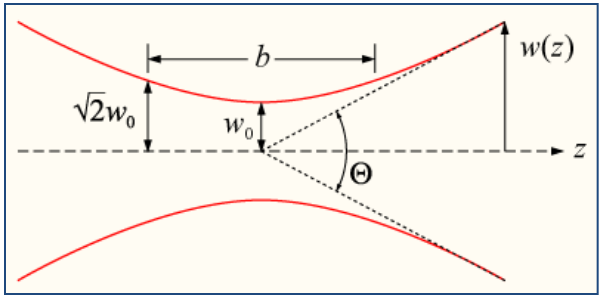
$$I(\mathbf{p}_v) = \sigma(p_r, \theta_r) W_{SFA}(p_r)$$

structure

Lasers

thousands times faster

Photoelectrons are collected from a **focused laser beam—Volume integration** is needed



$$\overline{I}(\mathbf{p}_v) = \sigma(p_r, \theta_r) \overline{W_{SFA}}(p_r)$$

Exp. e-spectra

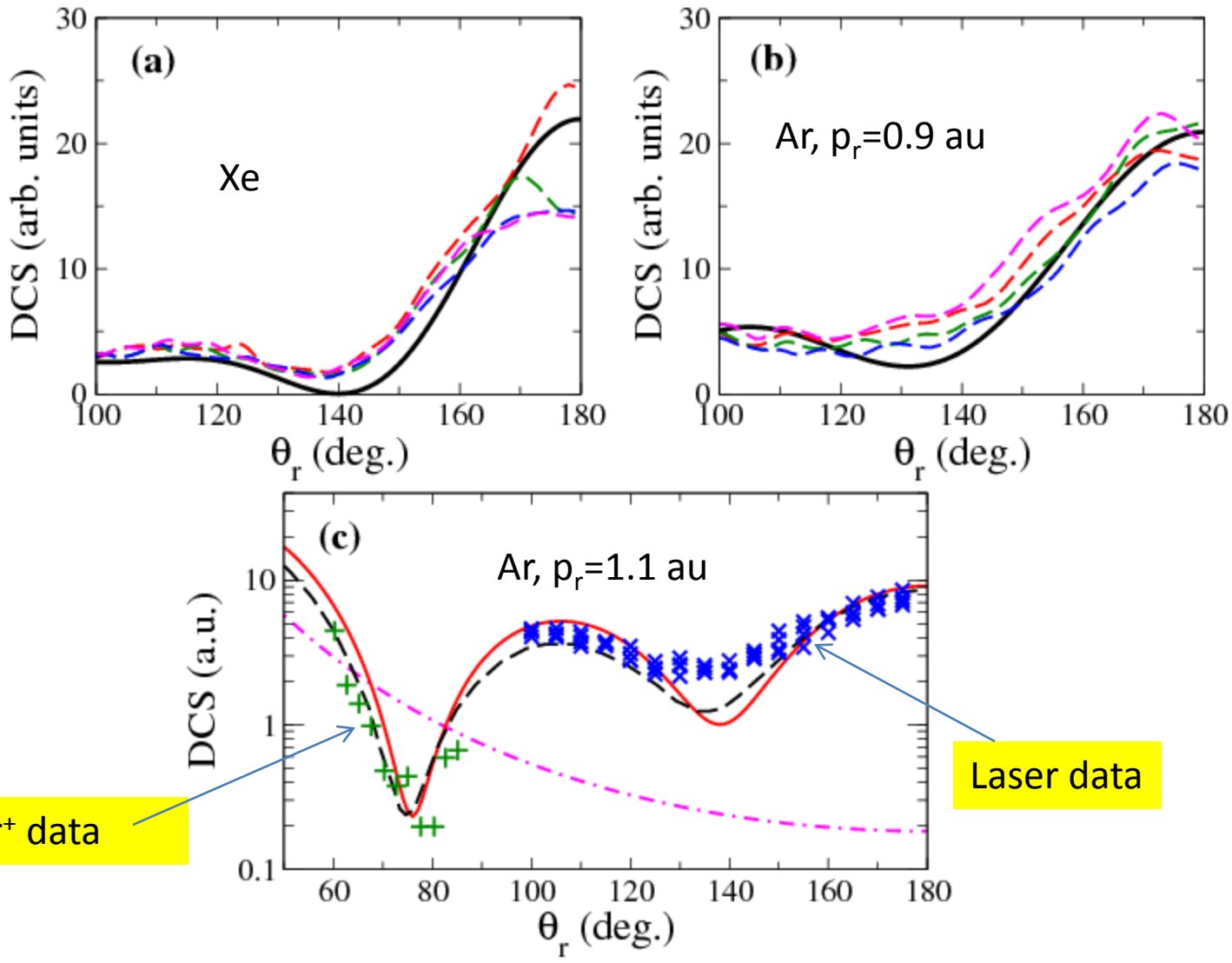
Volume-integrated w.p.

DCS can be extracted without knowing the laser parameters

DCS extracted from **experimental ATI** spectra– **independent of lasers**

EXP

Volume effect included



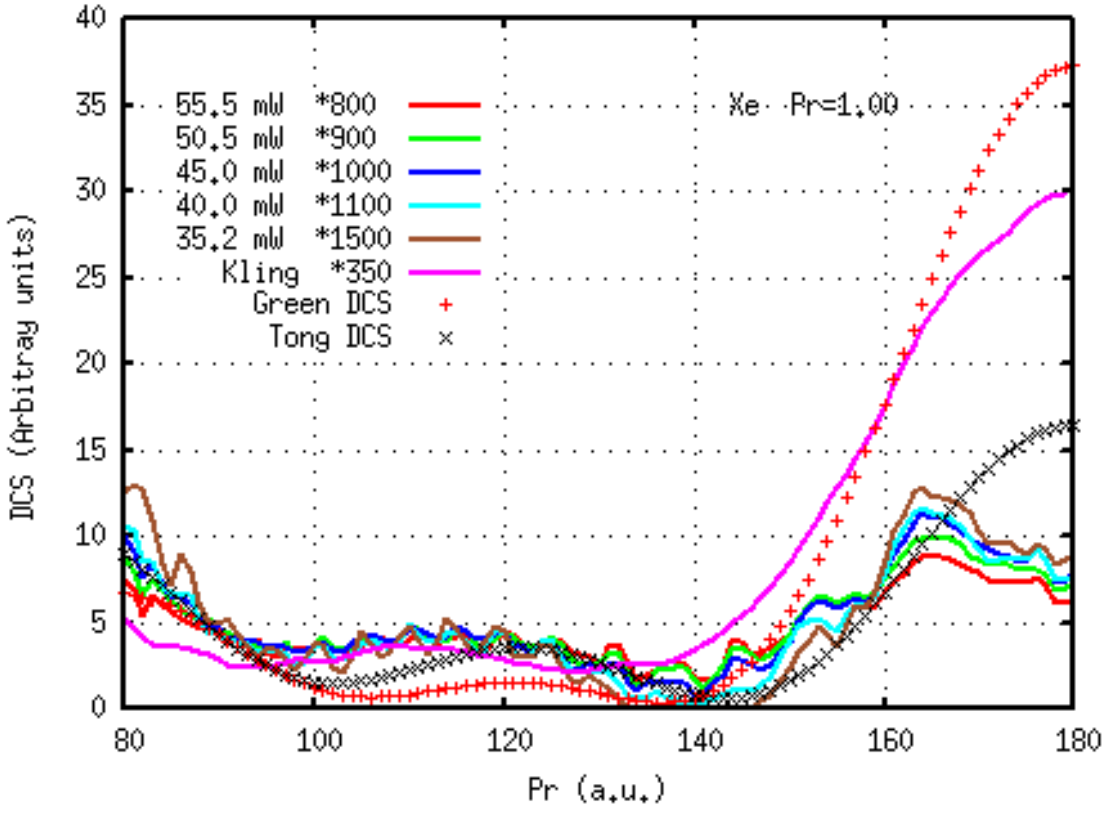
e+ Ar^+ data

Laser data

Exp. Data: Kling et al
Also: Ueda, Cocke

Experimentalists do not always get it right– theory stands to the test

From Lew (10/19/09) : When his postdoc Zhangjin Chen reduced both our images and some you had sent him, he found some persistent differences between the two sets of images. To make a long story short, we **have now traced this difference to an efficiency issue with the present VMI**:



Consistency Check: DCS extracted be independent of lasers used

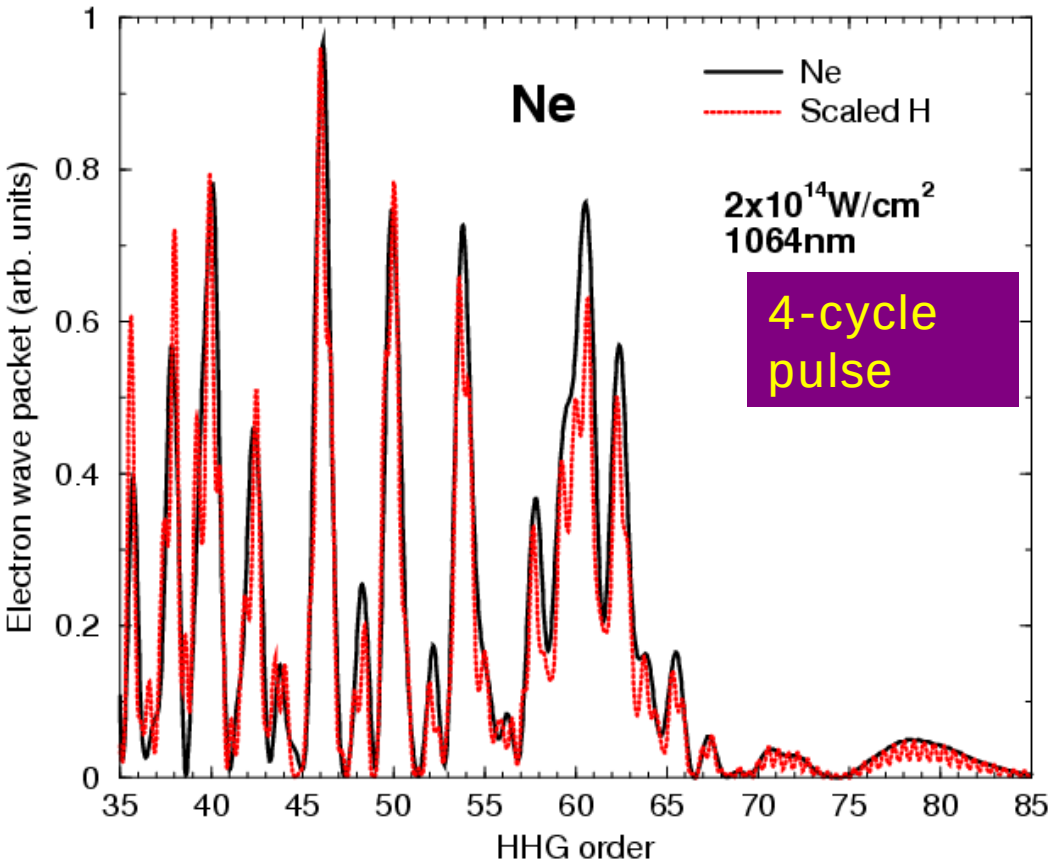
Next:

HHG

QRS

Photo-recombination  Photo-ionization

Wave-packets comparison from HHG



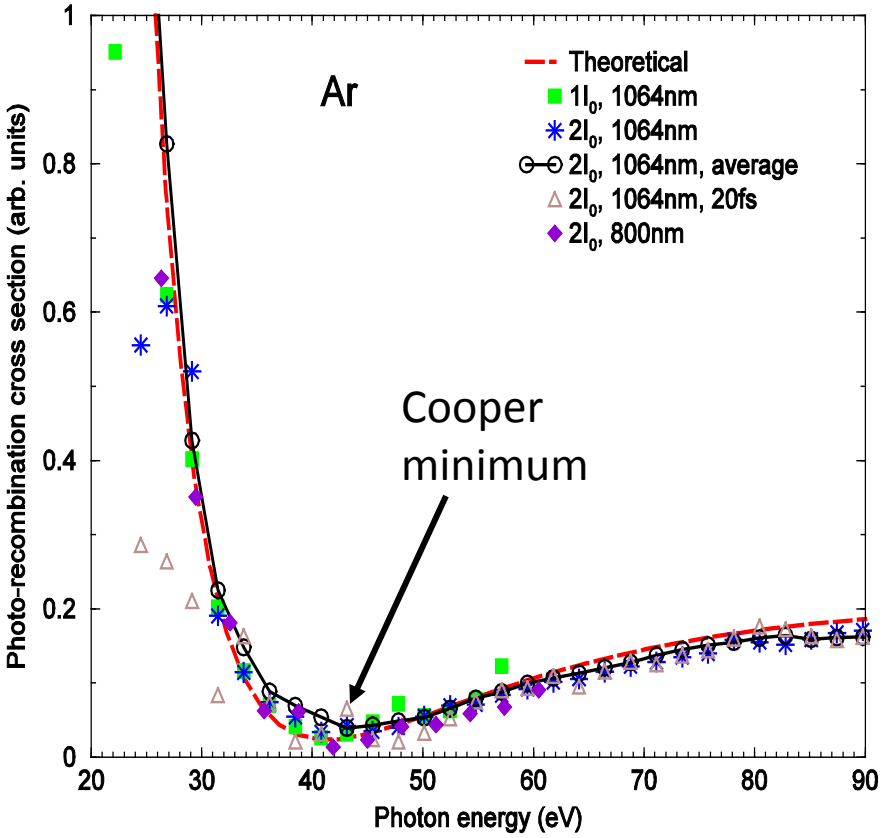
Compare Ne(2p0) with *scaled* H(1s) (with same I_p):

HHG spectra differ, but (normalized) ***wave-packets are very similar***

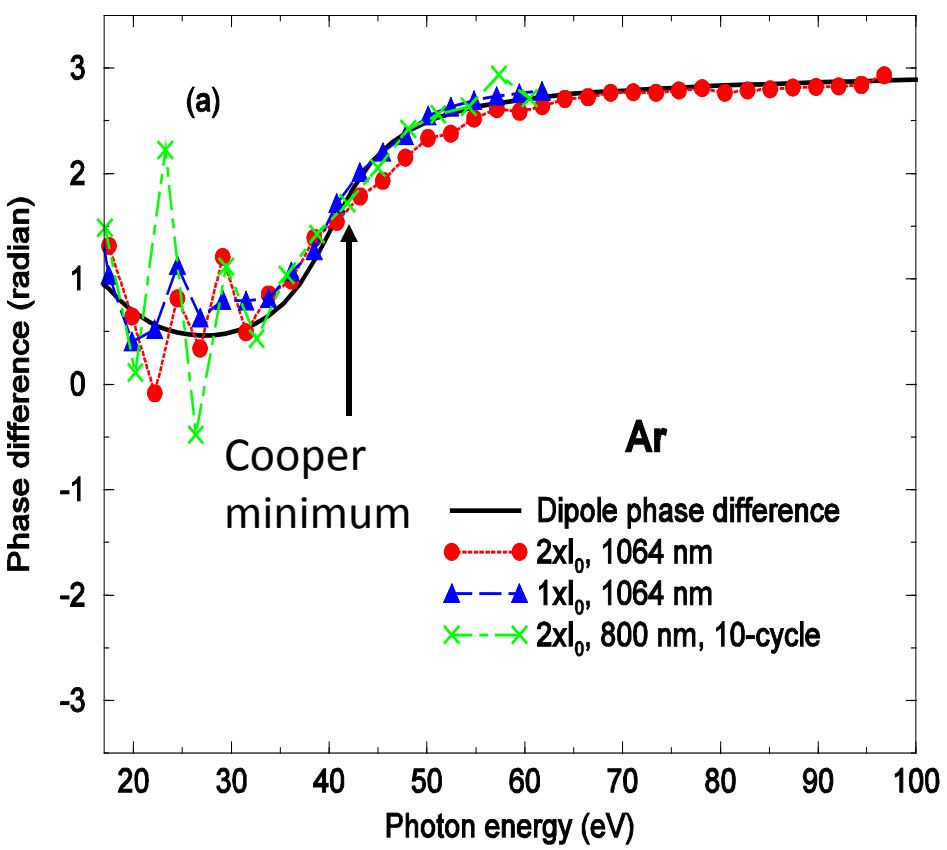
Extracted photo-recombination cross section & Phase

From TDSE

Cross section



Phase

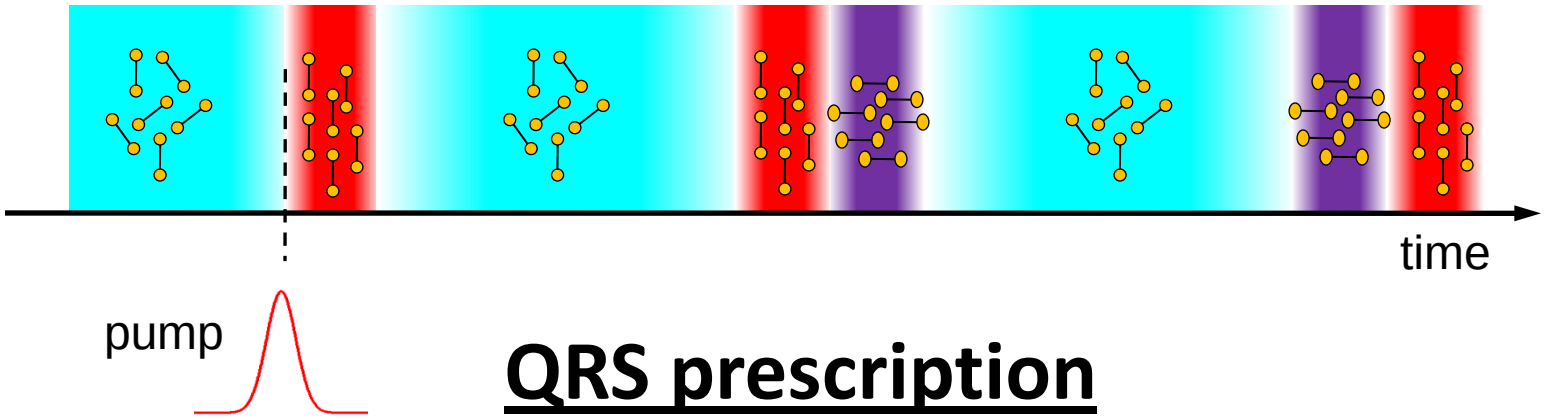


Differential photo-recombination cross section can be extracted with high accuracy!

Different lasers are used ($I_0=10^{14}$ W/cm^2)

QRS for HHG from **aligned molecules**

Impulsively aligning molecules with lasers – **probed at revival time**



QRS prescription

$$d(\omega,\theta) = N(\theta)W(\omega)e^{i\varphi^w}\sqrt{\sigma(k,\theta)}e^{i\phi(k,\theta)}$$

Tunneling rate MO-ADK

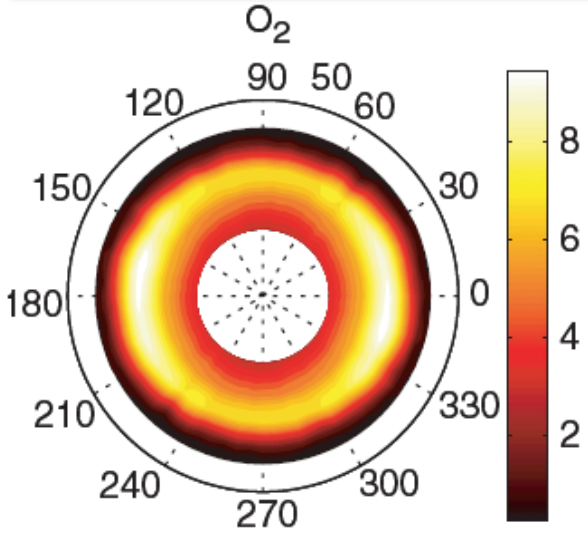
SFA2 or TDSE for atoms—independent of target

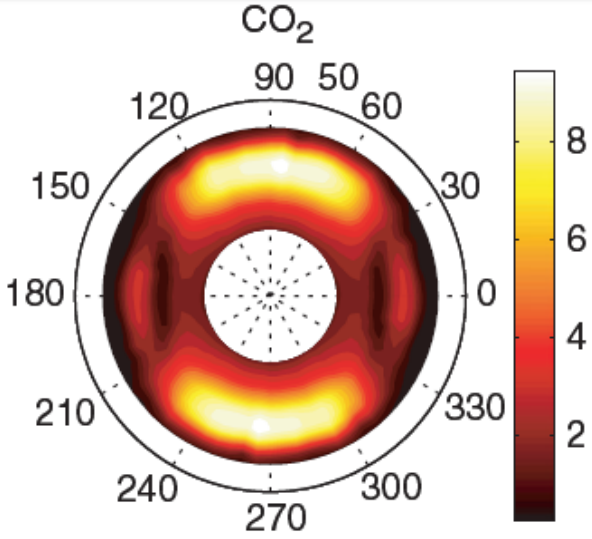
Photoionization code: From: Robert Lucchese

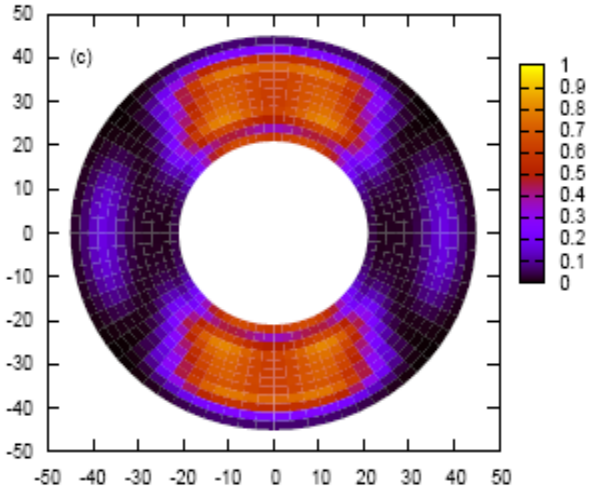
HHG spectra: O_2 vs CO_2

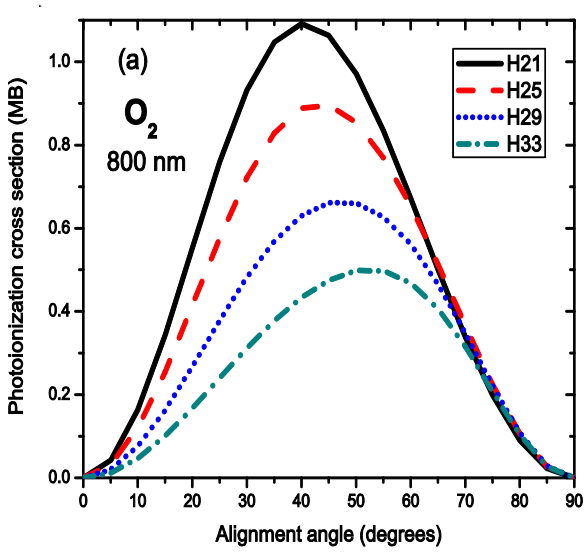
Experiment: Mairesse *et al, J. Mod. Optics* (2008)

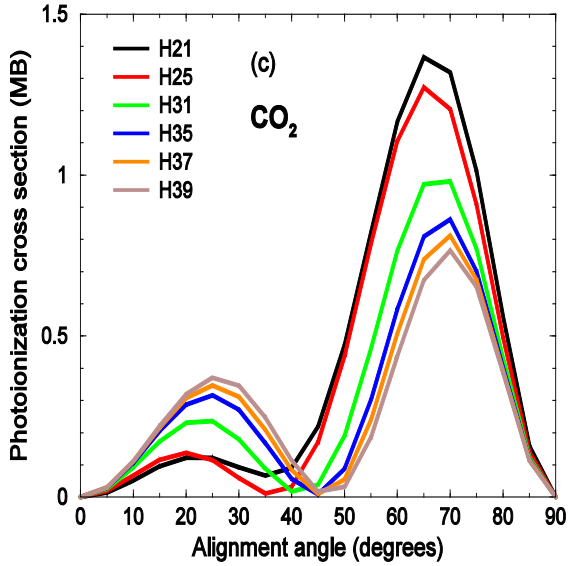
QRS











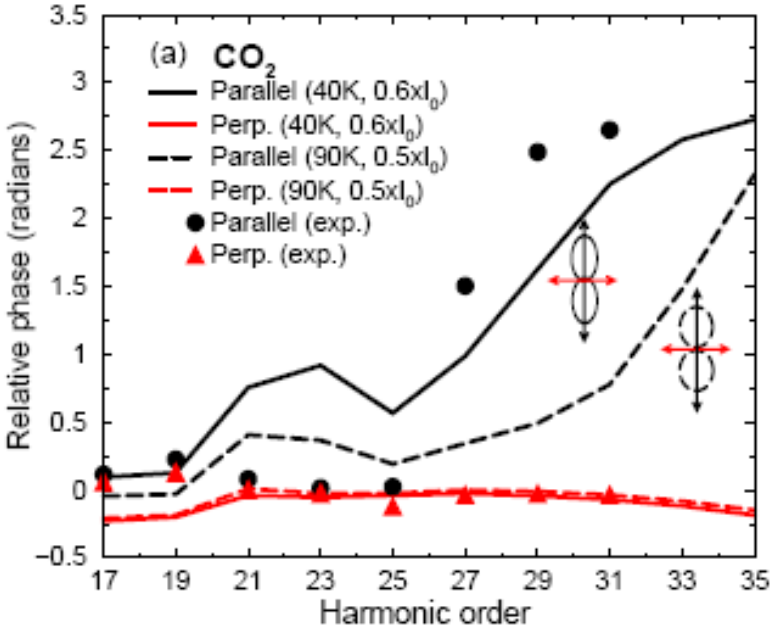
For Partially aligned molecules

Molecular frame photoionization angular distributions (MFPAD)

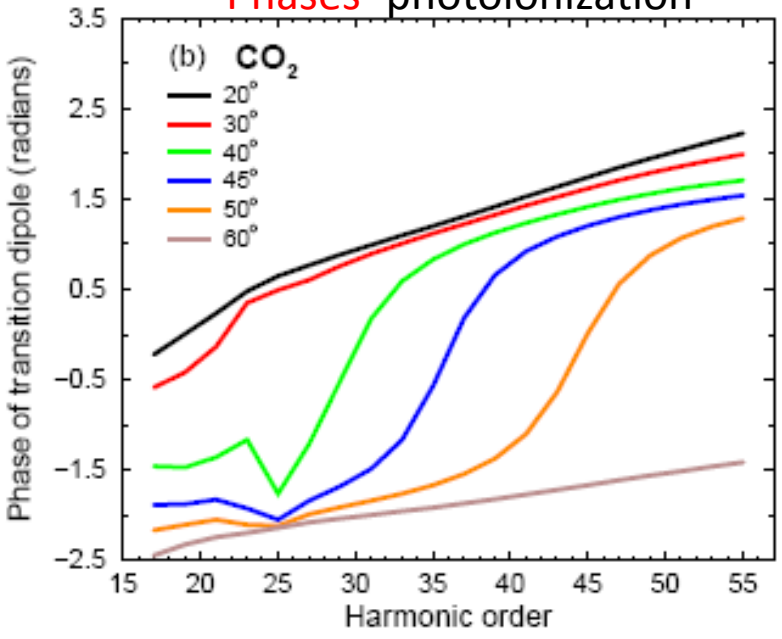
CO_2 HHG phases –mixed gas (+Kr) exp

Experiment: Boutu *et al*, *Nature Phys* **4**, 545 (2008)
Theory: QRS

Phases –HHG

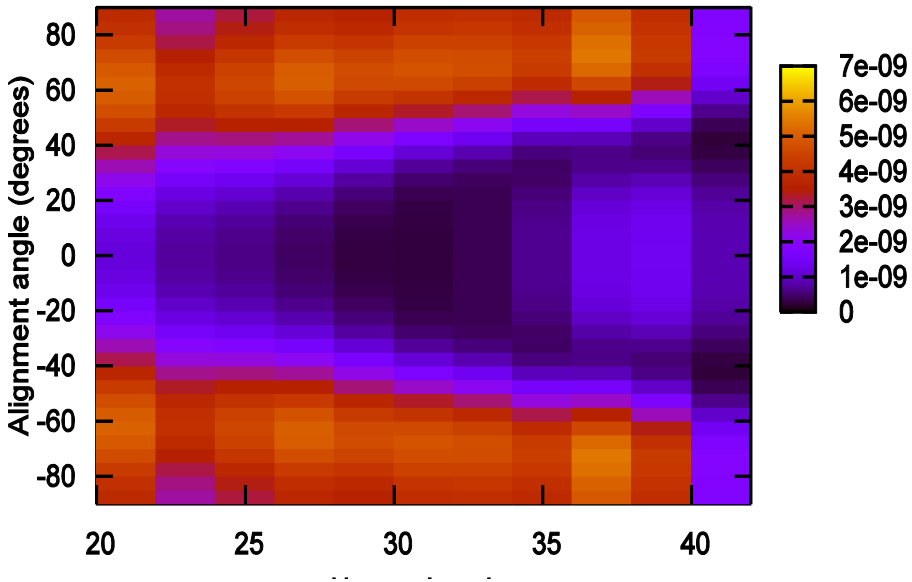


Phases -photoionization

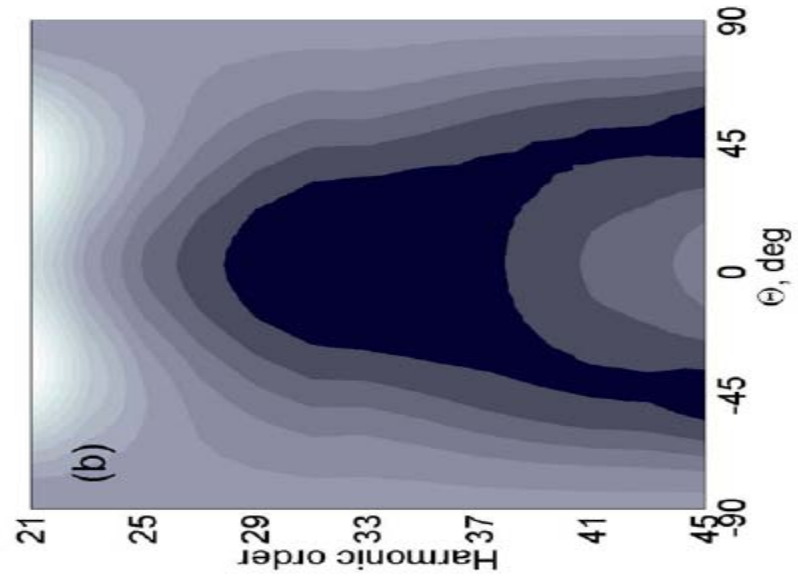


Phase jump is seen in the QRS, but not in the simpler models

HHG yield vs harmonic order & alignment angle

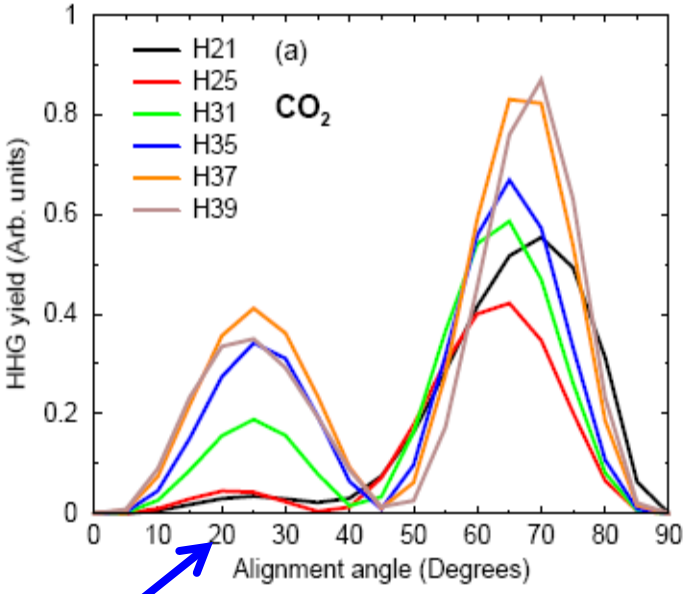


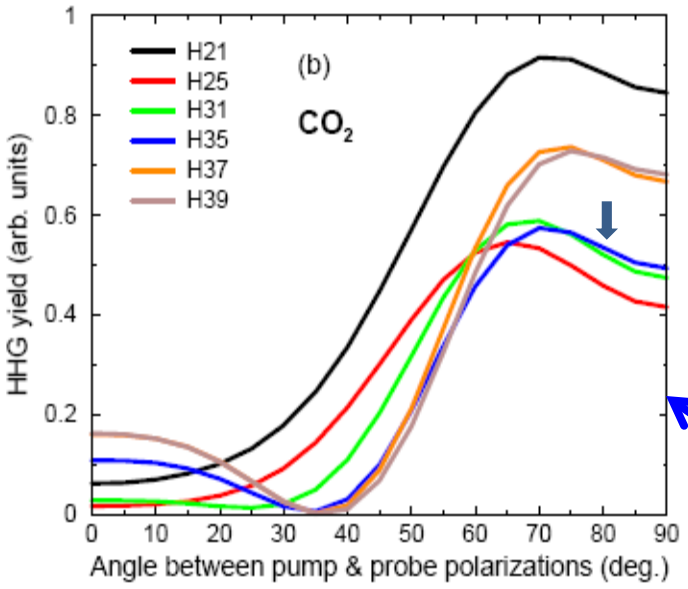
QRS



NRC:
Smirnova *et al*
PRL 2009

On the differences between theories

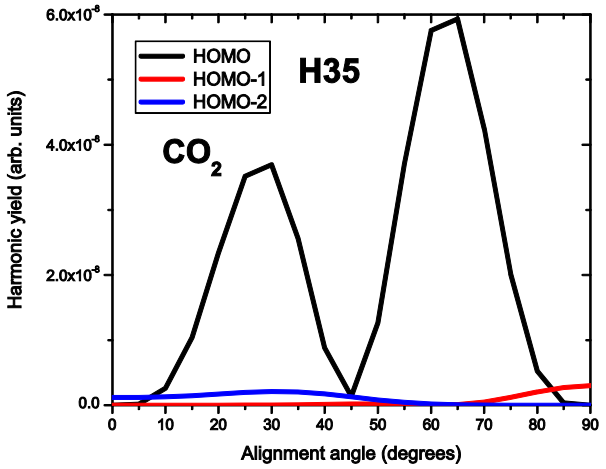


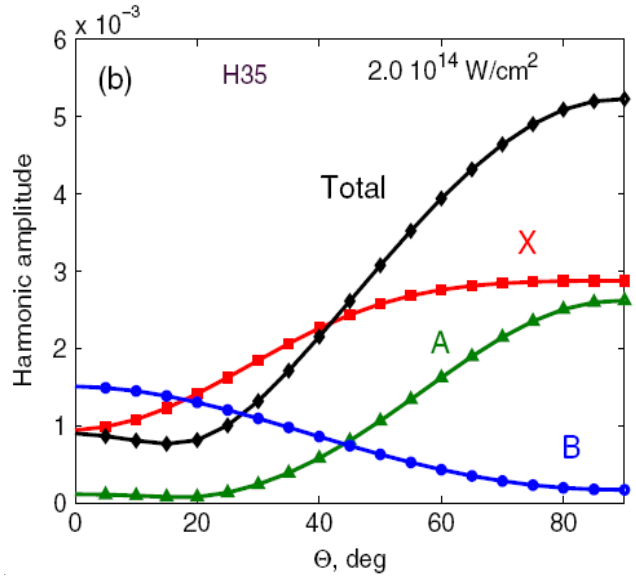


QRS

Partial alignment

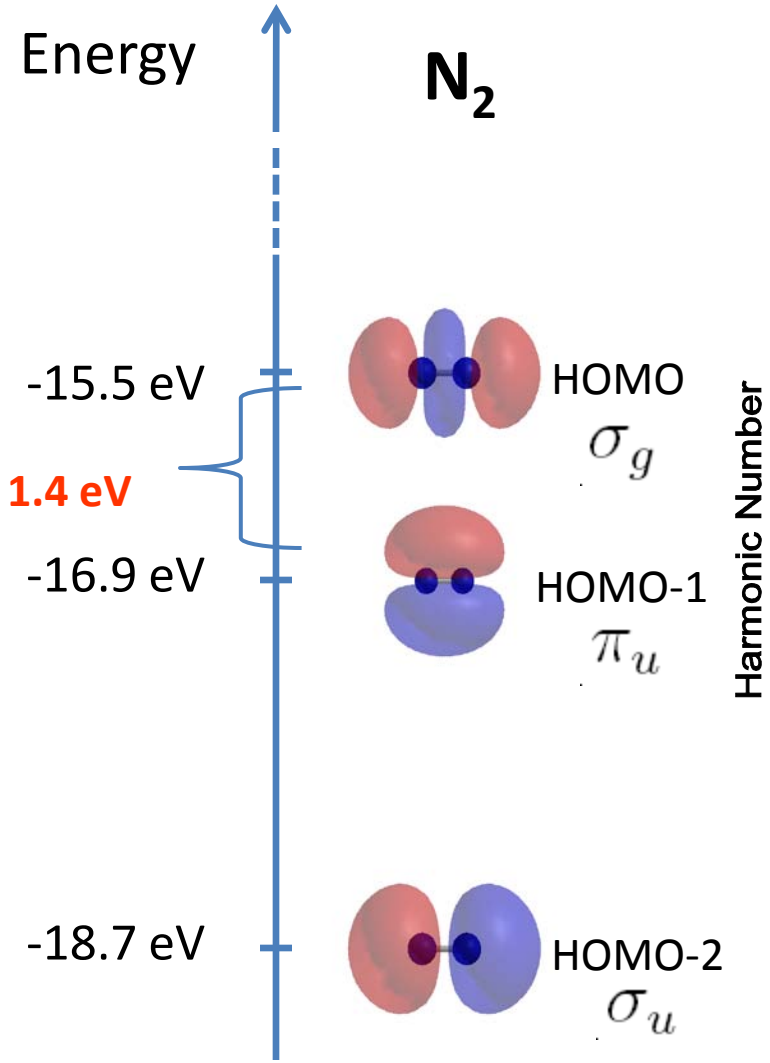
Fixed alignment



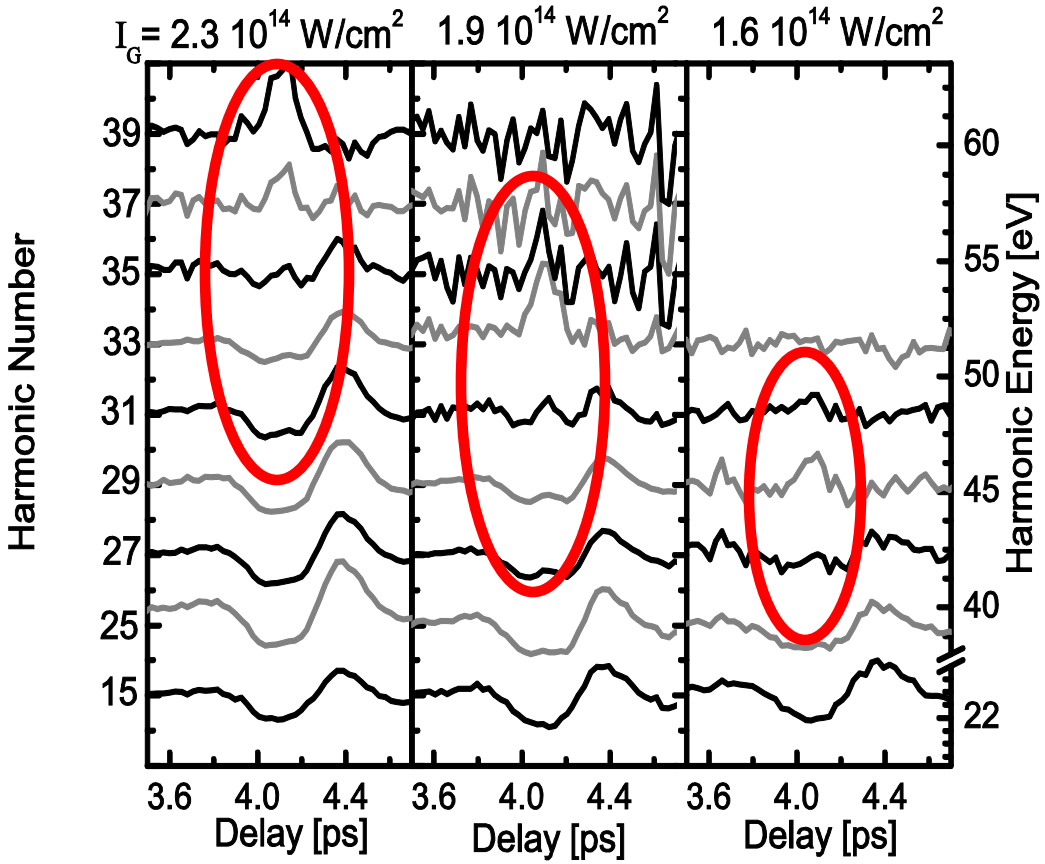


NRC: **H35**
Smirnova *et al*
PRL 2009

Influence of multiple orbitals



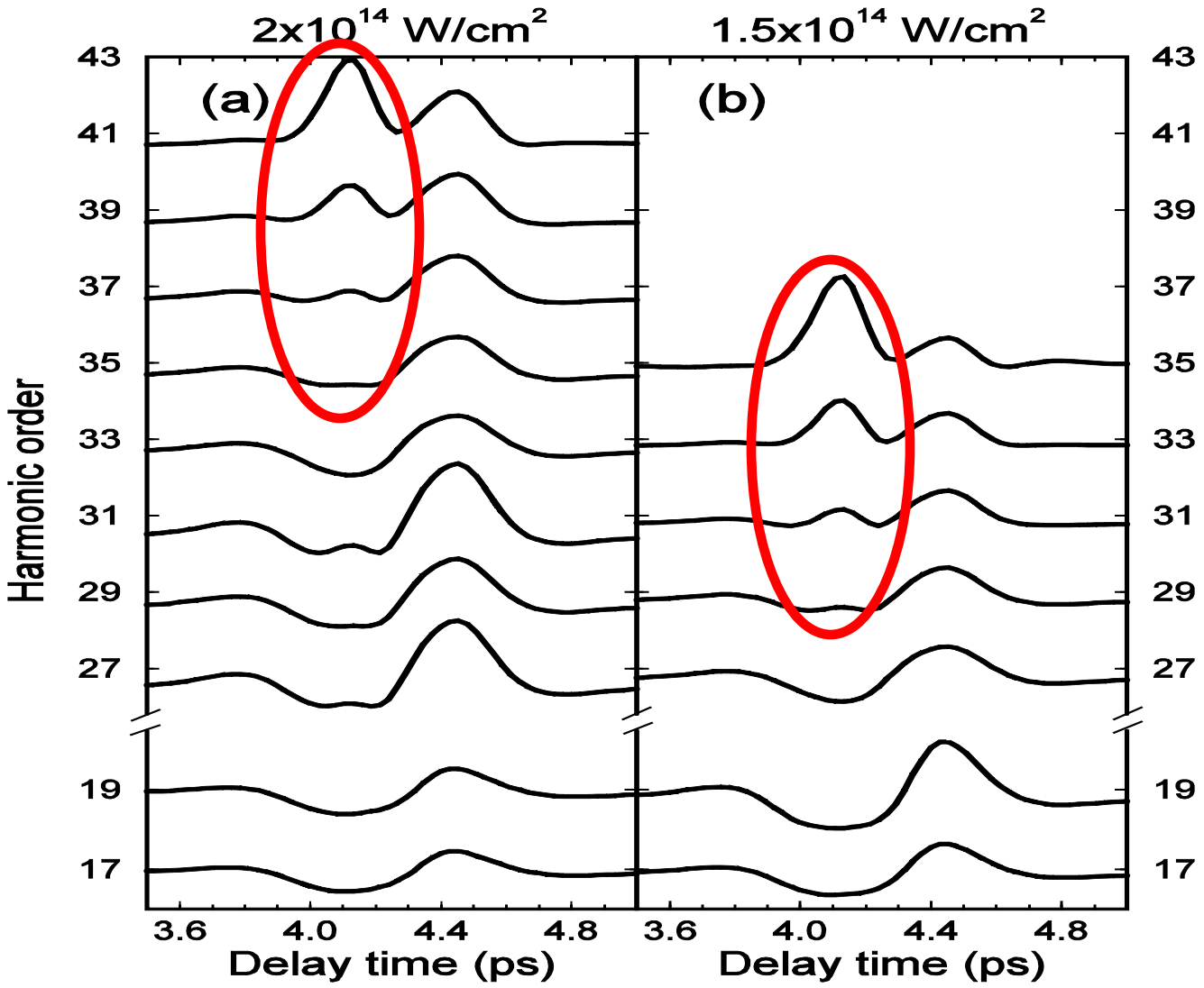
McFarland *et al*, Science (2008)



Pump ⊥ Probe

QRS

To appear-- JPB

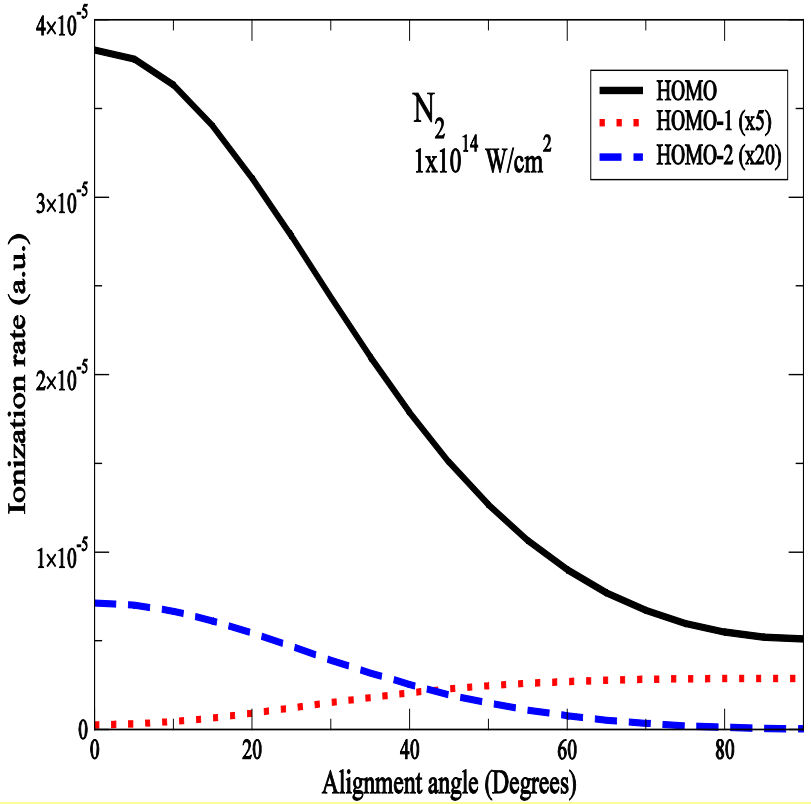


Ionization rates: Laser intensity dependence

HOMO: $3\sigma_g$, Ip=15.58 eV
HOMO-1 : $1\pi_u$, Ip=16.93 eV
HOMO-2: $2\sigma_u$, Ip=18.73 eV

Note factor of **5x** (in HOMO-1) and **20x** (in HOMO-2)

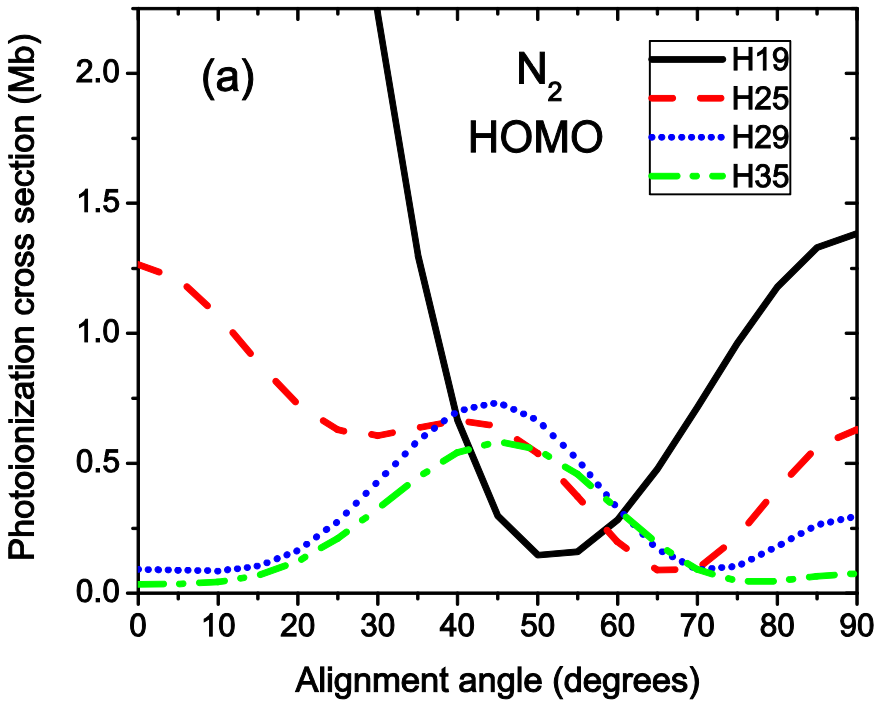
MO-ADK

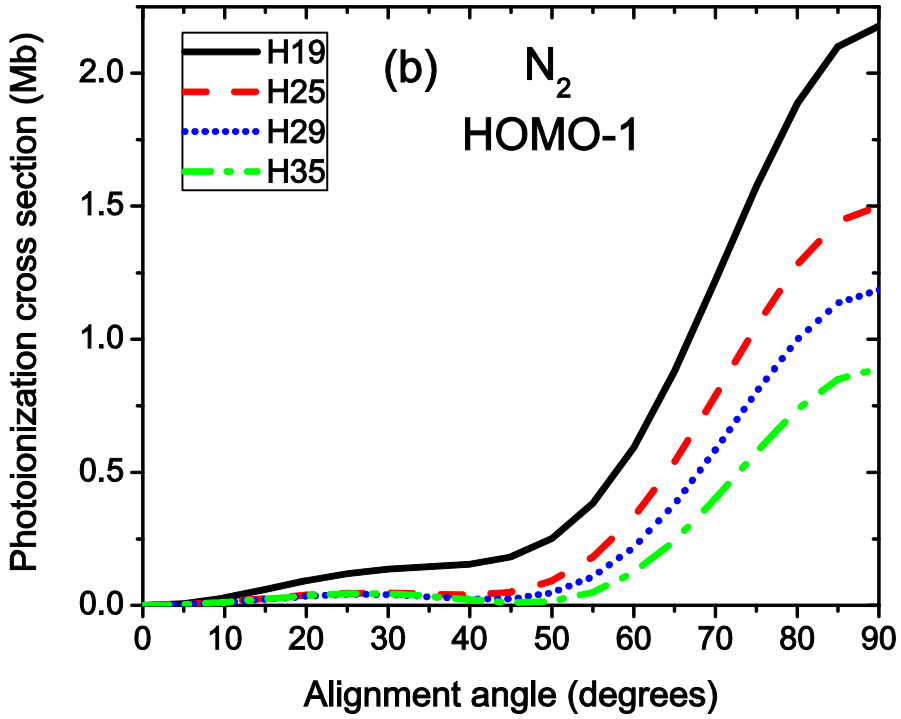


$$d(\omega,\theta) \sim N(\theta)W(\omega)e^{i\varphi^w(\theta)}\sqrt{\sigma(k,\theta)}e^{i\phi(k,\theta)}$$

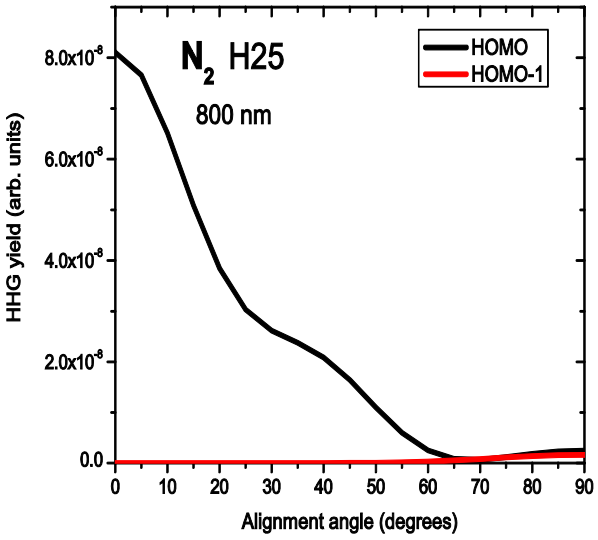
Photoionization cross sections:

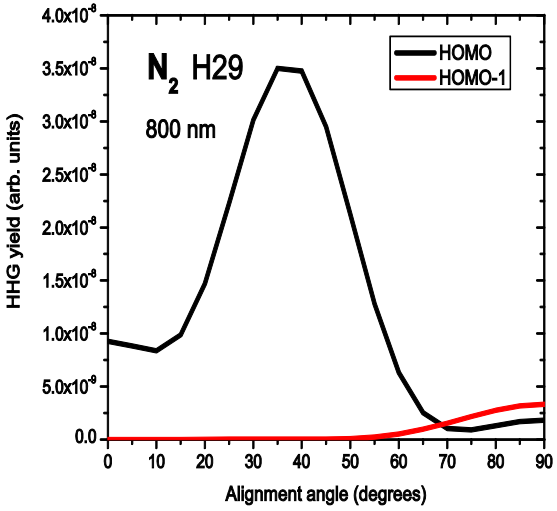
HOMO vs HOMO-1





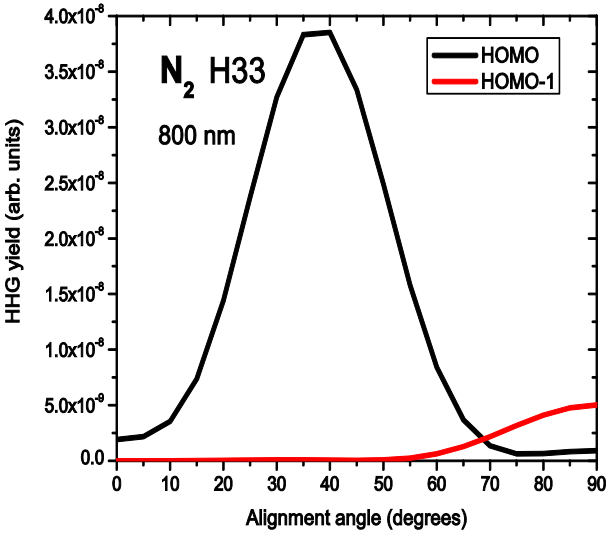
QRS: Contributions from HOMO vs HOMO-1

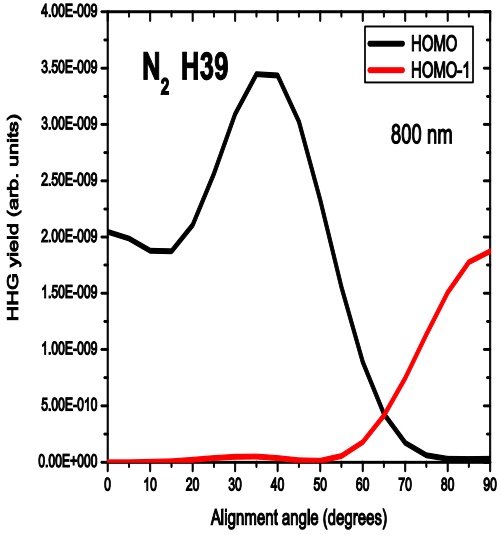




$2x10^{14}$ W/cm^2

Cut-off=**H35**





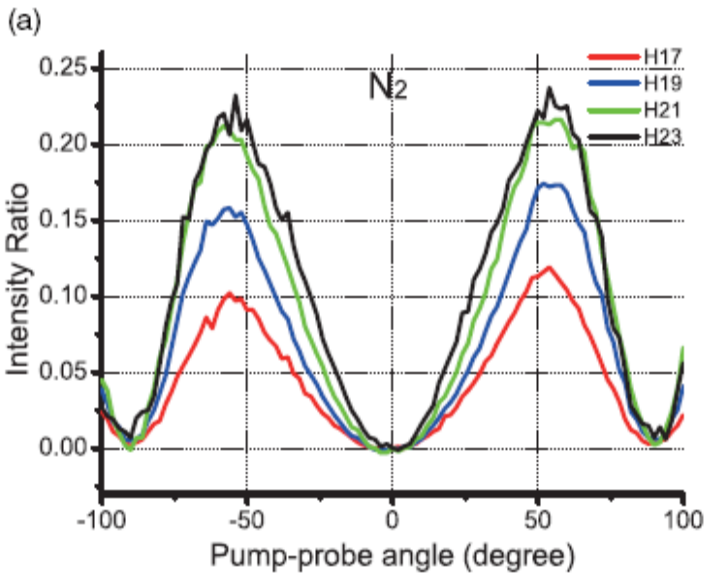
Ellipticity of the HHG from aligned N_2

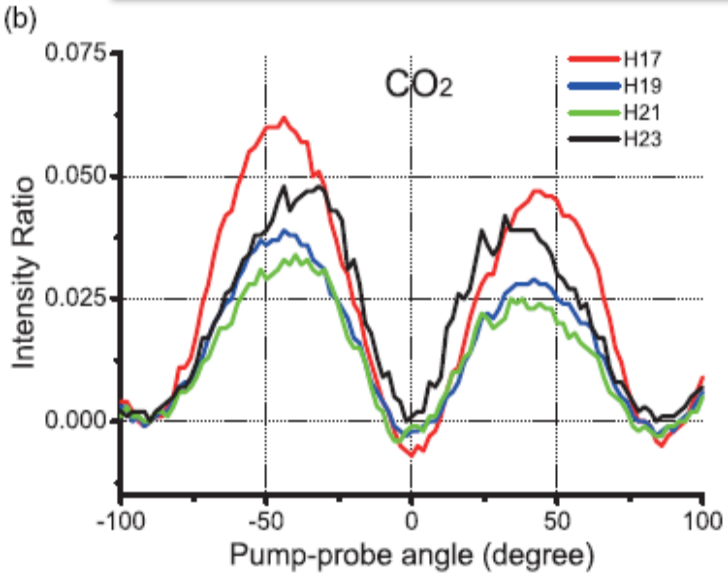
Intensity ratio=perp/parallel

JILA exp.: Zhou *et al*, PRL 2009

N2

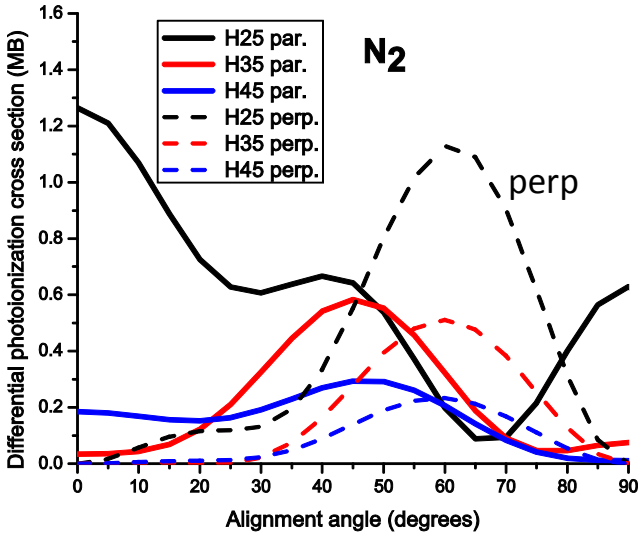
Exp.

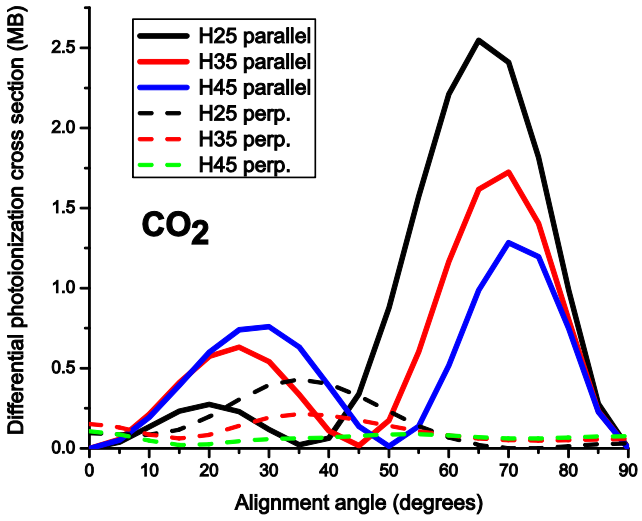




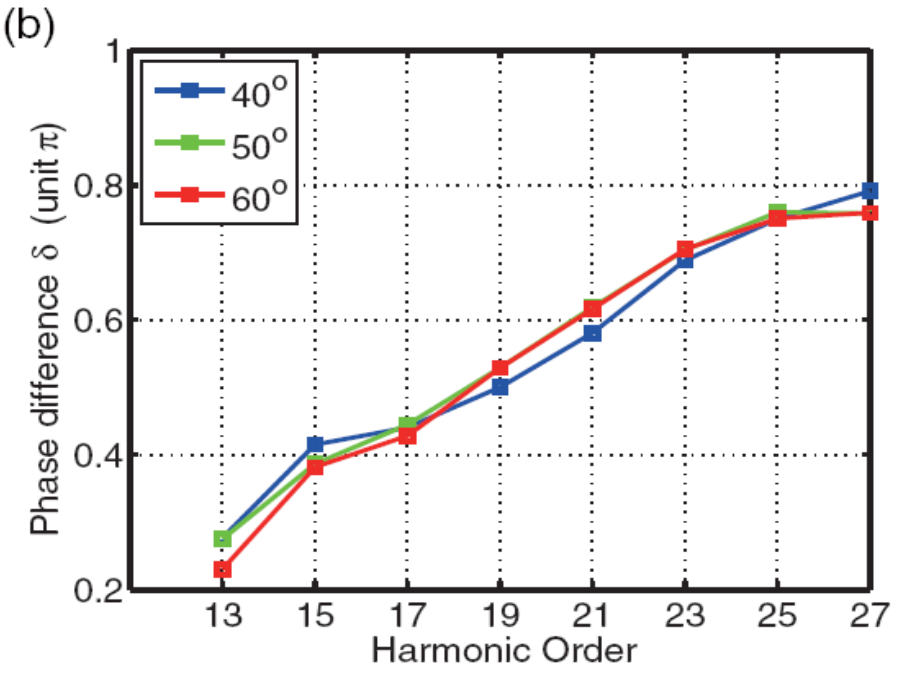
CO2

QRS

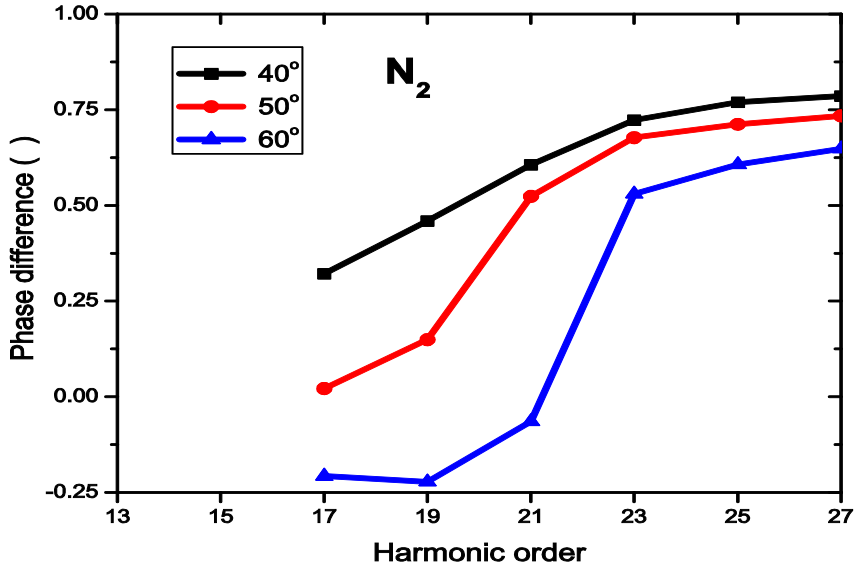




Cross section (Theory)



JILA exp.:
Zhou *et al*, PRL 2009



QRS
Fixed alignment
(**need to average over partial alignment** to compare with exp.)

Laser-induced electron diffraction – HATI electron spectra from molecules

First: Need electron-molecular ion DCS from aligned molecules

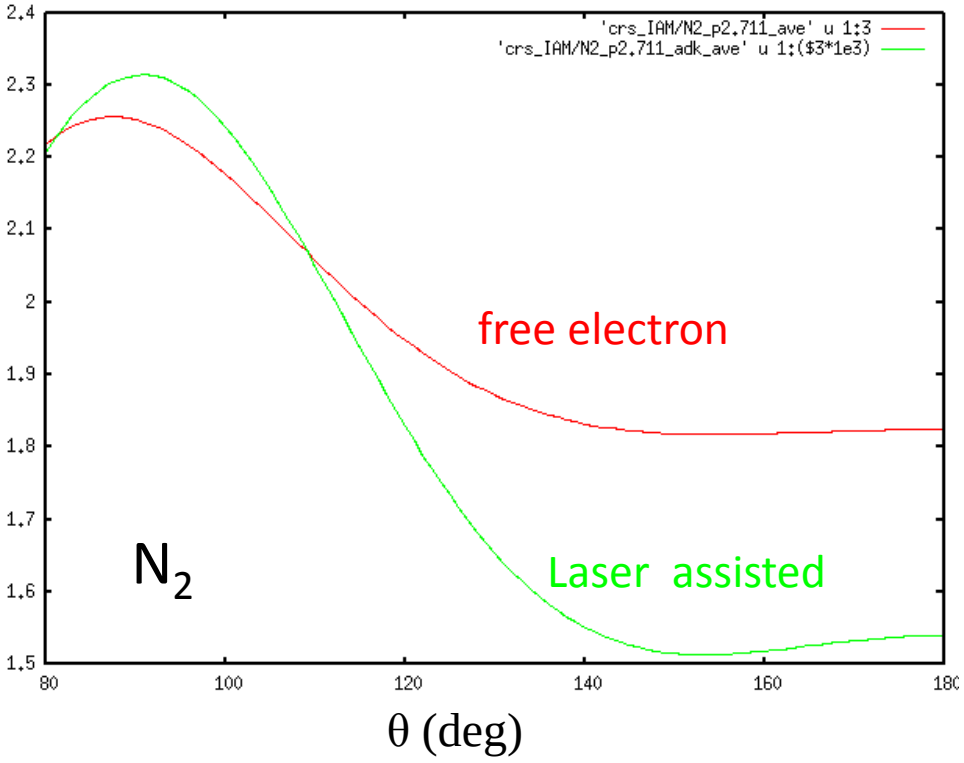
New!

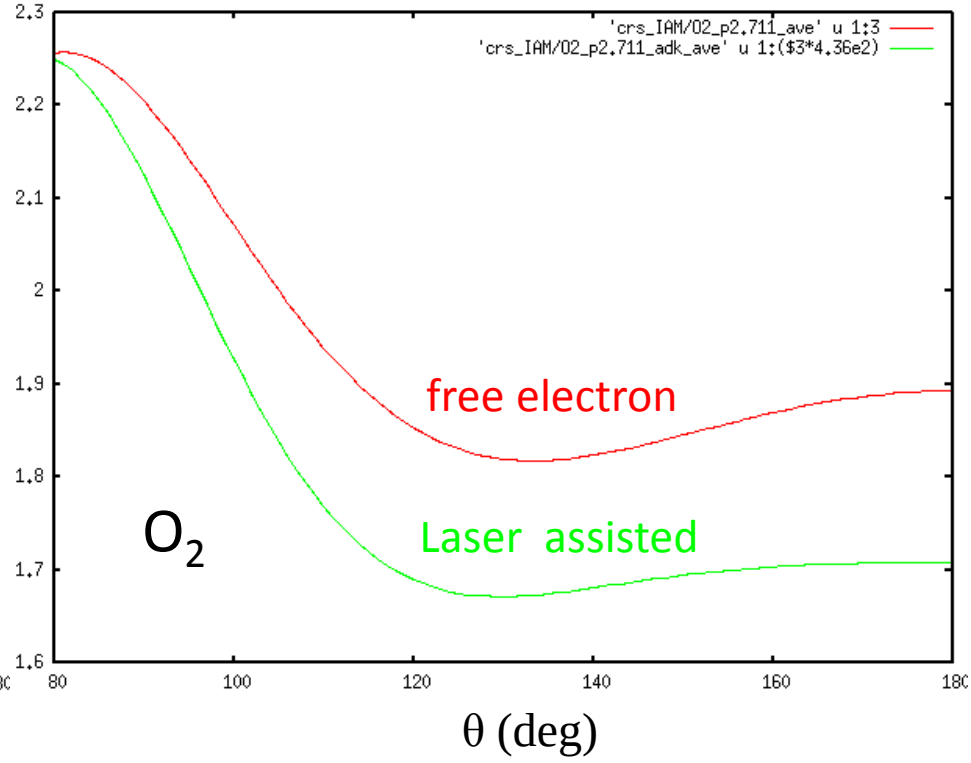
Simpler models used so far

DCS "extracted" from HATI for isotropic N2 and O2

Small differences between N2 and O2!

50 eV electrons





DCS vary strongly with Internuclear Distance: O_2

Sensitive variation with R !!

For Isotropic distributed molecules

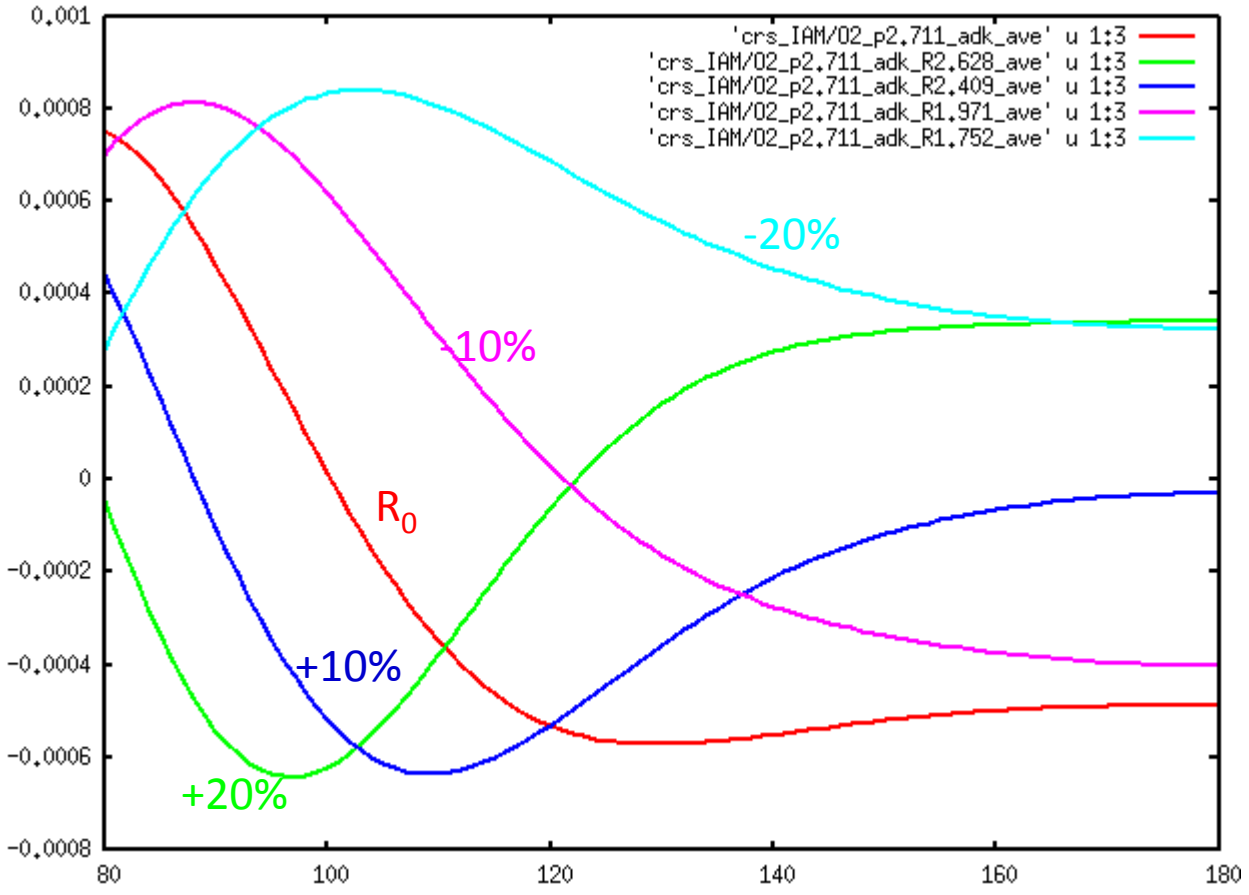
O_2: R_0=2.19 a.u.

+20%: R=2.628 a.u.

+10%: R=2.409 a.u.

-10%: R=1.971 a.u.

-20%: R=1.752 a.u.



Emission angle θ (deg)

Interference term *v.s.* Internuclear Distance: N_2

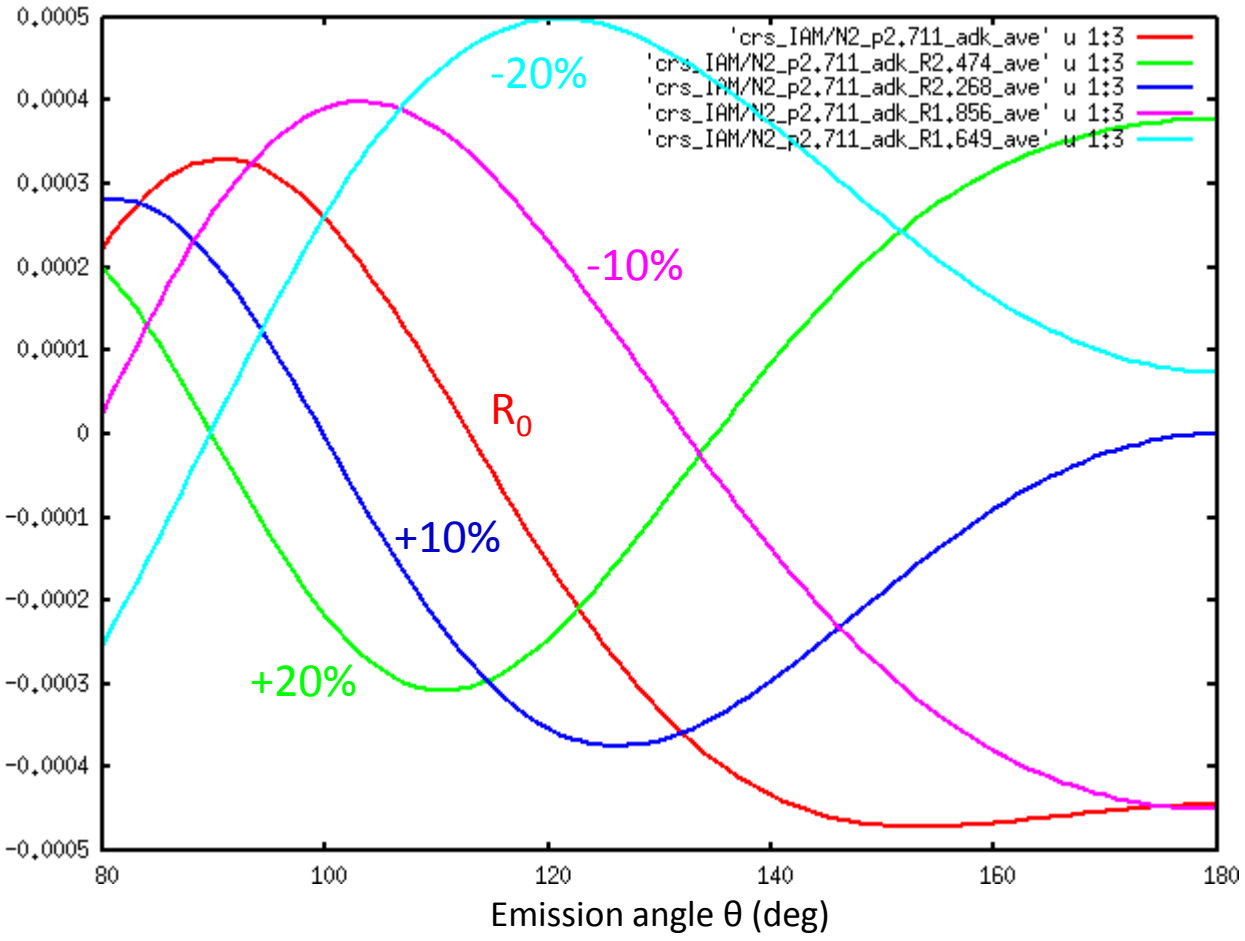
N_2: R_0=2.062 a.u.

+20%: R=2.474 a.u.

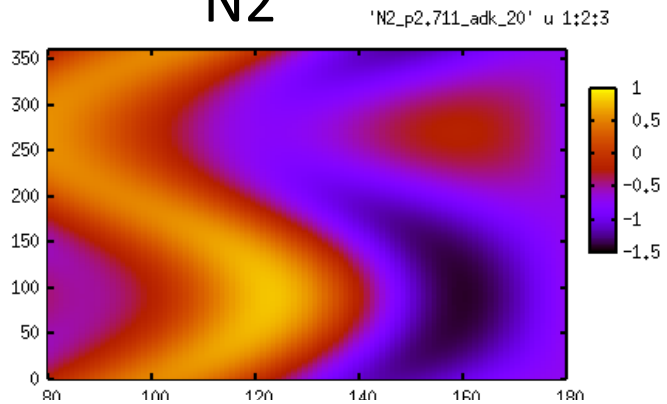
+10%: R=2.268 a.u.

-10%: R=1.856 a.u.

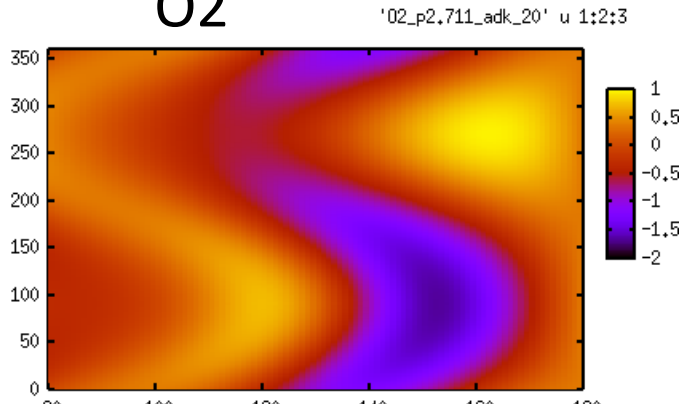
-20%: R=1.649 a.u.



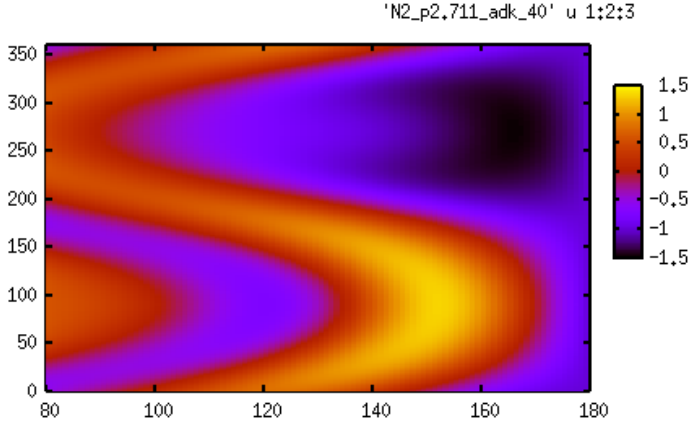
N2

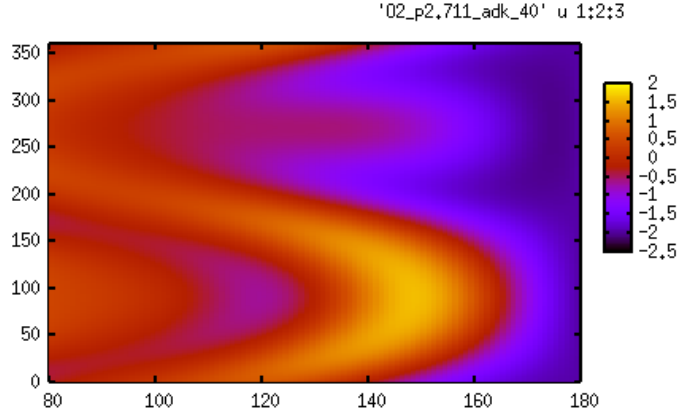


O2

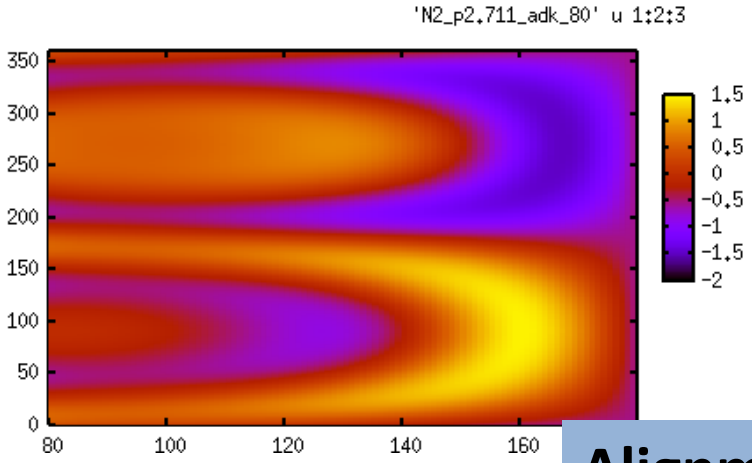


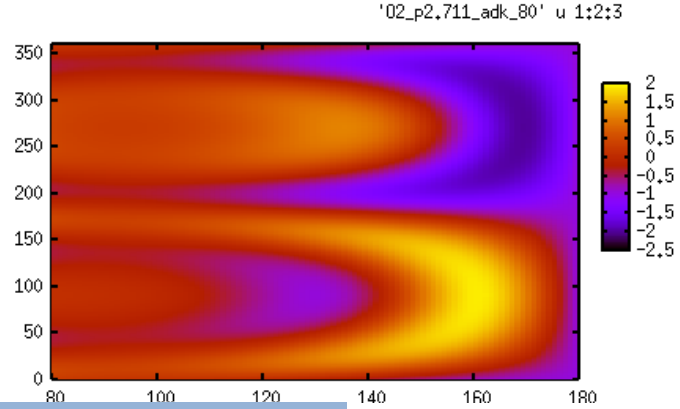
20 deg





40



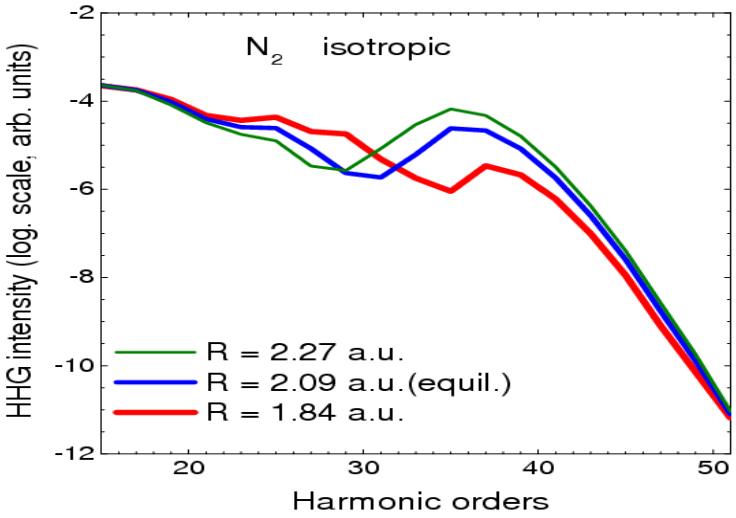


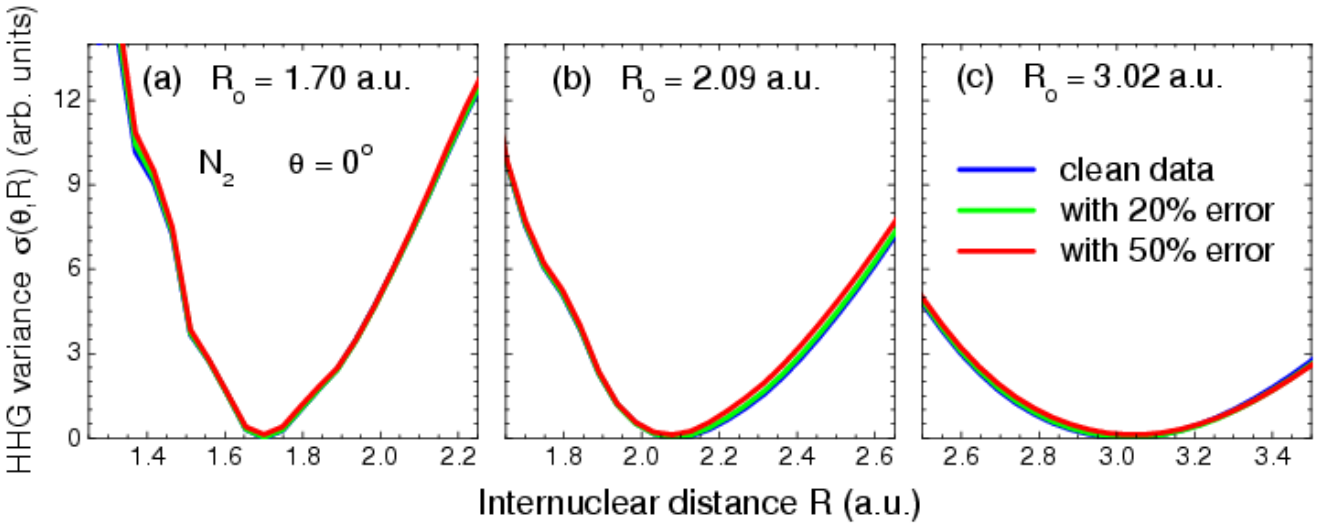
80

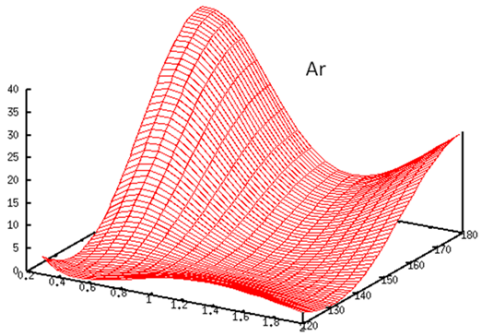
Alignment dependence

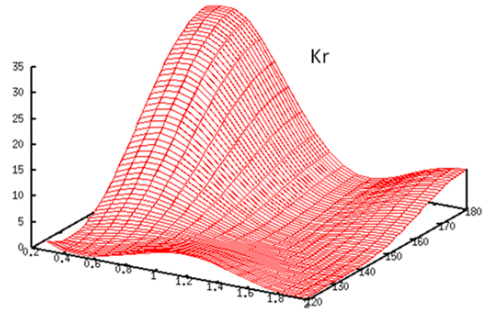
Simple examples of **structure retrieval** from **HHG** and from **HATI**

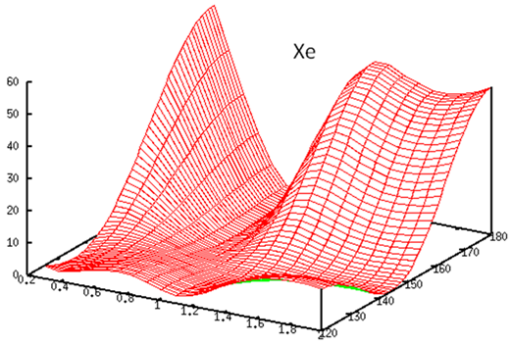
HHG depends on R's for non-aligned molecules





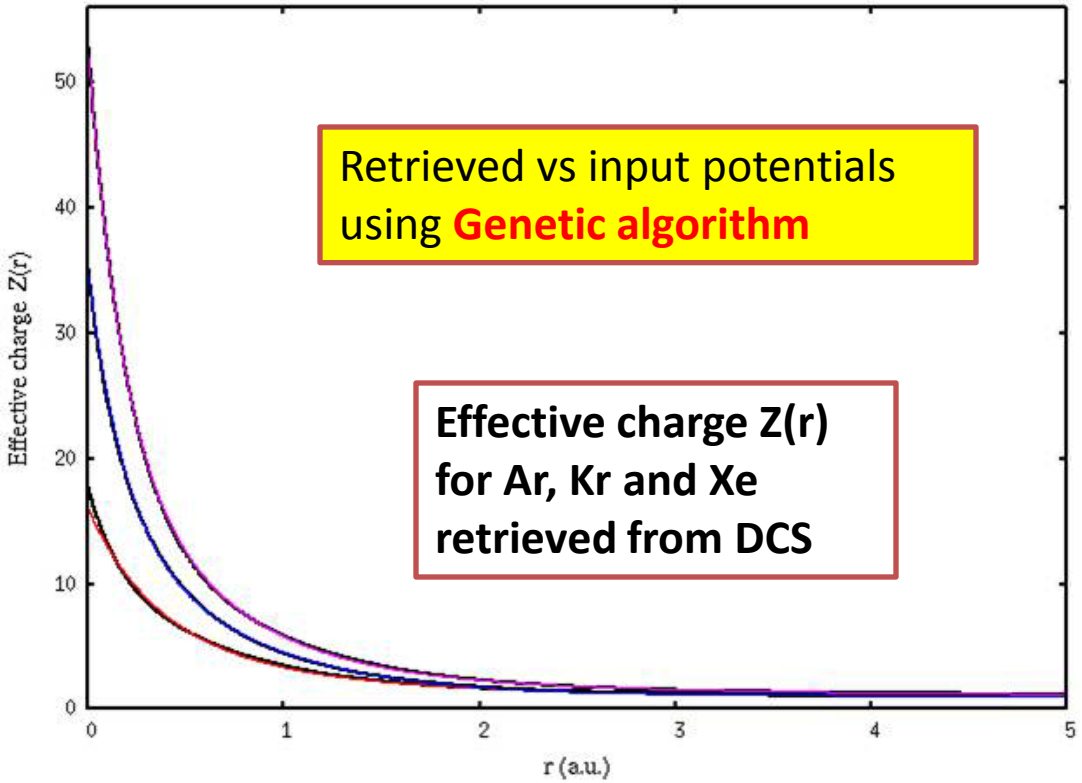






Retrieving atomic potential from elastic differential scattering cross sections

$$V(r) = -Z(r)/r$$



Retrieved vs input potentials using **Genetic algorithm**

Effective charge Z(r) for Ar, Kr and Xe retrieved from DCS

Summary and Comments:

1. **Based on QRS, DCS and PICS can be retrieved from HATI and HHG.**

2. **Electron diffraction is sensitive to the electron density –good for positions of atoms (bond length and bond angles) in the molecule**
3. **Light atoms in the molecules are harder to "see".**
4. **Can use lasers of different wavelengths and intensities to extract laser-independent DCS.**
5. **Electron diffraction is less sensitive to molecular bonds, and electronic states are preferably retrieved from HHG**

NEXT:

Generalize to dynamic systems– wave packet,….

Experimental data are needed

•Goal of dynamic imaging of molecules---

• DCS to retrieve bond angles and bond lengths

• HHG to retrieve electronic states (XFEL's cannot probe chemical bonds)

•Robust retrieval methods yet to be developed

• **Tomography is not endorsed !**

References on QRS –

First paper: 2008 PRL

QRS for HATI: Chen et al Phys. Rev. A. 79, 033409 (2009). 20 pages

QRS for HHG: Le et al Phys. Rev. A80, 013401 (2009). 20 pages

16 other papers on QRS in 2008-9
Including applications to NSDI and laser retrieval

A topical review will appear in the first half of 2010 in J phys B