Modelling strong-field processes in real* molecules

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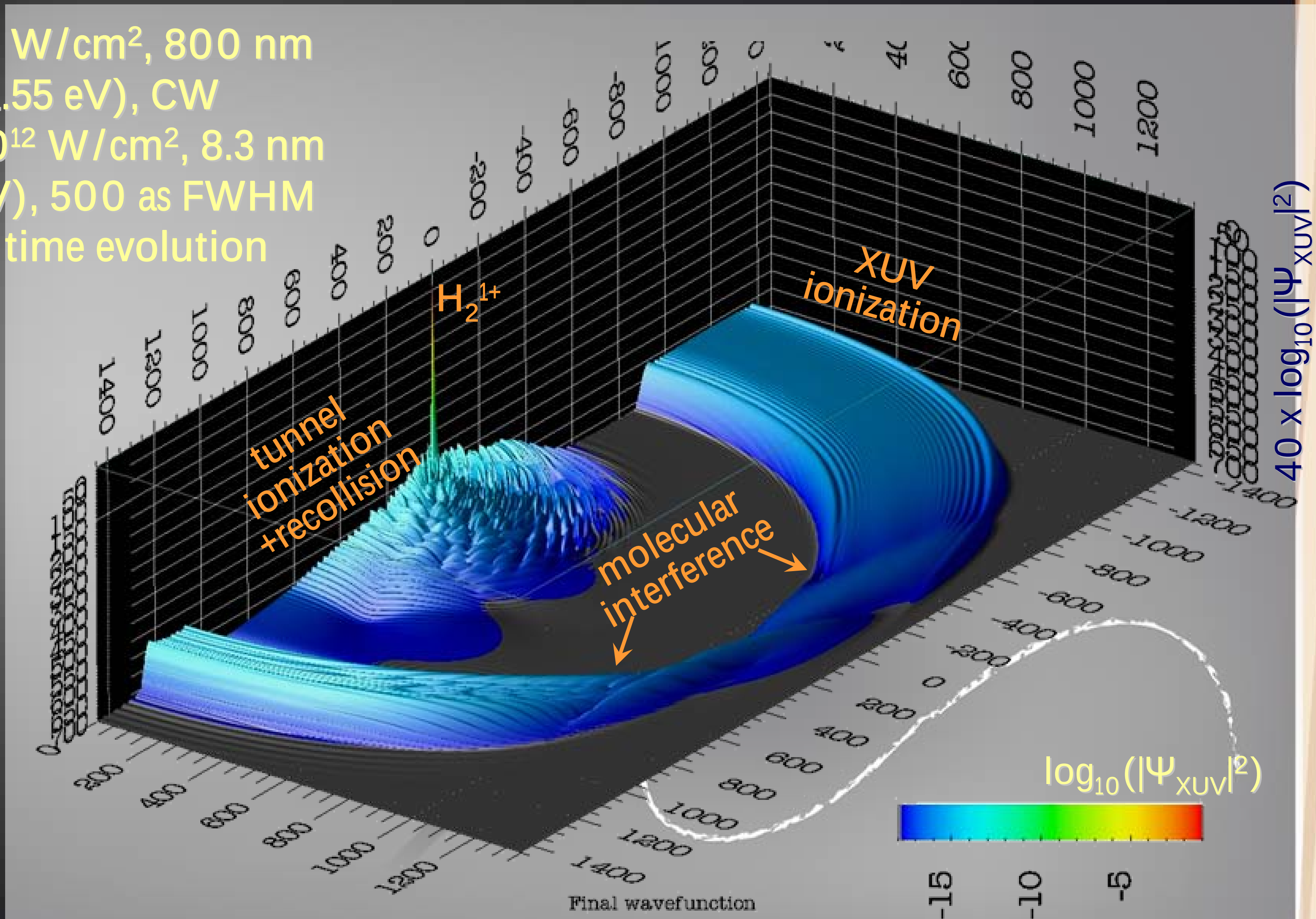
*: the available reality quotient may vary

National Research Council Canada
Conseil national de recherches Canada
Canada

Bart Simpson, "Skinner's Sense of Snow" (2000)

Strong field example: H_2^+ in a two-colour field

IR: 10^{13} W/cm², 800 nm
(1.55 eV), CW
XUV: 10^{12} W/cm², 8.3 nm
(150 eV), 500 as FWHM
13 fs time evolution



Watching many-electron molecules in strong fields: The Spanner Approach

- The “active” electron undergoes large-amplitude motion
  - grid-based techniques are indicated
- Remaining (n-1)-electrons remain in the vicinity of the nuclei
  - Localized basis sets are best
- Correlations are:
  - important for the bound electrons
  - may be important between bound and continuum electrons
  - Unimportant (?) between the continuum electrons

Anti-symmetry is overrated
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Dealing with the antisymmetry

$$|\Psi(t)\rangle = \hat{A}\,|\Psi_p(t)\rangle$$

n-electron w.f. antisymmetric in all coordinates

"proxy" w.f. antisymmetric in first (n-1) coordinates

$$\hat{A} = \frac{1}{\sqrt{n}}\left(1 - \sum_{j=1}^{n-1} \hat{P}_{jn}\right)$$ ← antisymmetrizer

$$\hat{U}(t,t_0)\,|\Psi(t_0)\rangle = \hat{U}(t,t_0)\,\hat{A}\,|\Psi_p(t)\rangle$$

$$= \hat{A}\,\hat{U}(t,t_0)\,|\Psi_p(t)\rangle$$

↑ time evolution operator

$$i\frac{\partial}{\partial t}\hat{U}(t,t_0) = \hat{H}(t)\,\hat{U}(t,t_0)\,, \quad \hat{U}(t,t_0) = \hat{I}$$

If propagating the proxy is easier, we win!

Spanner wavefunction Ansatz

Anti-symmetric — NOT anti-symmetric

$$|\Psi_p(t)\rangle = b(t)|\tilde{N}\rangle + \sum_m{}' \left[a_m(t)|S_m\rangle + |X_m(t)\rangle\right]$$

(n-1)-electron cation eigenstate

$$|S_m\rangle = |\tilde{\phi}^S_m\rangle|I_m\rangle$$

normalized "spanner" orbital

$$|\phi^S_m\rangle = \langle I_m|N\rangle$$

Represented on grid

$$|X_m\rangle = |X_m(t)\rangle|I_m\rangle$$

excited/continuum part of n-th electron

$$|\tilde{N}\rangle = N_{\tilde{N}}\left(\hat{I} - \sum_m{}' \hat{P}^S_m\right)|N\rangle$$

neutral ground state

part of the neutral orthogonal to all ions

$$\hat{P}^{\tilde{N}}|\Psi_p(t)\rangle = b(t)|\tilde{N}\rangle$$

$$\hat{P}^S_m|\Psi_p(t)\rangle = a_m(t)|S_m\rangle$$

$$\hat{P}^X_m|\Psi_p(t)\rangle = |X_m(t)|S_m\rangle$$

Spanner & Patchkovskii, PRA 80, 083411 (2009); Note similarities to the R-matrix Ansatz

Spanner propagator: Multi-channel

$$|\Psi_p(t)\rangle = b(t)|\tilde{N}\rangle + \sum_m{}' \left[a_m(t)|S_m\rangle + |X_m(t)\rangle \right]$$

$$i\frac{\partial}{\partial t} b(t) = \langle \tilde{N}| H^F(t) |\tilde{N}\rangle b(t) + \sum_k{}' \langle \tilde{N}| H^F(t) |S_k\rangle a_k(t) + \sum_k{}' \langle \tilde{N}| H^F(t) |X_k(t)\rangle$$

$$i\frac{\partial}{\partial t} a_m(t) = \langle S_m| H^F(t) |\tilde{N}\rangle b(t) + \sum_k{}' \langle S_m| H^F(t) |S_k\rangle a_k(t) + \sum_k \langle S_m| H^F(t) |X_k(t)\rangle$$

$$i\frac{\partial}{\partial t} |X_m(t)\rangle = \hat{R}^S_m \langle \mathcal{I}_m| H^F(t) |\tilde{N}\rangle b(t) + \sum_m \hat{R}^S_m \langle \mathcal{I}_m| H^F(t) |S_k\rangle a_k(t) + \sum_k \hat{R}^S_m \langle \mathcal{I}_m| H^F(t) |X_k\rangle$$

$$\hat{R}^S_m = \left(1 - |\tilde{\Phi}^S_m\rangle\langle \Phi^S_m|\right)$$

Source: Spanner & Patchkovskii, PRA 80, 083411 (2009)

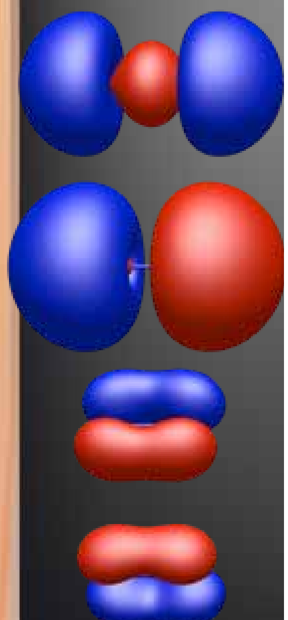
Ingredients of the Spanner propagator

- State energies (neutral & ions)
- Dipole and transition moments
- Dyson and "craddle" orbitals
- Multiplicative ion core potentials
- Transition potentials

Directly from MCSCF/MCQDPT2 (state energies; dipole and transition moments)

Postprocessing of MCSCF wavefunctions (Dyson and "craddle" orbitals)

From 1-RDMs; post-processing of MCSCF wfs. (multiplicative ion core potentials; transition potentials)

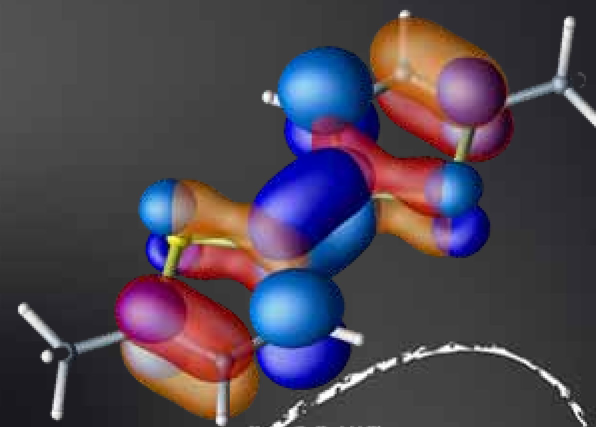


$$\varphi_i^{D} \sim \langle I_i | N \rangle$$

$$\varphi_i^{C,z} \sim \langle I_i | \sum_{k=1}^{n-1} z_k | N \rangle$$

- · ···

$$N_2^+(X^2\Sigma_g^+) \leftarrow N(X^1\Sigma_g^+)$$



Singular-value decomposition of transition 1-rdm of S_1<-S_0 in bis-thiophene

$$\rho^{ab}(r_1, r_1') = N \int \Psi_a^*(r_1 \ldots r_N) \Psi_b(r_1' \ldots r_N) \, dr_2 \ldots dr_N$$

The Strong Field Approximation has so many drawbacks and “wrongs” that fly into the face of any rigorous quantum theory that it is amazing it was published …

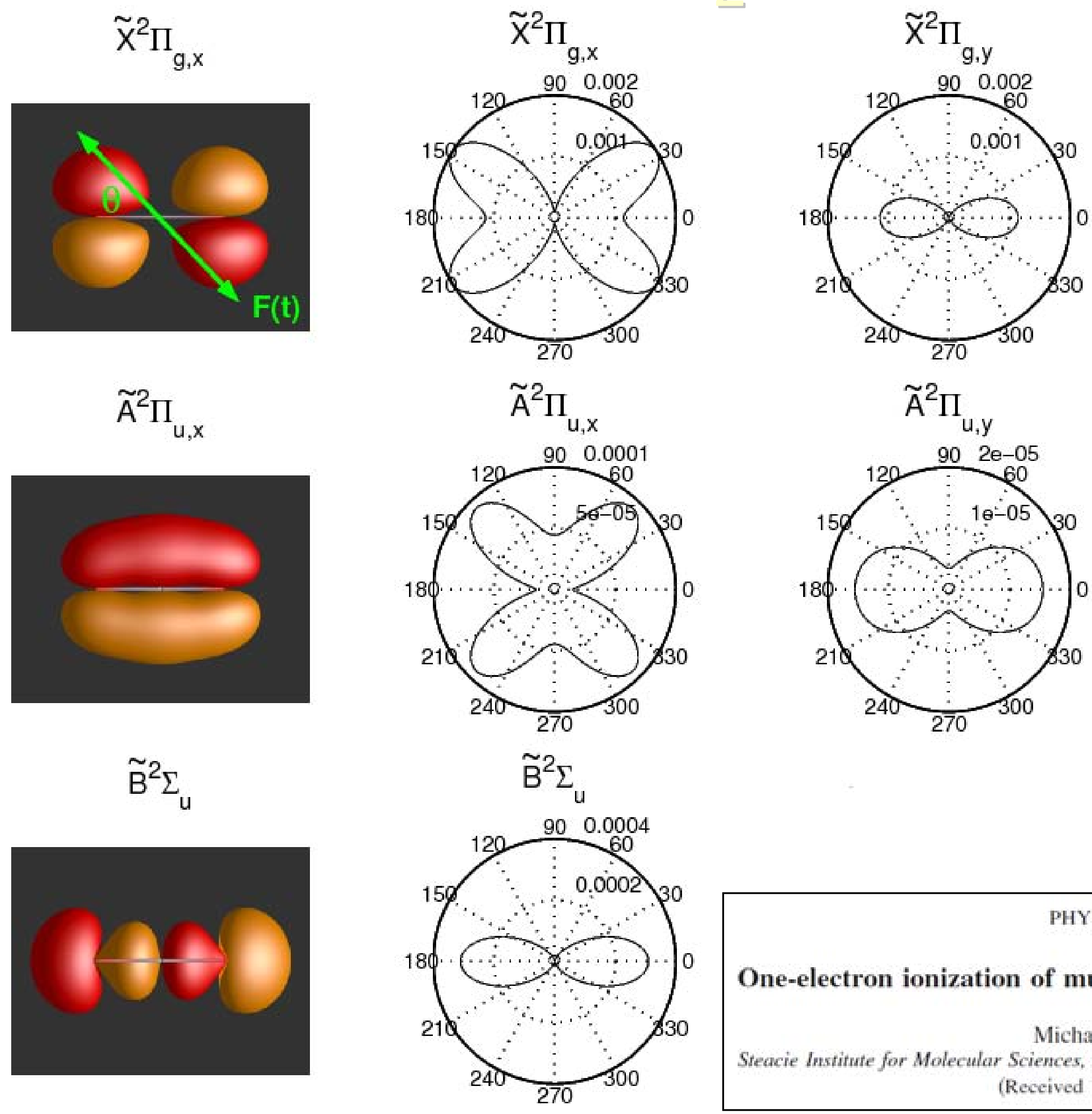
M. Yu Ivanov, Lecture notes on Strong Field Approximation

Some numerical examples

- Ionization in strong fields
  - Small molecules: CO_2; CO; HCl
  - N_2O_4
  - n-C_4H_{10}, 1-C_4H_8, C_4H_6
- High harmonics in molecules
  - Structural minimum: The case of peripatetic immovable object

ALL RESULTS ARE PRELIMINARY

CO_2 Ionization



Ionization rosettes are: Total ionization yield for laser polarization at angle θ from the molecular axis

Single-cycle pulse
800 nm
$1.5*10^{14}$ W/cm^2

PHYSICAL REVIEW A **80**, 063411 (2009)

One-electron ionization of multielectron systems in strong nonresonant laser fields

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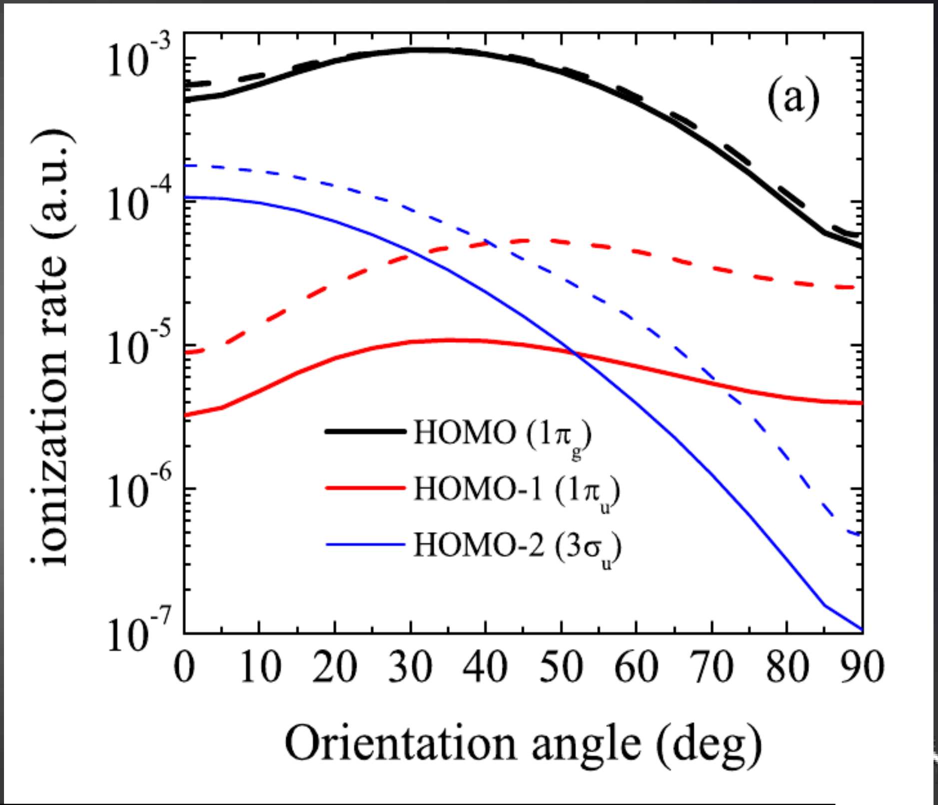
(Received 1 August 2009; published 7 December 2009)

CO_2 Ionization

CO_2

Present method

MO-ADK



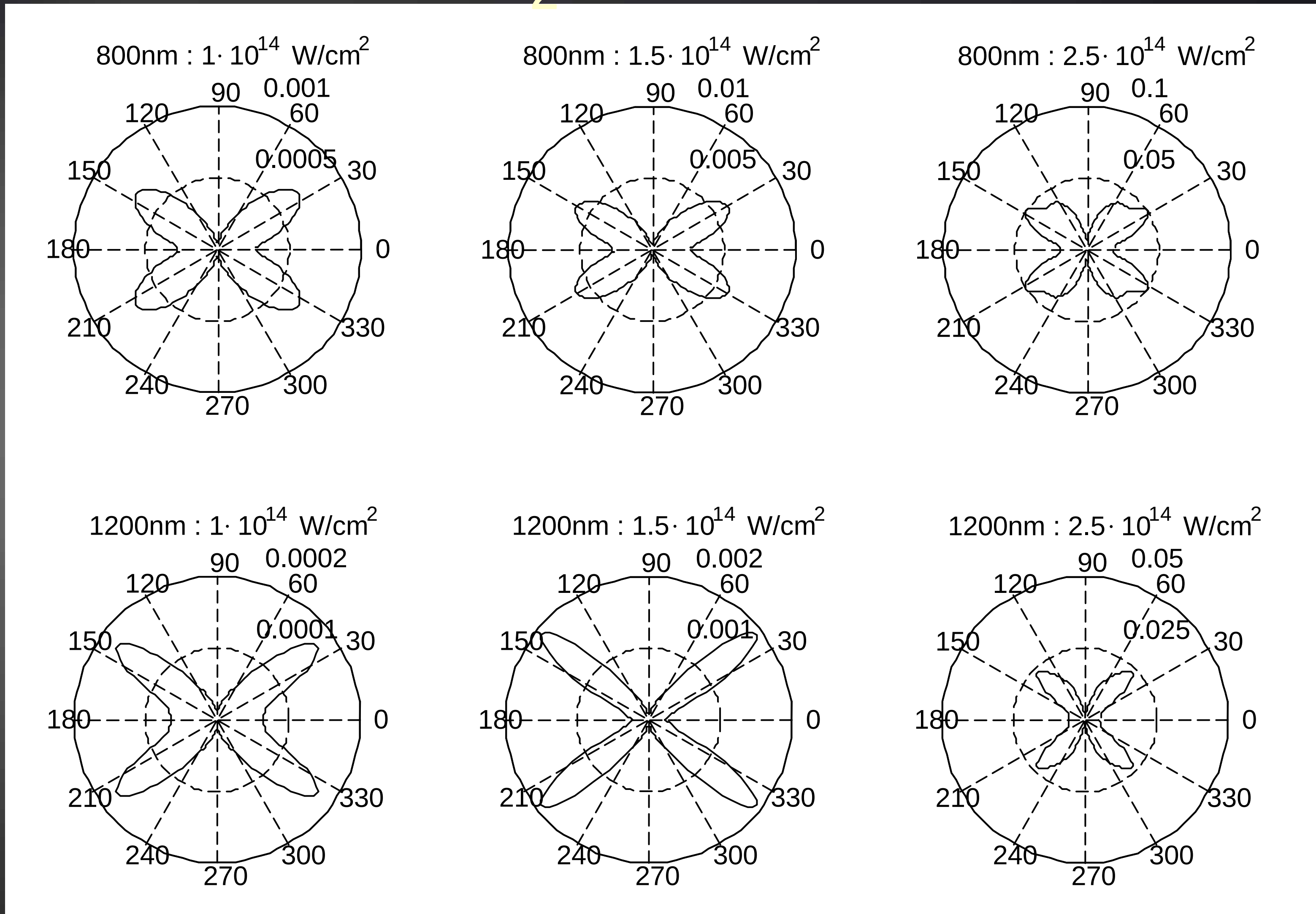
New determination of structure parameters in strong field tunneling ionization theory of molecules

Song-Feng Zhao,[1,2] Cheng Jin,[1,2] Anh-Thu Le,[1] T. F. Jiang,[1,3] and C. D. Lin[1]

[1]*J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, Kansas 66506-2604, USA*
[2]*College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou, Gansu 730070, People's Republic of China*
[3]*Institute of Physics, National Chiao-Tung University, Hsinchu 30010 Taiwan*

(Dated: January 21, 2010)

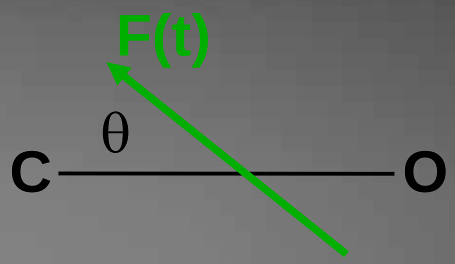
CO_2 Ionization

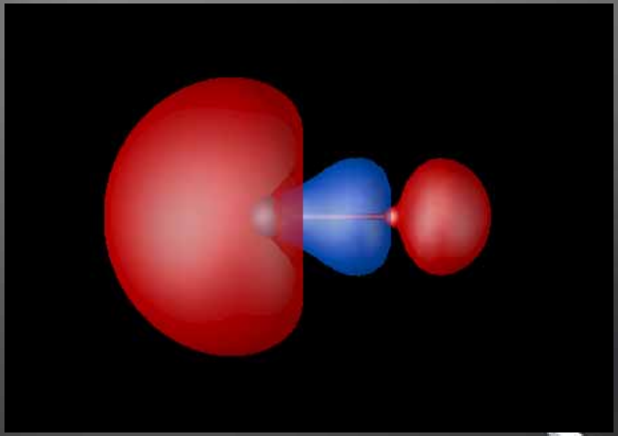


Our ionization yields dependent on wavelength and intensity and pulse duration

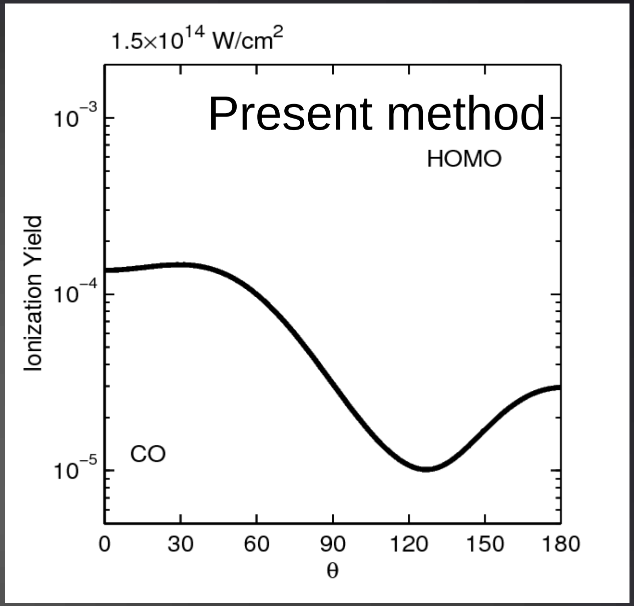
Total ionization yield for laser polarization at angle θ from the molecular axis

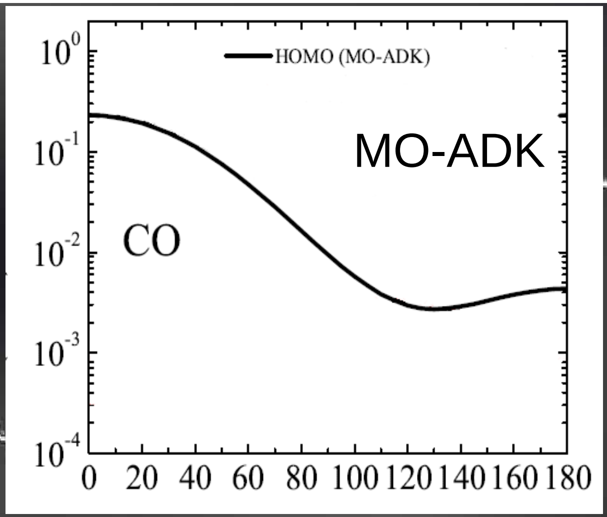
CO Ionization





Used a half-cycle pulse (800 nm) to see asymmetry in ionization yield

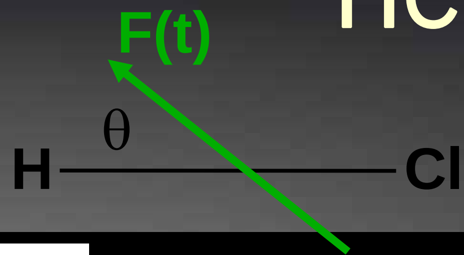


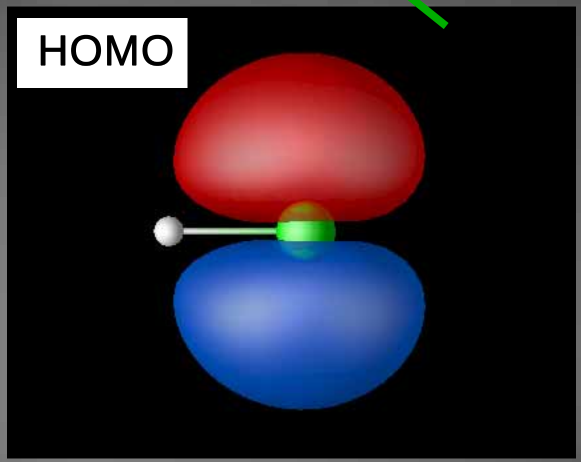


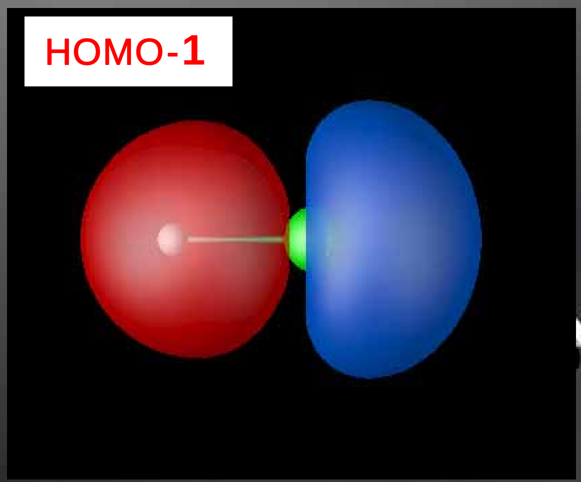
Total ionization yield for laser polarization at angle θ from the molecular axis

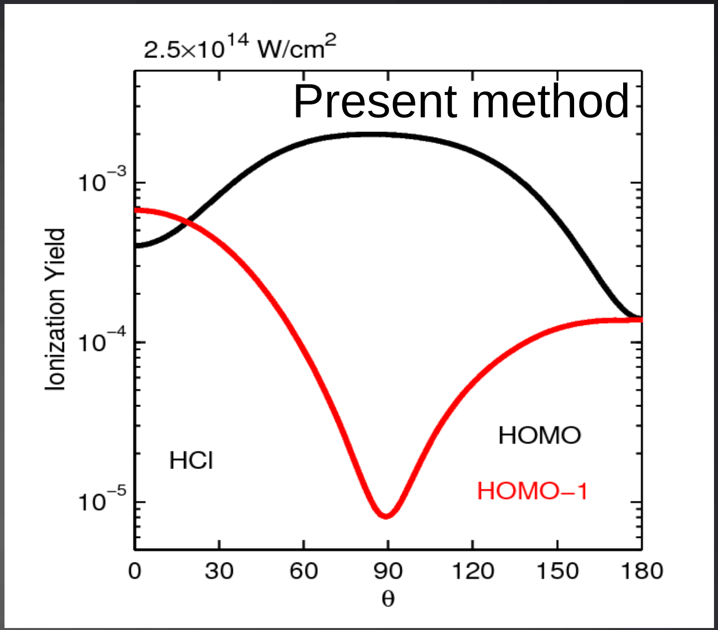
Unpublished results

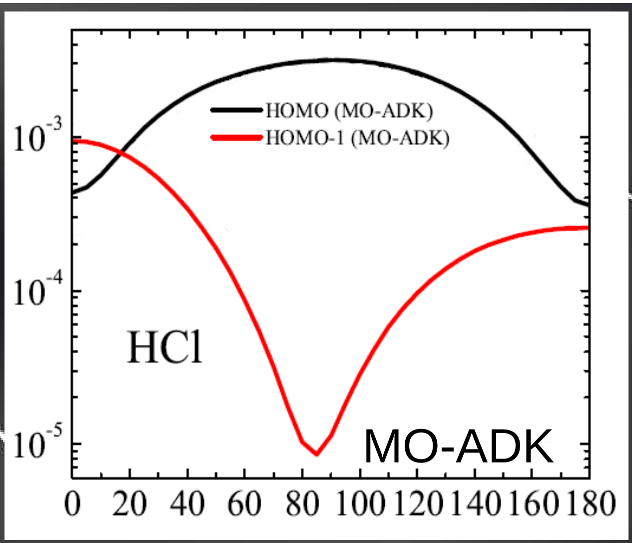
HCl Ionization











Total ionization yield for laser polarization at angle θ from the molecular axis

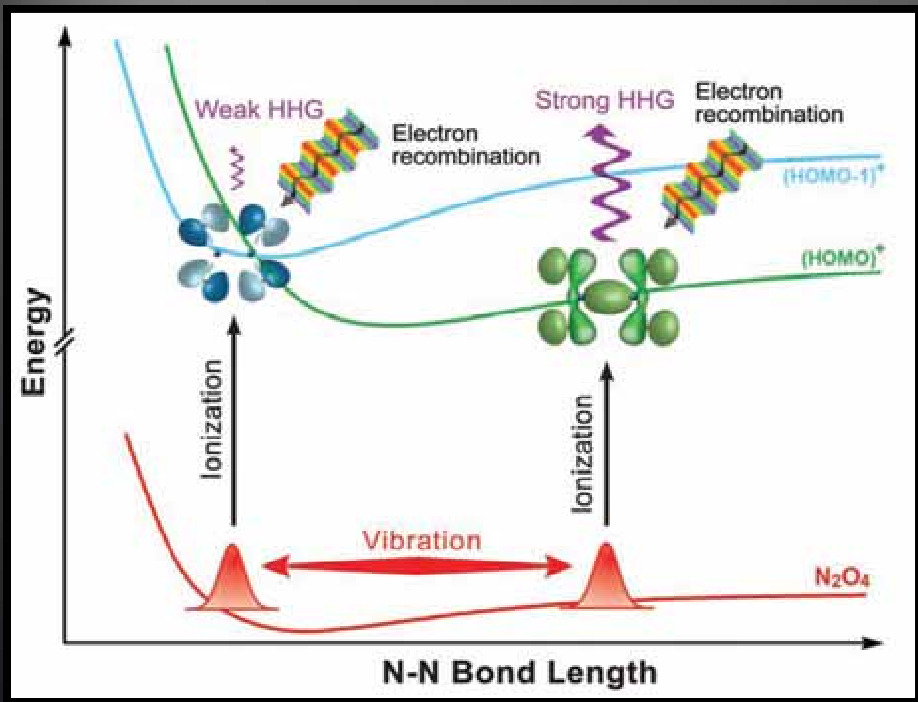
Unpublished results

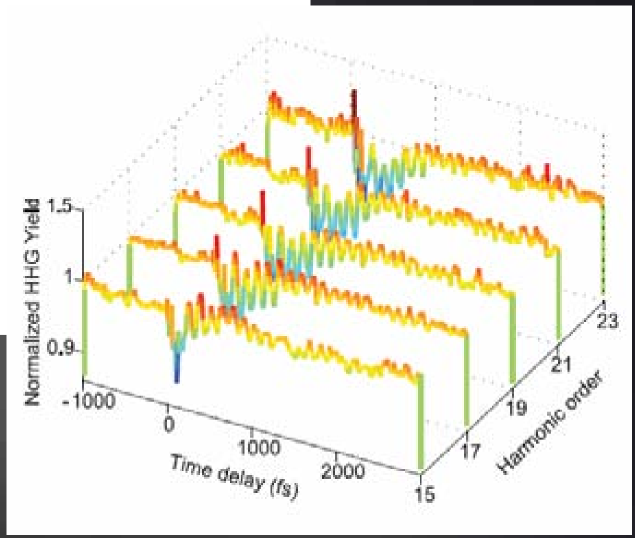
N_2O_4

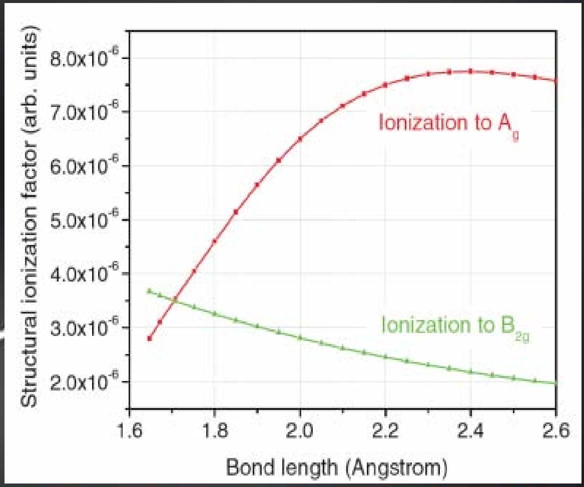
RESEARCH ARTICLES
www.sciencemag.org SCIENCE VOL 322 21 NOVEMBER 2008

Time-Resolved Dynamics in N_2O_4 Probed Using High Harmonic Generation

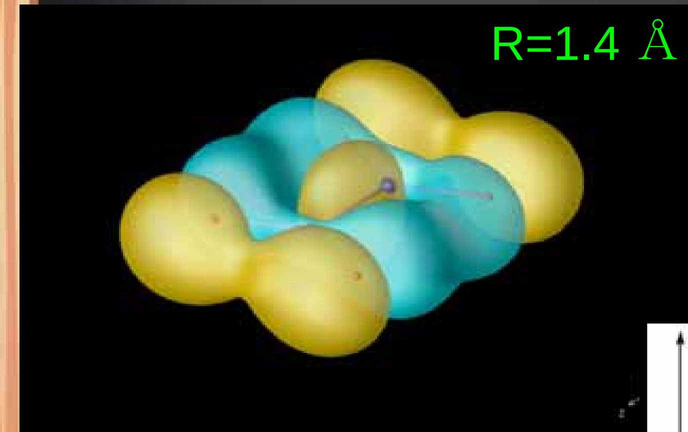
Wen Li,[1]* Xibin Zhou,[1] Robynne Lock,[1] Serguei Patchkovskii,[2] Albert Stolow,[2] Henry C. Kapteyn,[1] Margaret M. Murnane[1]





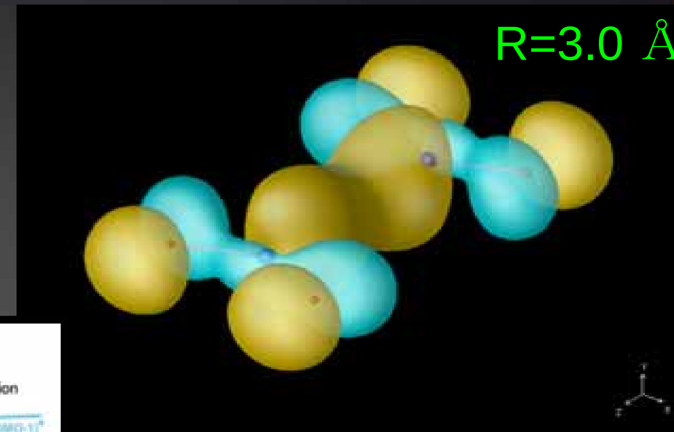


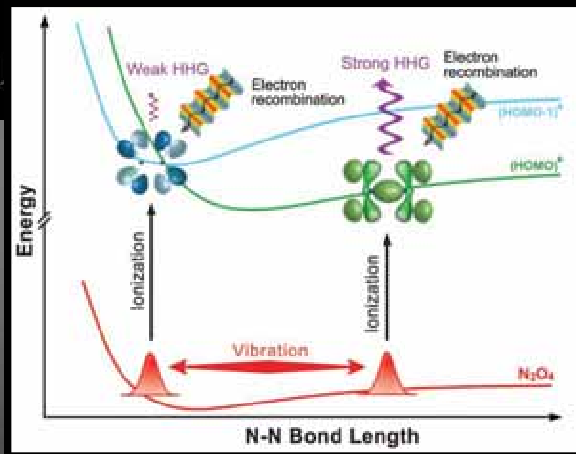
N_2O_4: A_g ionization channel

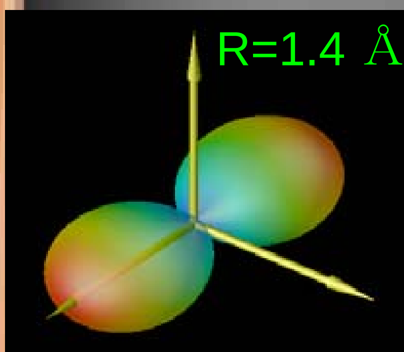


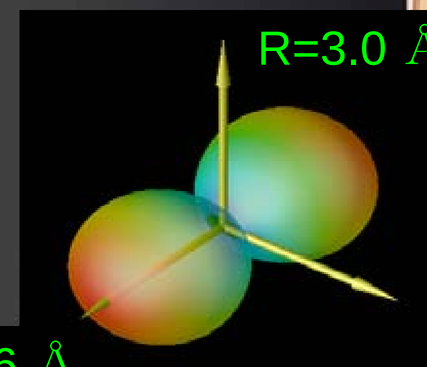
800 nm, 10^{14} W/cm^2, 1 cycle

Total yield: 0.008-0.012

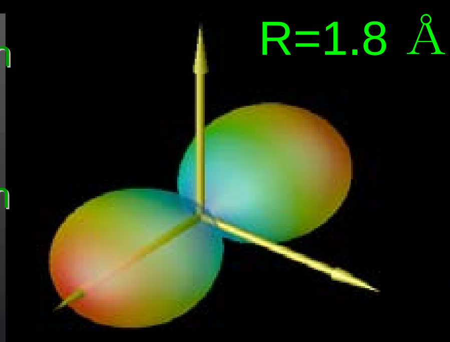


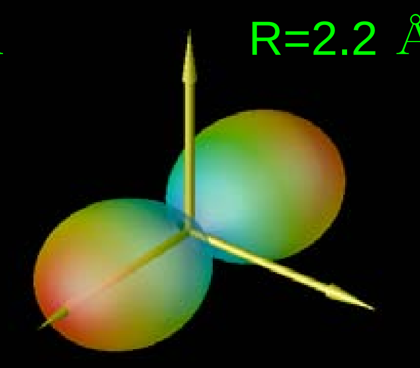


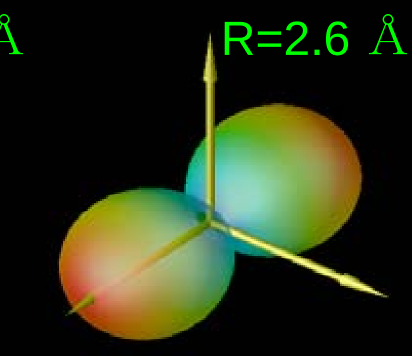




Total ionization yield for laser polarization at angles φ,θ from the molecular axis

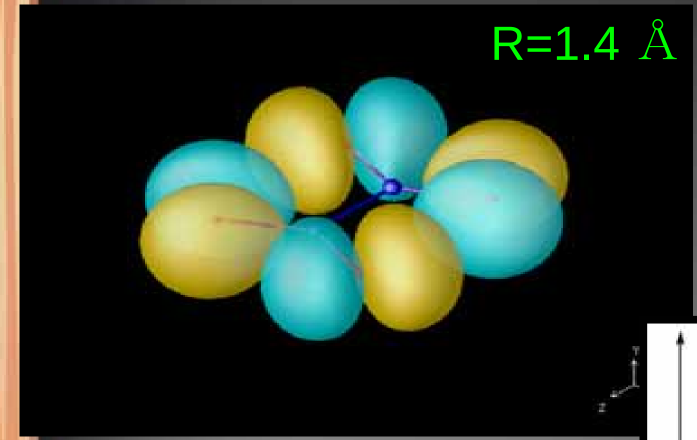






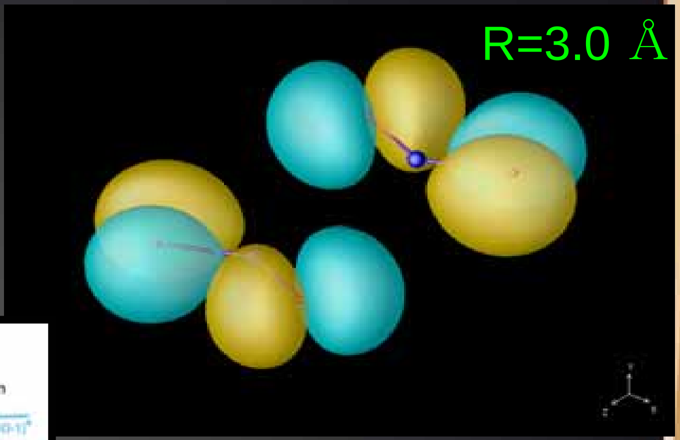
Unpublished results

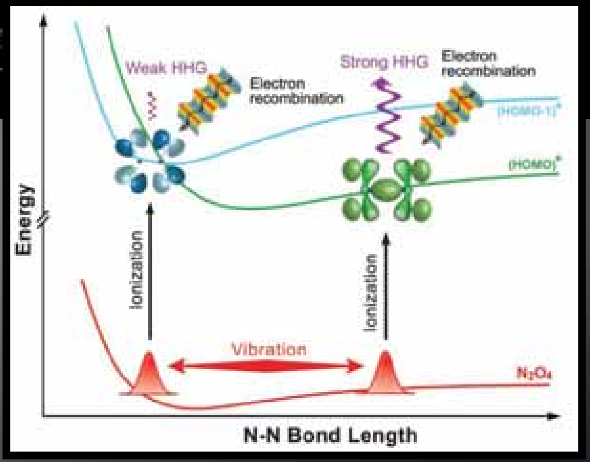
N_2O_4: B_{2g} ionization channel

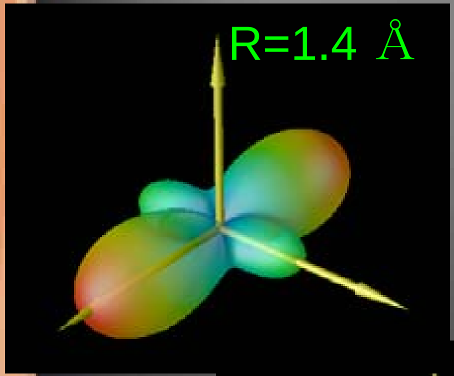


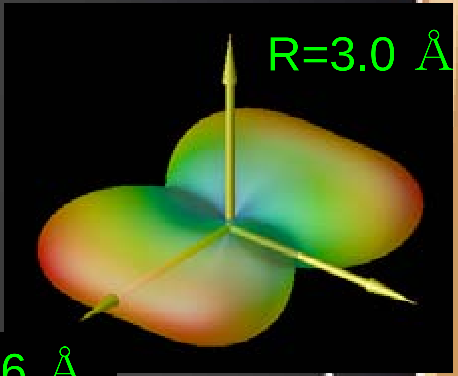
800 nm, 10^{14} W/cm^2, 1 cycle

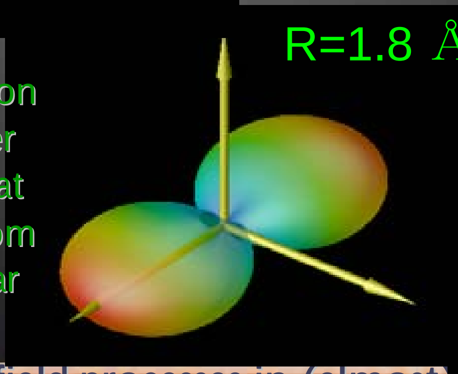
Total yield: < 0.001

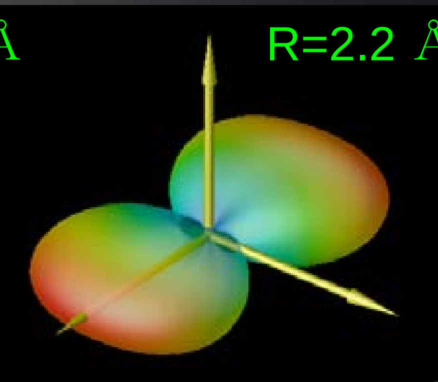


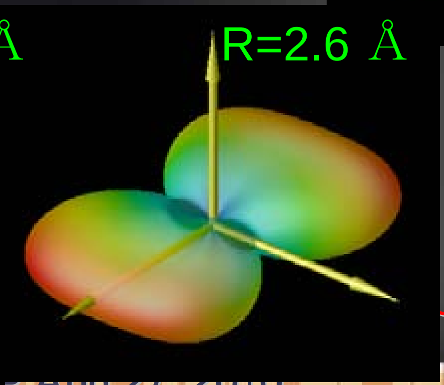










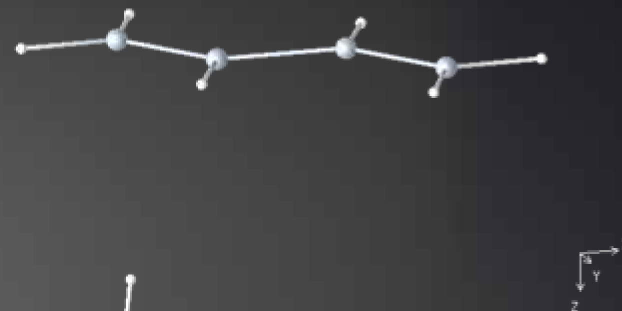


Total ionization yield for laser polarization at angles φ,θ from the molecular axis

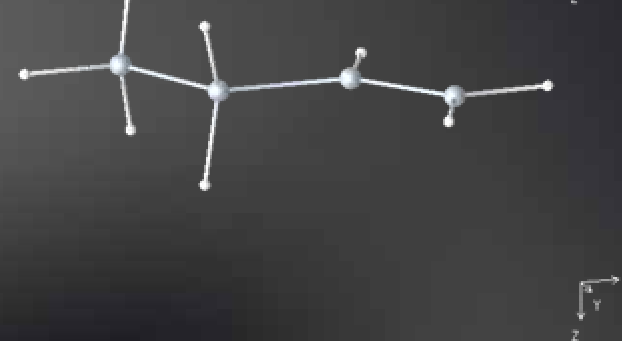
Unpublished results

Hydrocarbons

C_4H_6: 1,3-Butadiene

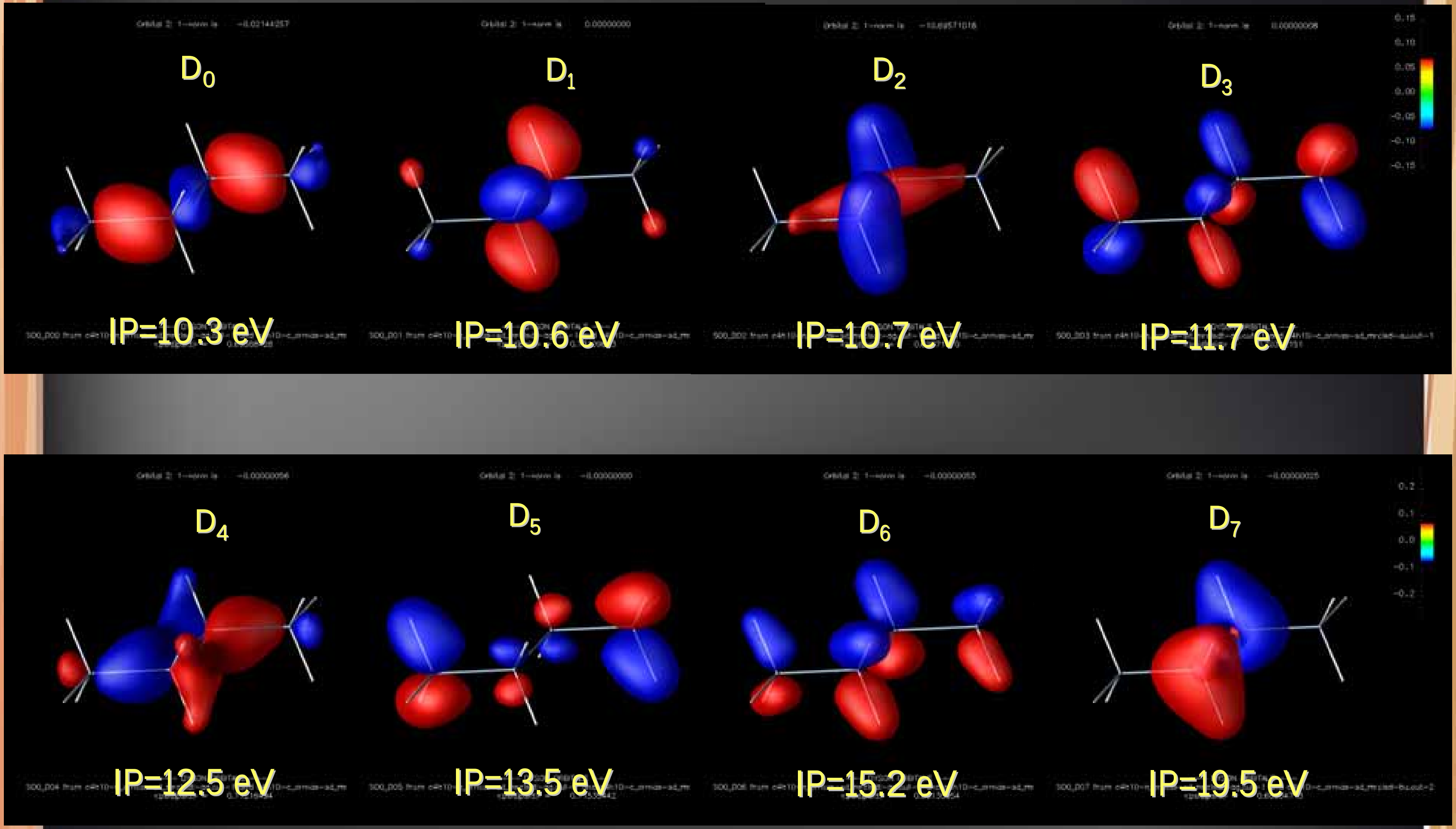


C_4H_8: 1-Butene

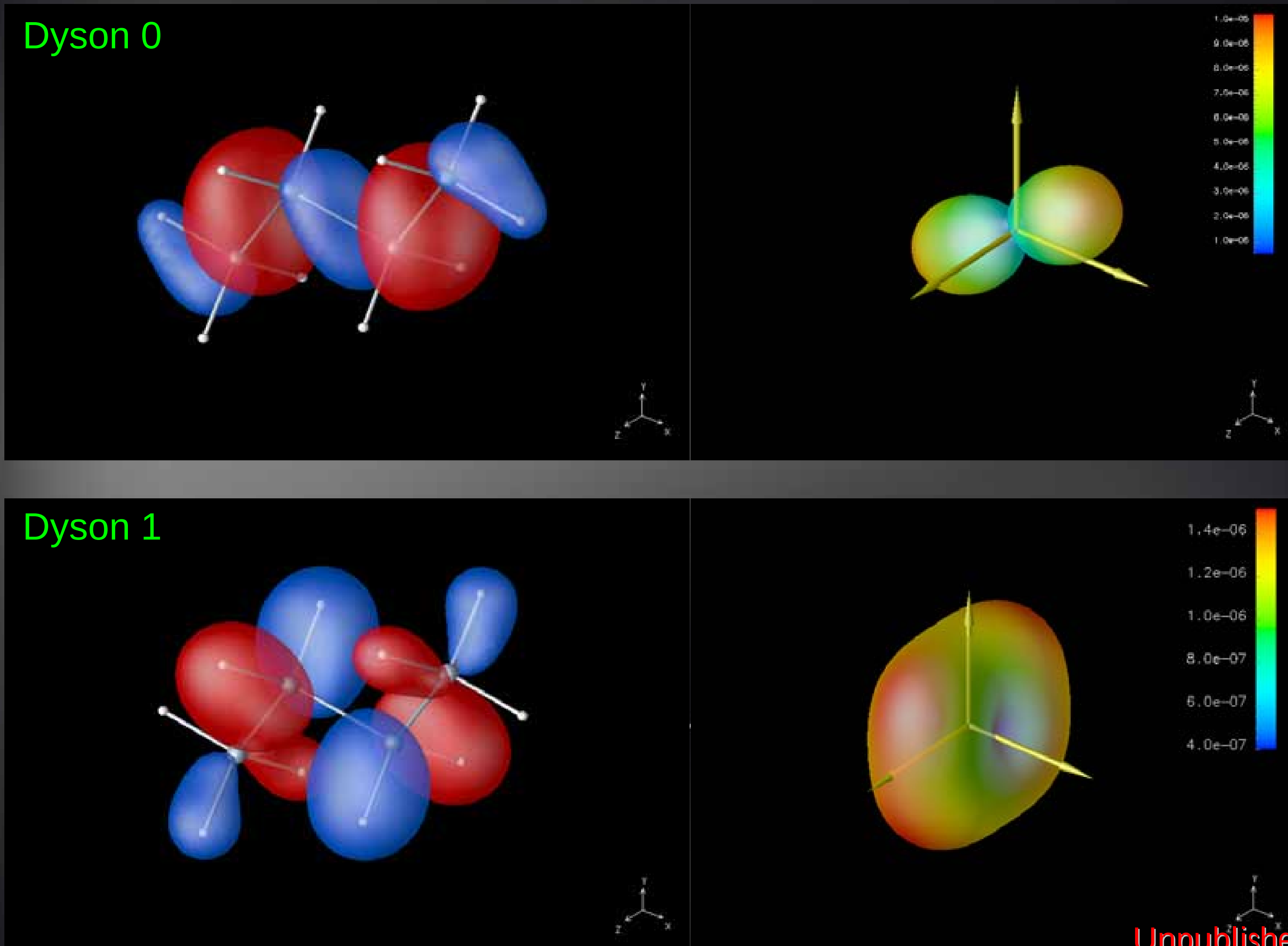


C_4H_{10}: Butane

C_4H_{10}: Ionization channels

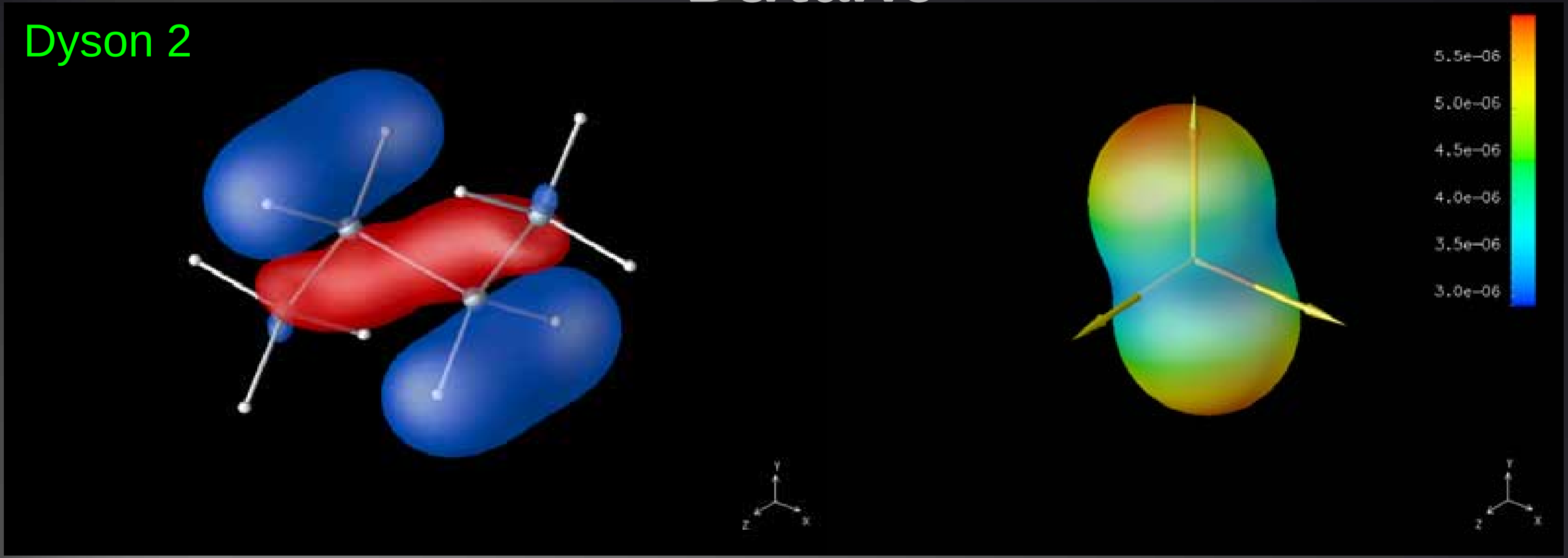


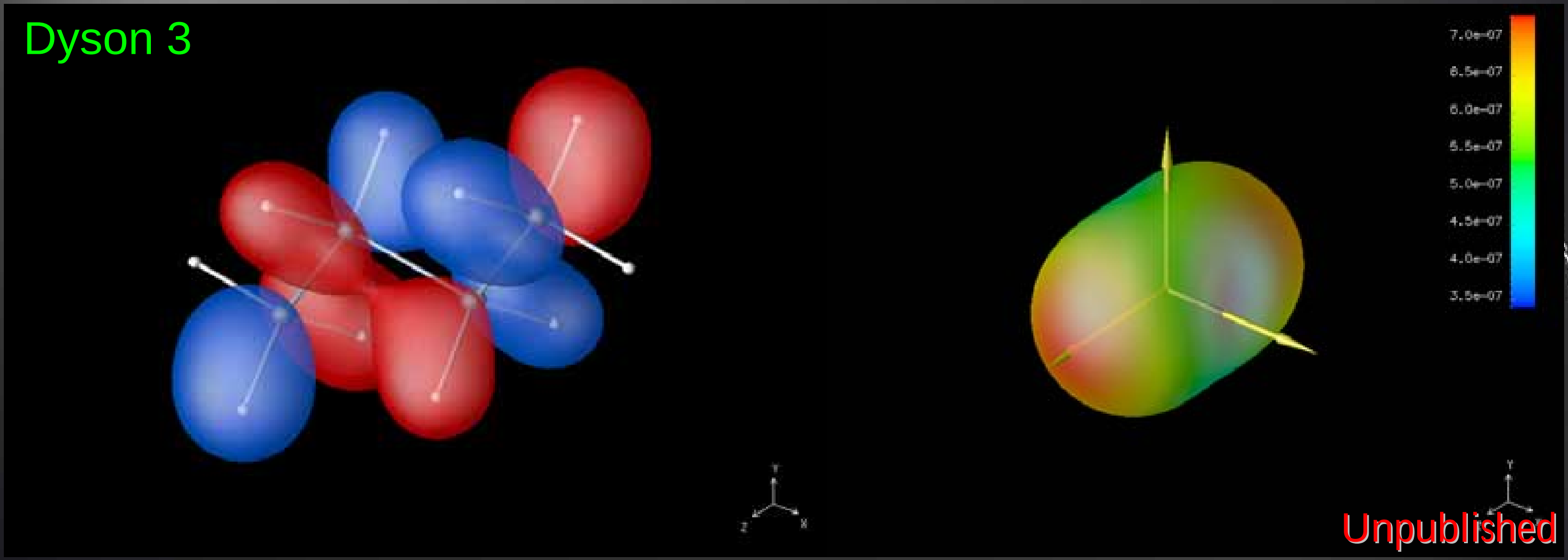
Butane



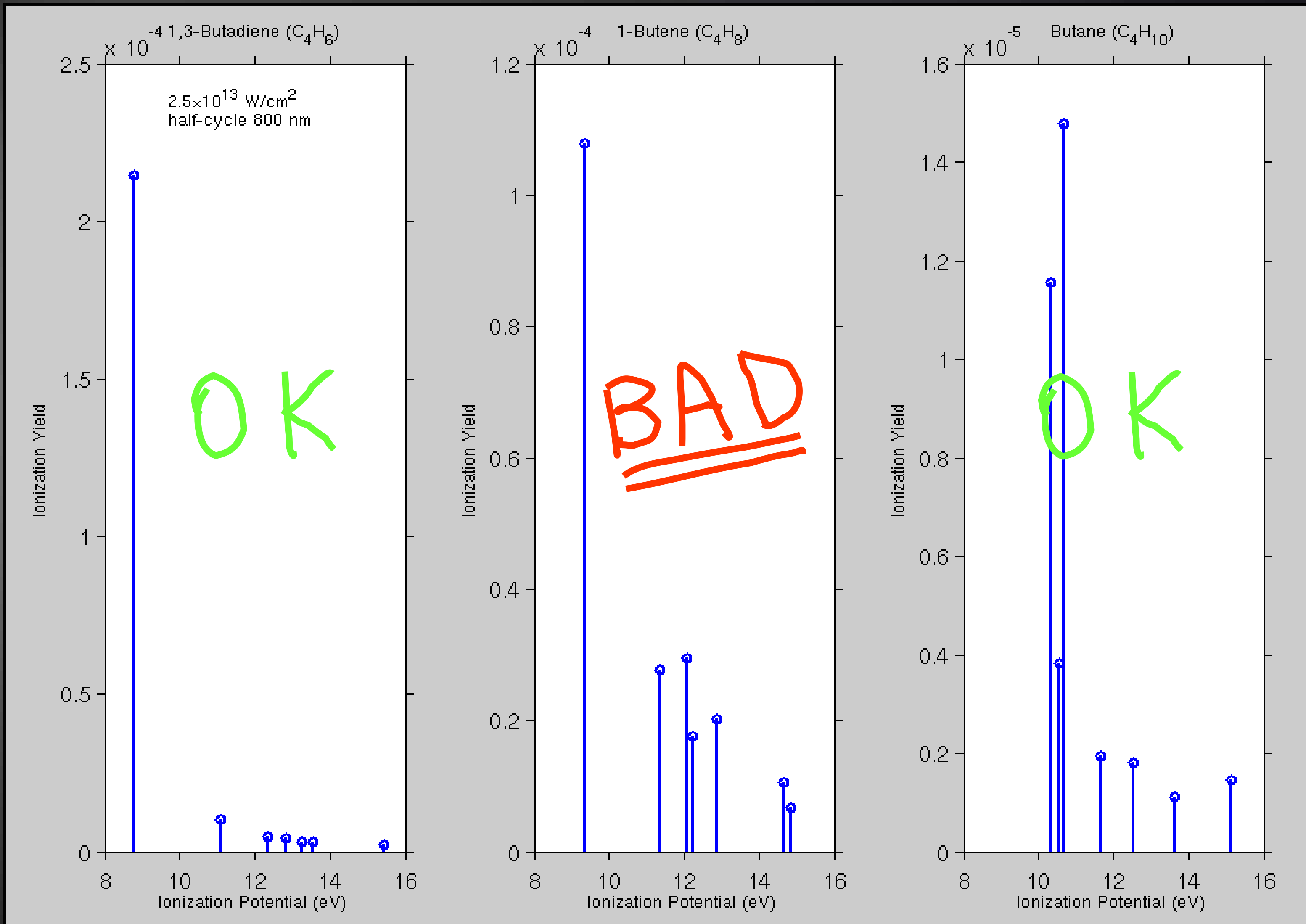
Unpublished results

Butane


Dyson 2
5.5e-06
5.0e-06
4.5e-06
4.0e-06
3.5e-06
3.0e-06

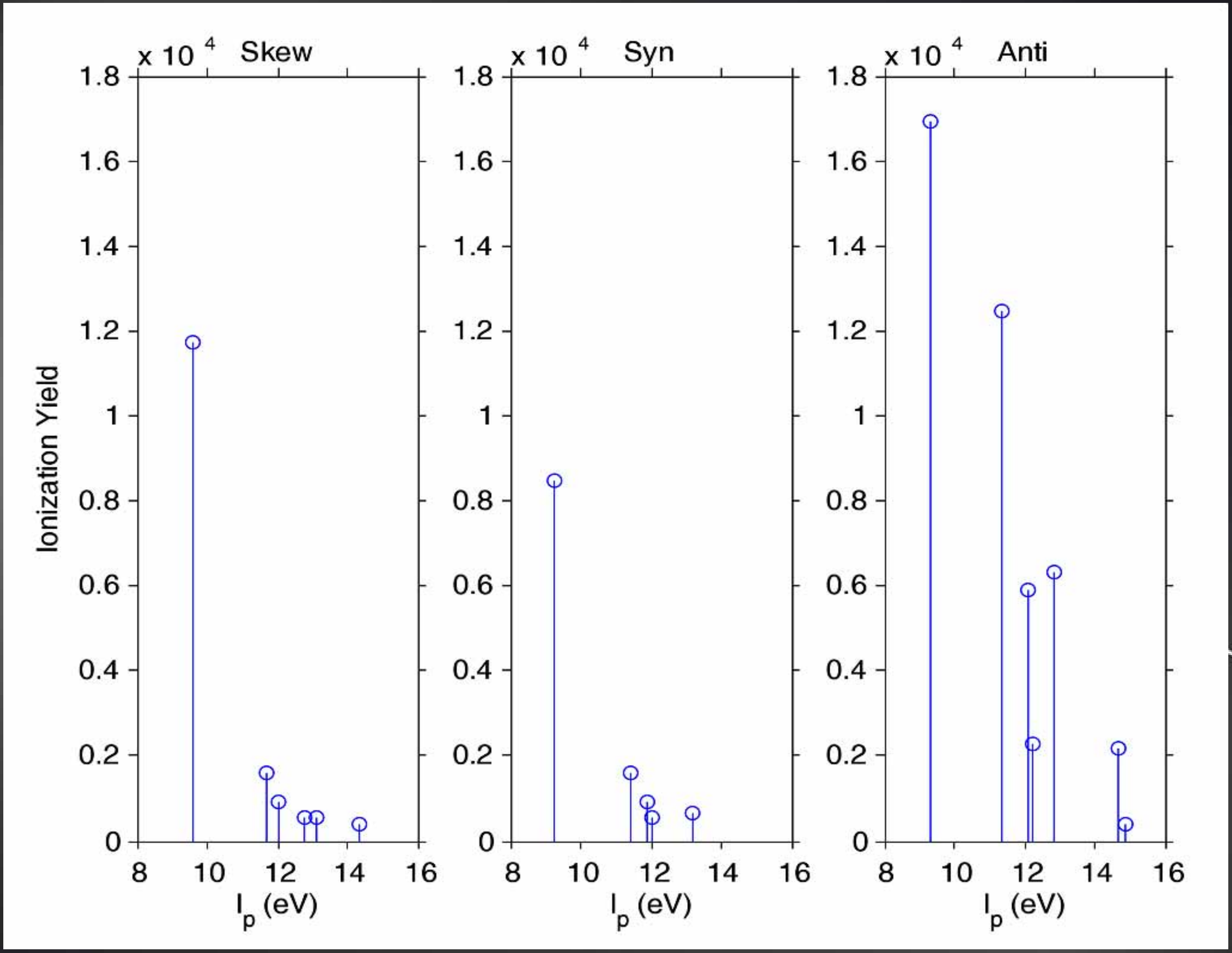

Dyson 3
7.0e-07
6.5e-07
6.0e-07
5.5e-07
5.0e-07
4.5e-07
4.0e-07
3.5e-07
Unpublished results

Butane-Butene-Butadiene

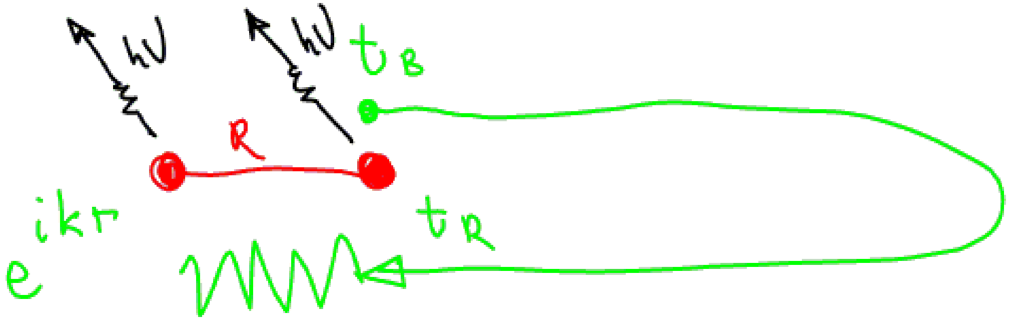


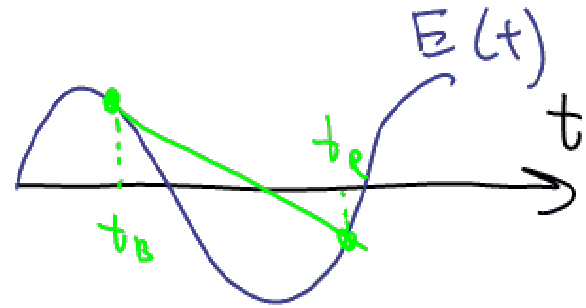
Unpublished results

1-Butene: Conformations matter



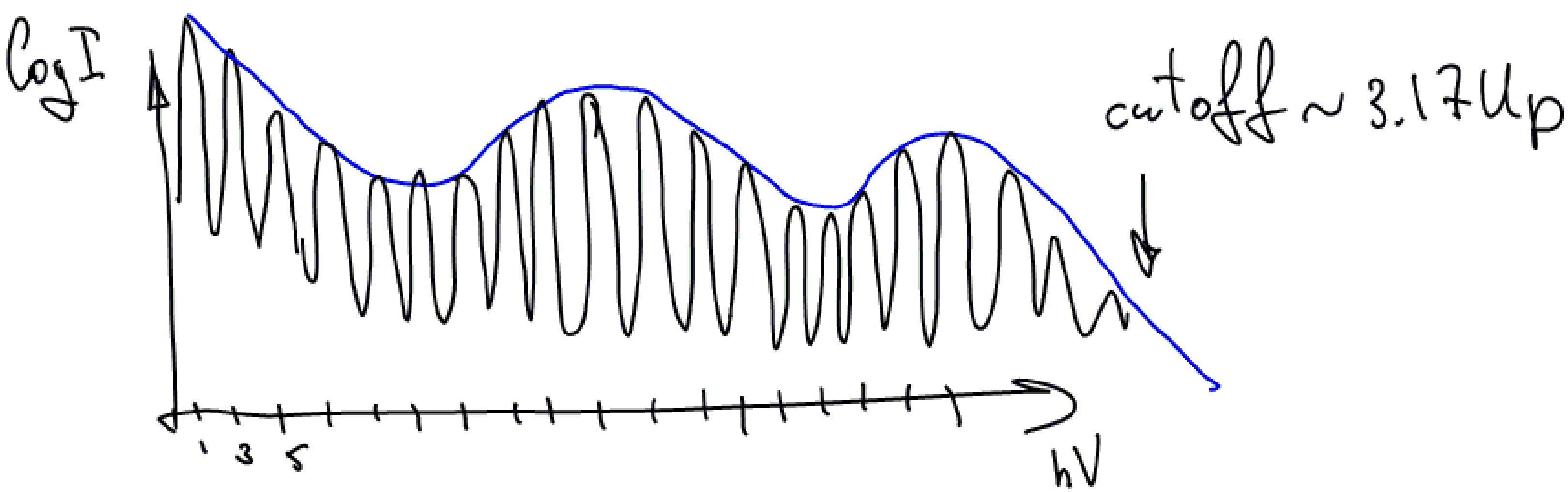
Structural minima in High-Harmonics spectra



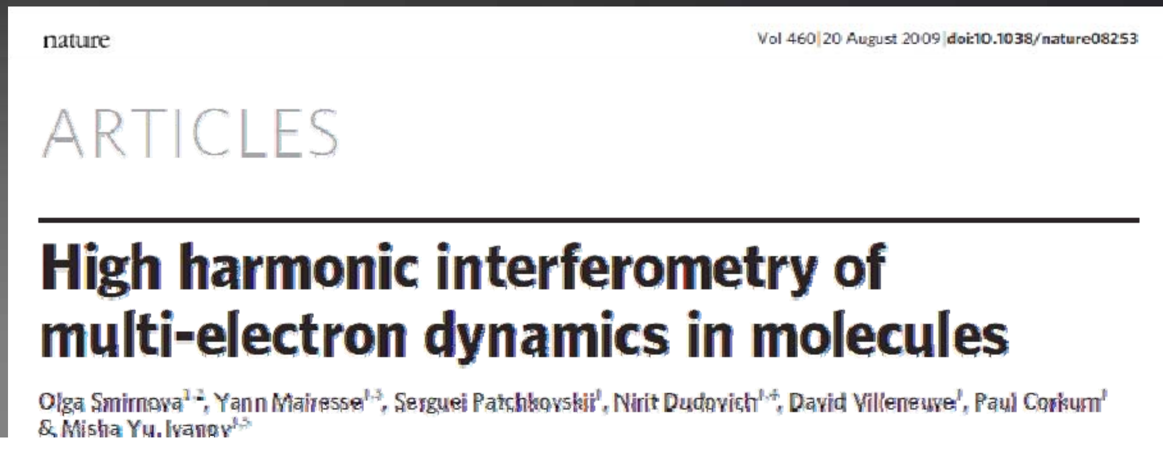


constructive: $2\pi n = Rk = R\sqrt{2h\nu}$

destructive: $2\pi n + \pi = Rk = R\sqrt{2h\nu}$



The case of peripatetic immovable object

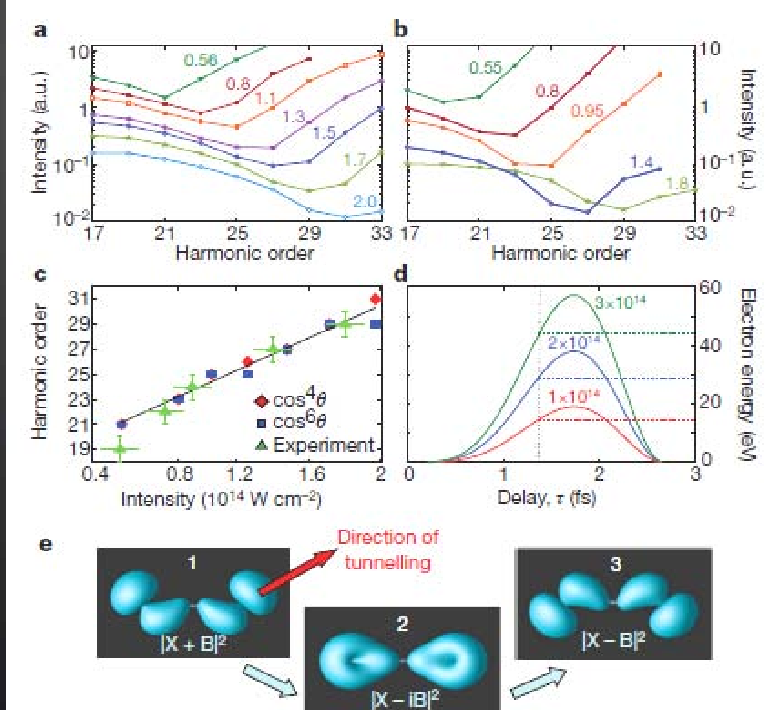


nature | Vol 460 | 20 August 2009 | doi:10.1038/nature08253

ARTICLES

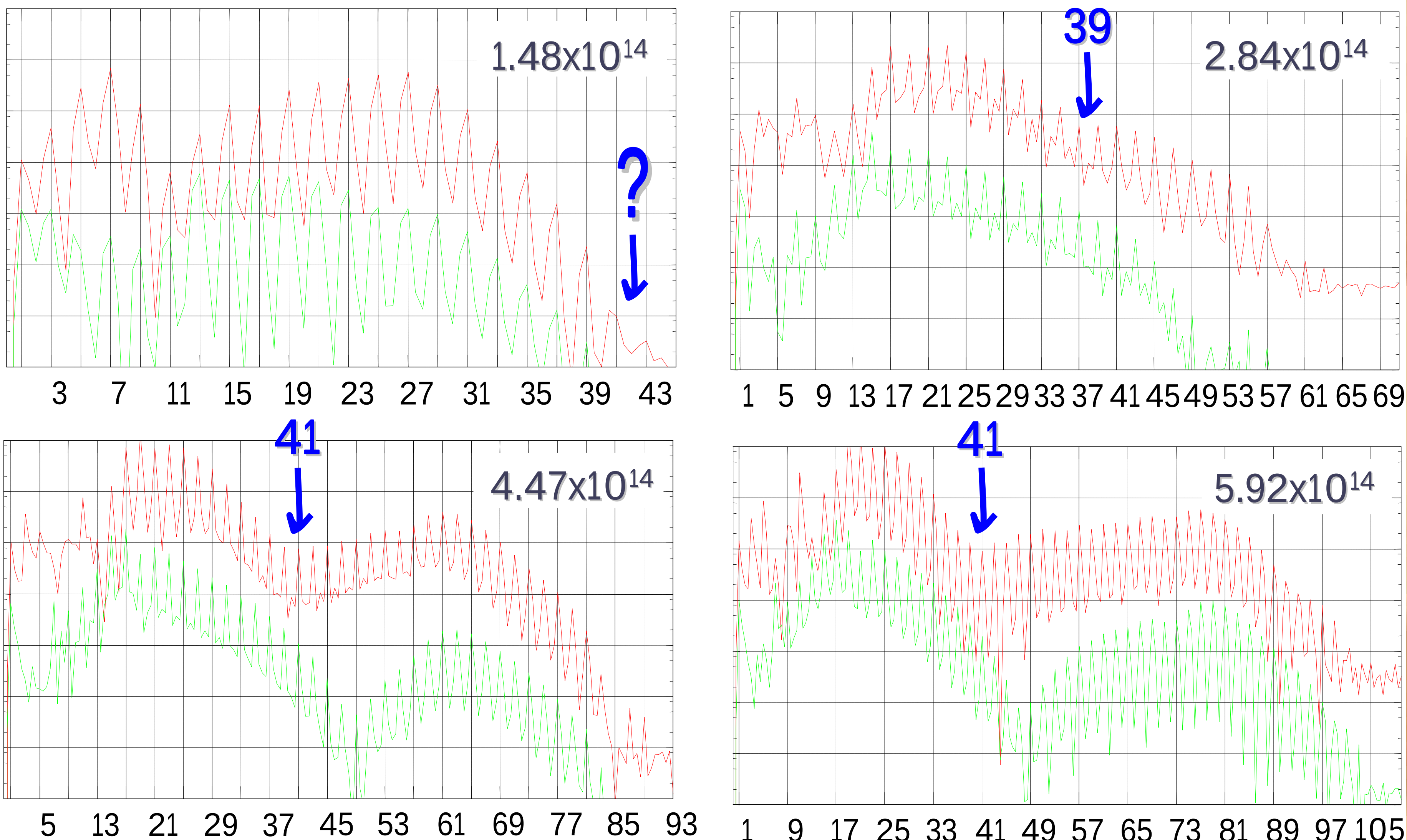
High harmonic interferometry of multi-electron dynamics in molecules

Olga Smirnova[1,2], Yann Mairesse[1,3], Serguei Patchkovskii[1], Nirit Dudovich[1,4], David Villeneuve[1], Paul Corkum[1] & Misha Yu. Ivanov[1,5]



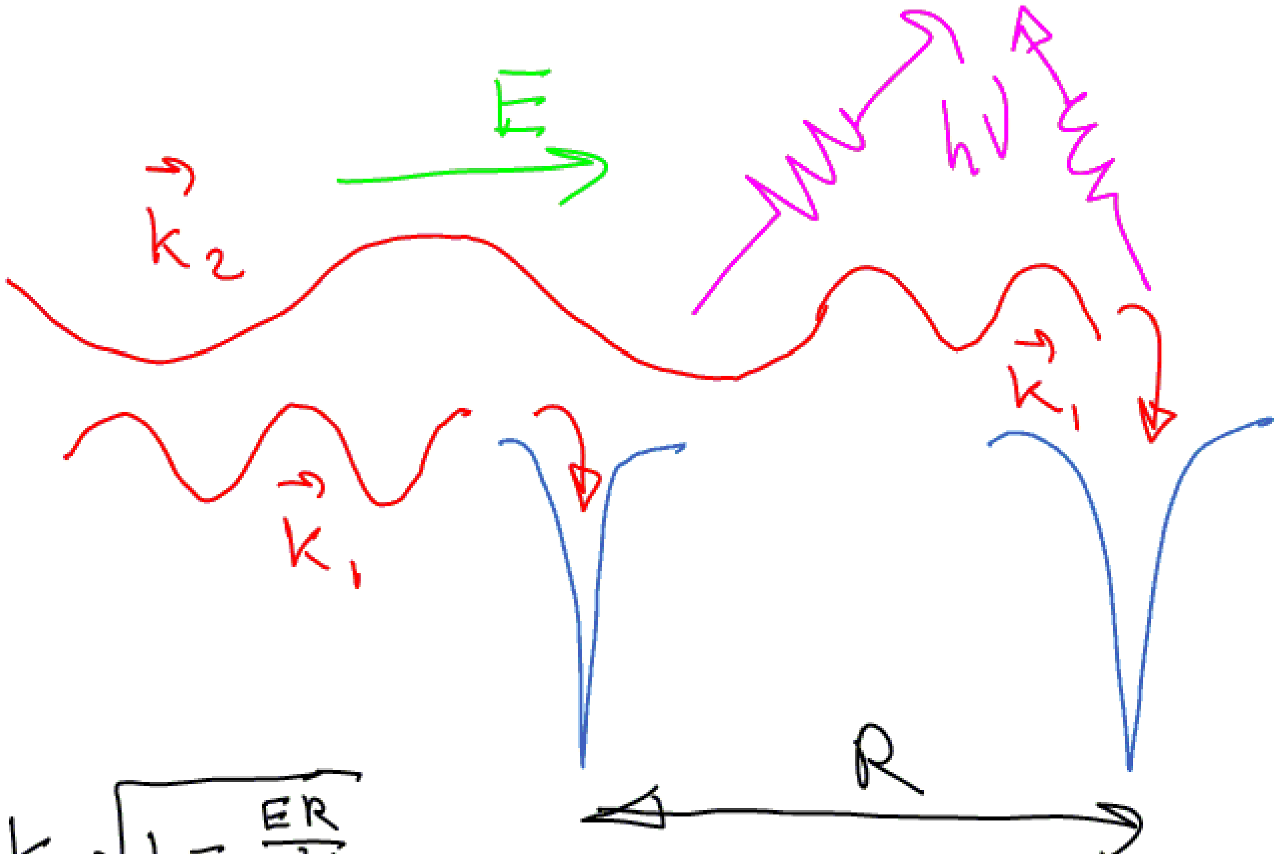
(Simplified) moral of the story: dynamical minima move with field intensity; structural minima don't

N_2 (R_e=1.098Å), CW, 800 nm, E ∥ Z, E ⊥ Z



Unpublished results

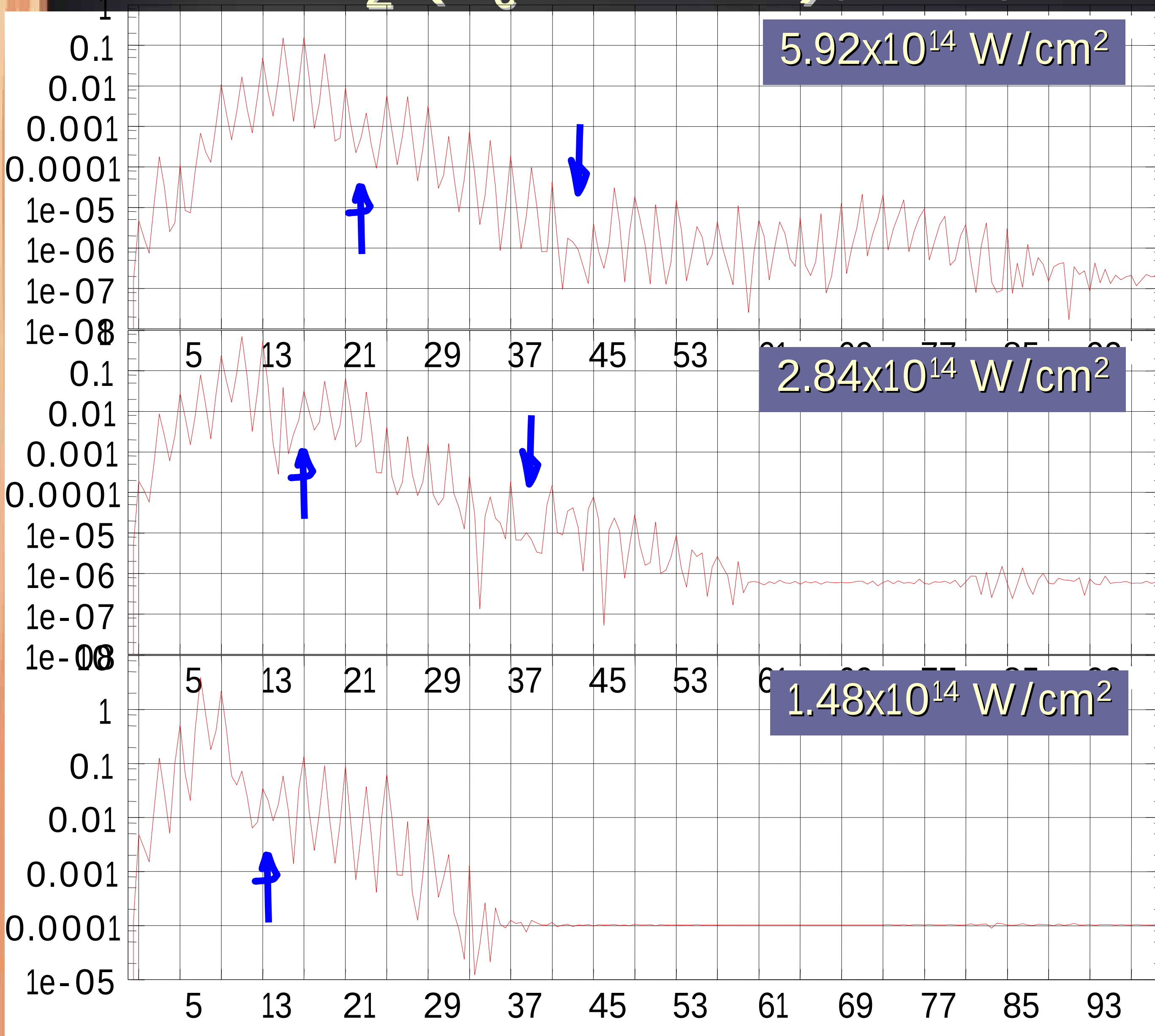
What about larger molecules?

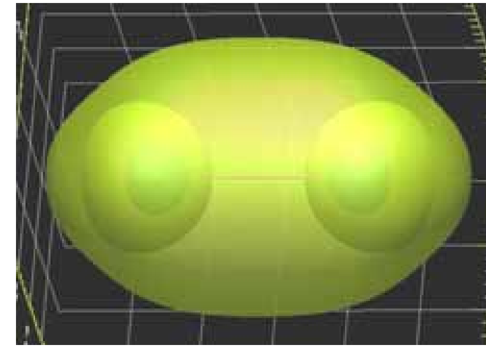


$$K_2 \sim k_1 \sqrt{1 - \frac{ER}{k_1^2/2}}$$

Also see: Chen, Liu, and Hu, PRA 79, 033405 (2009)
Figuero de Morisson Faria, Laser Phys. 19, 797 (2009)

K_2 (R_e=3.905Å), CW, 800 nm





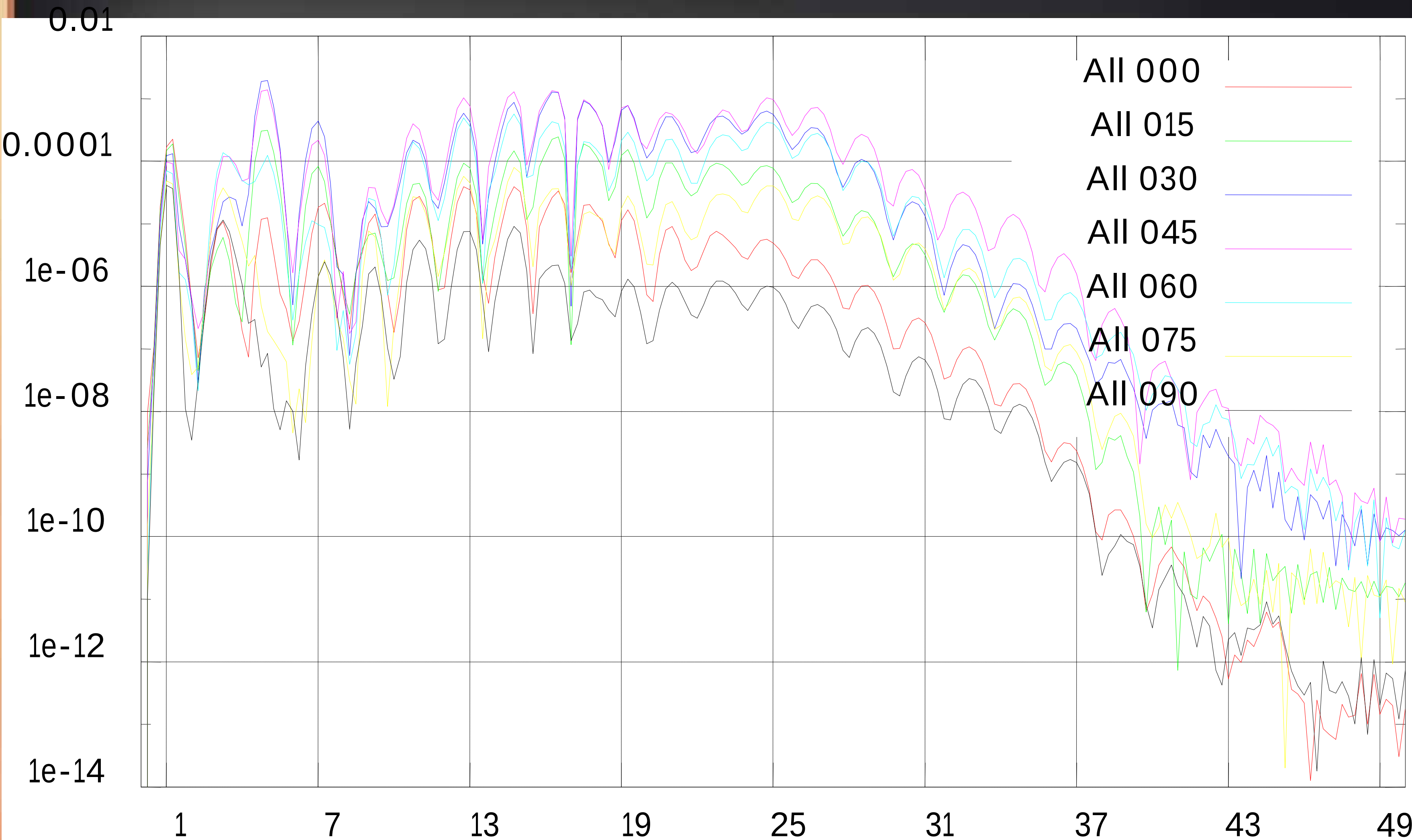
$pR = \pi(2n+1)$

n	$(p^2/2)/(\hbar\omega_0)$
~~0~~	~~1.6~~
1	14.3
2	39.7
3	77.9

IP≈4.6eV

Unpublished results

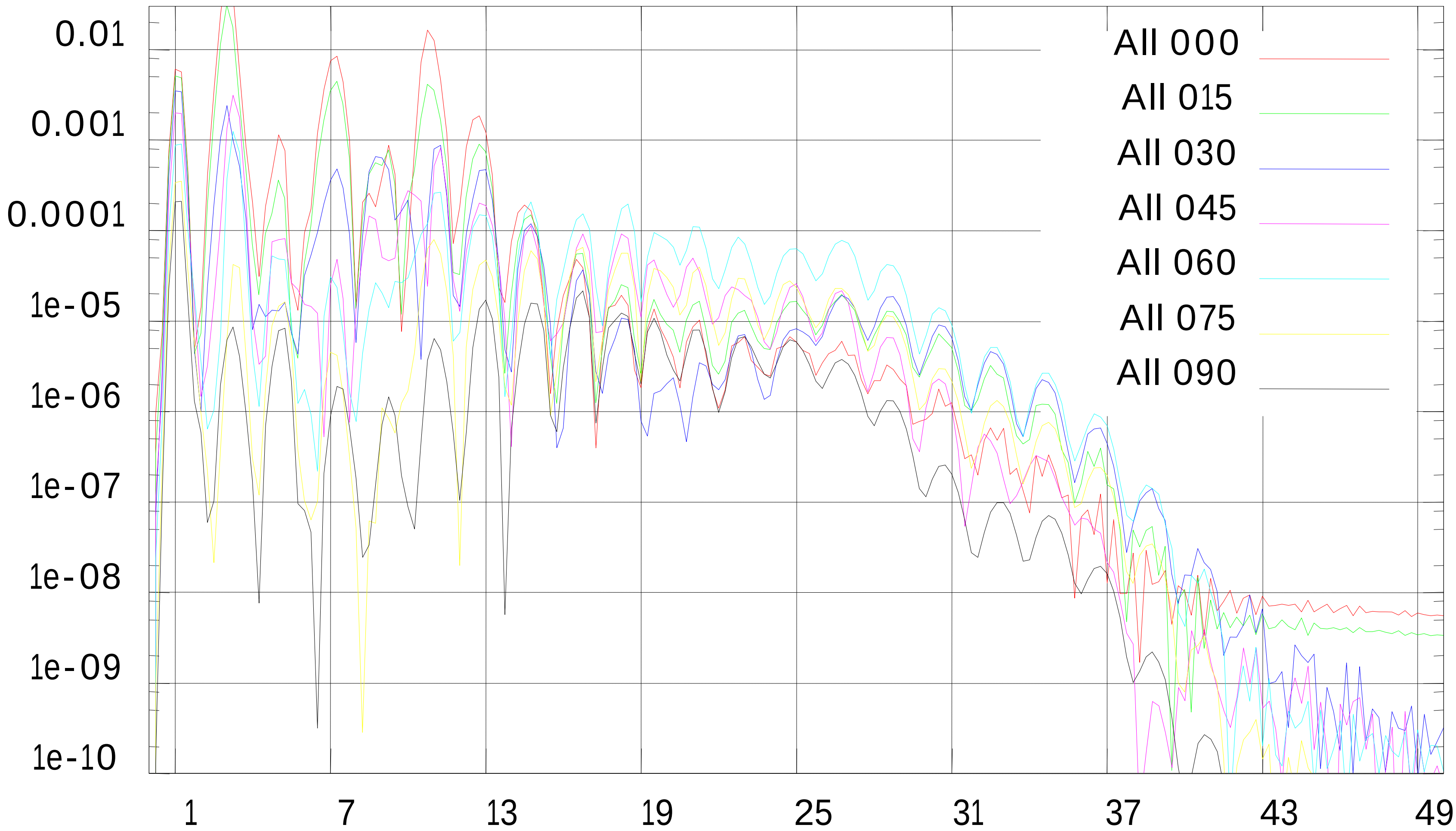
O_2 harmonics



800 nm, 1.5x10[14] W/cm², 5.5 fs FWHM, sin² envelope

Unpublished results

CO_2 harmonics



800 nm, 1.5×10^{14} W/cm^2, 5.5 fs FWHM, $\sin^2$ envelope

Unpublished results

Thank you for listening!