Time-resolved Molecular Electron Dynamics

8-10-2014 & 9-10-2014

Max-Born-Institut

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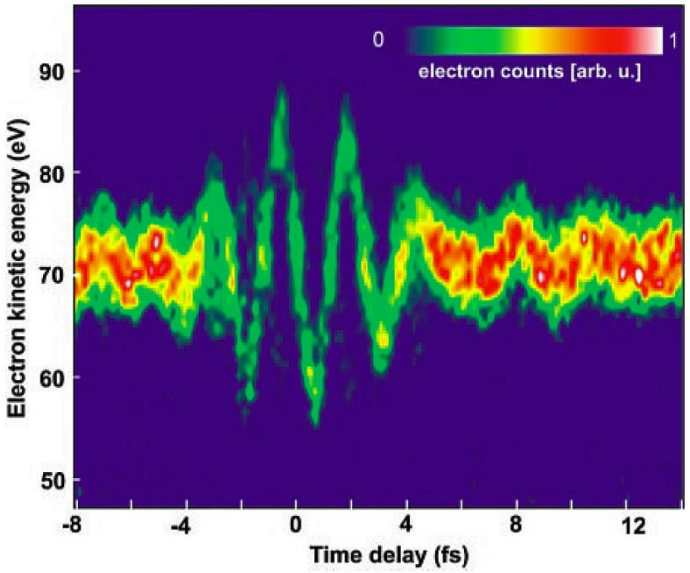
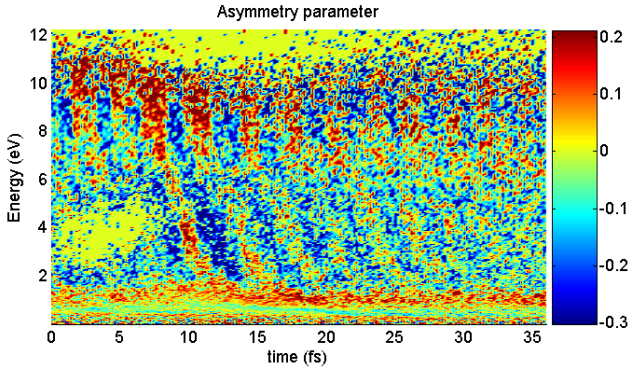
Today and tomorrow

- High harmonic generation and attosecond laser pulses
  - Atoms in intense laser fields
  - Generation of attosecond laser pulses
  - Characterization of attosecond laser pulses

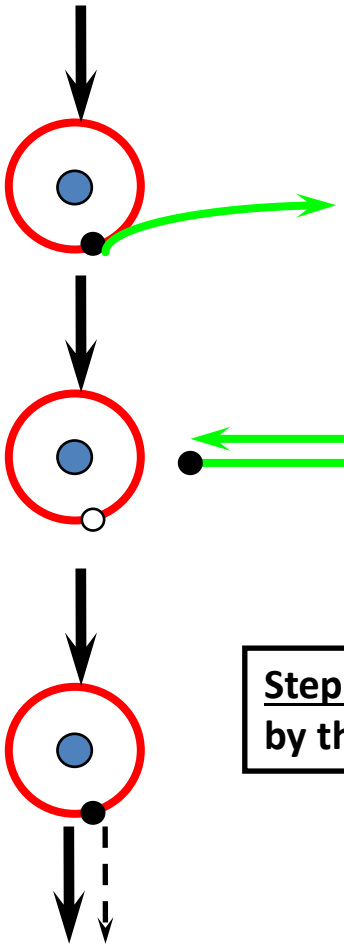


- Attosecond pump-probe spectroscopy
  - Attosecond experiments – atoms
  - Attosecond experiments – molecules



Making attosecond laser pulses

Intense near-infrared femtosecond laser

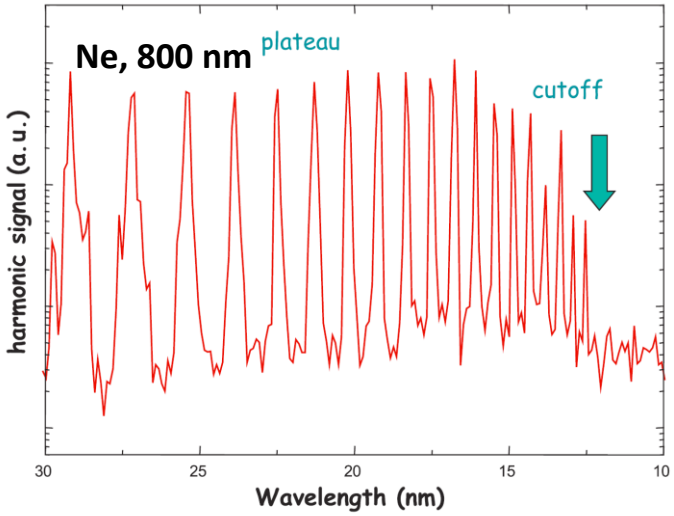


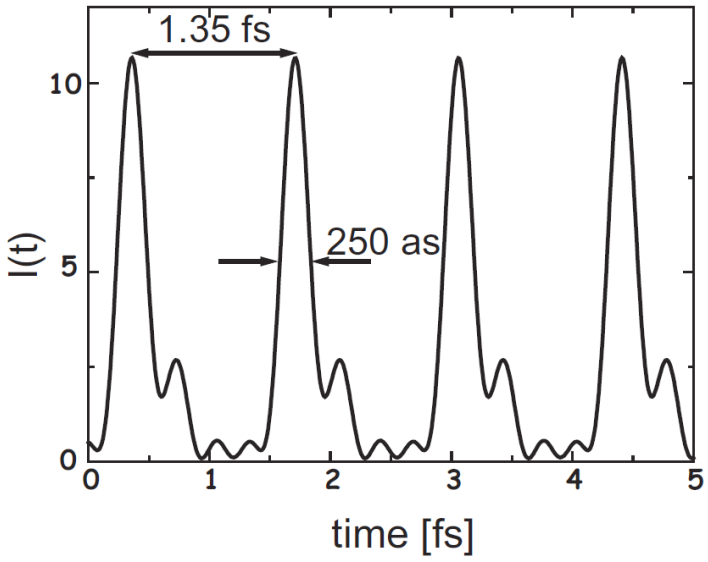
Step 1: ionization and removal of an electron from the positive ion core

Step 2: acceleration of the electron in the oscillatory laser field

Step 3: recombination, accompanied by the emission of an XUV photon

Intense near-infrared femtosecond laser + XUV radiation





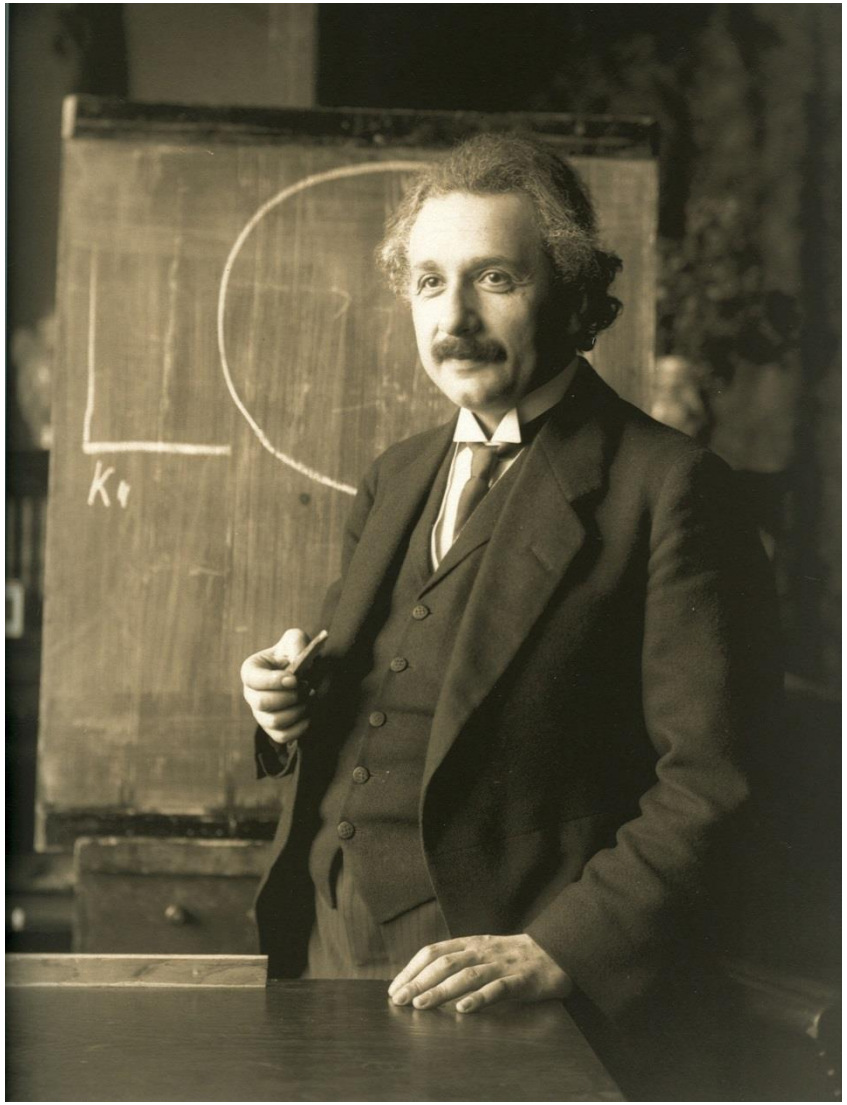
P. Agostini and L. DiMauro, Rep.Prog.Phys. 67, 813 (2004)

1905: Simple photo-effect

132

6. *Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt;*
von A. Einstein.

Zwischen den theoretischen Vorstellungen, welche sich die Physiker über die Gase und andere ponderable Körper gebildet haben, und der Maxwellschen Theorie der elektromagnetischen Prozesse im sogenannten leeren Raume besteht



146 *A. Einstein.*

versehenes Elektron wird, wenn es die Oberfläche erreicht hat, einen Teil seiner kinetischen Energie eingebüßt haben. Außerdem wird anzunehmen sein, daß jedes Elektron beim Verlassen des Körpers eine (für den Körper charakteristische) Arbeit P zu leisten hat, wenn es den Körper verläßt. Mit der größten Normalgeschwindigkeit werden die unmittelbar an der Oberfläche normal zu dieser erregten Elektronen den Körper verlassen. Die kinetische Energie solcher Elektronen ist

$$\frac{R}{N}\beta\nu - P.$$

Ist der Körper zum positiven Potential Π geladen und von Leitern vom Potential Null umgeben und ist Π eben imstande, einen Elektrizitätsverlust des Körpers zu verhindern

A. Einstein, Annalen der Physik 322, 132 (1905)

Multi-Photon Ionization

SOVIET PHYSICS JETP VOLUME 23, NUMBER 1 JULY, 1966

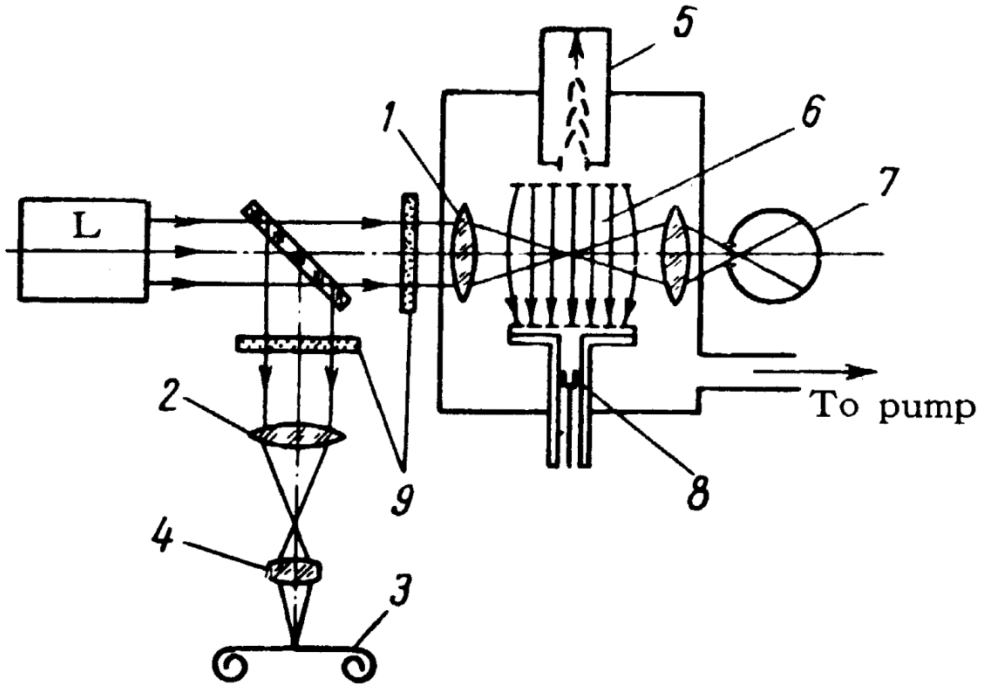
MANY-PHOTON IONIZATION OF THE XENON ATOM BY RUBY LASER RADIATION

G. S. VORONOV and N. B. DELONE

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor August 27, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 50, 78-84 (January, 1966)



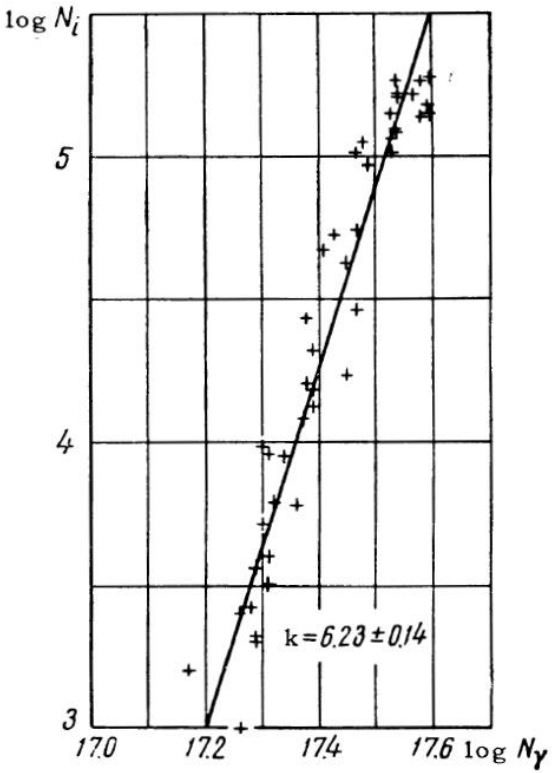


FIG. 2. Dependence of the number of ions formed N_i on the number of photons N_γ which have traversed the focusing region.

Multi-Photon Ionization

According to perturbation theory, the rate of n-photon absorption is given as

$$W_{fi}^{(n)} = \frac{2\pi}{\hbar}(2\pi\alpha\hbar)^n I_{laser}^n \left|\tilde{T}_{fi}^{(n)}\right|^2 \rho_f(E_f)$$

laser intensity

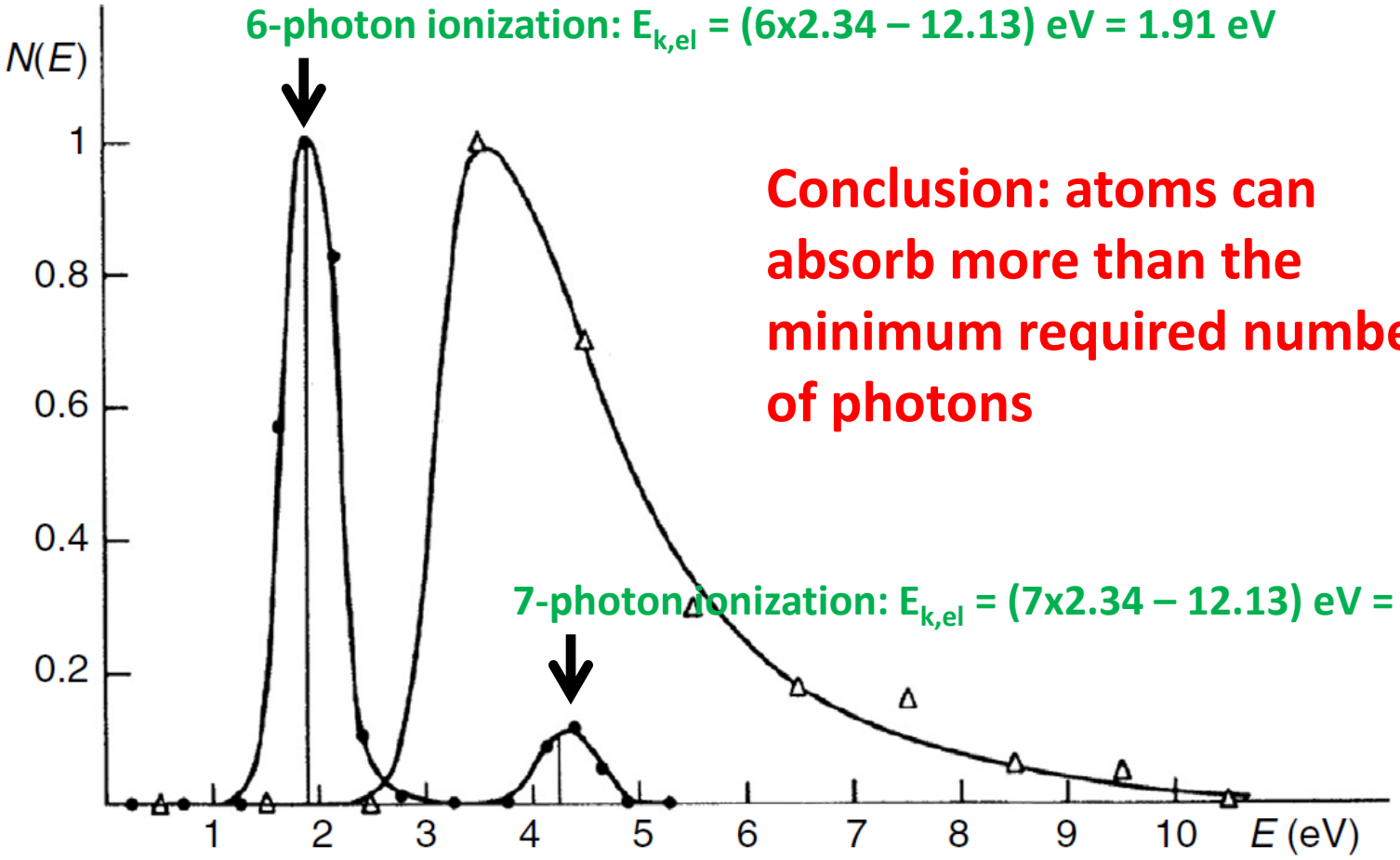
final state density

N-photon matrix element

Therefore, the lowest-order perturbation theory (LOPT) ionization rate is proportional to $I_{laser}^{n_0}$, where n_0 is the minimum number of photons needed

C.J. Joachain, N.J. Kylstra and R.M. Potvliege, Atoms in Intense Laser Fields, (Cambridge University Press, 2012)

Above-Threshold Ionization



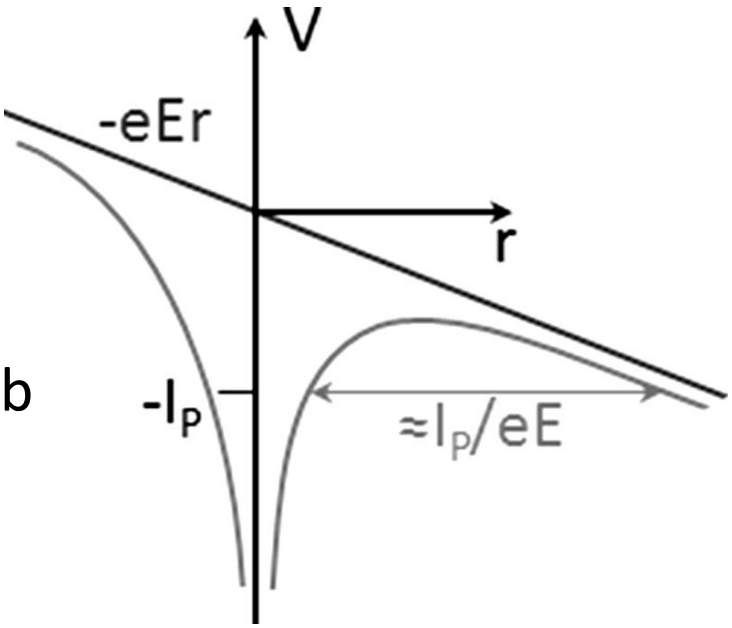
Conclusion: atoms can absorb more than the minimum required number of photons

Energy spectra of electrons produced by multiphoton ionization of xenon atoms, for two photon energies. Triangles: ω = 1.17 eV; Circles: ω =2.34 eV

P. Agostini et al., Phys. Rev. Lett. 42, 1127 (1979)

Distortion of the Coulomb potential

$$V(z) = -\frac{1}{z} - E_{laser} z$$



For sufficiently strong laser fields the electron can tunnel through the Coulomb + laser field potential, or pass over the saddlepoint in this potential

Saddlepoint: $\frac{\partial V(z)}{\partial z} = \frac{1}{z^2} - E_{laser} = 0$

$$z_{Saddle} = \frac{1}{\sqrt{E_{laser}}}; V(z_{saddle}) = -2\sqrt{E_{laser}}$$

Over-the-barrier ionization: $IP = -2\sqrt{E_{laser}}; E_{laser} = \frac{IP^2}{4}; I_{laser,OTB} = \frac{IP^4}{16}$

Distortion of the Coulomb potential

Over-the-barrier ionization: $I_{laser,OTB} = \frac{IP^4}{16}$

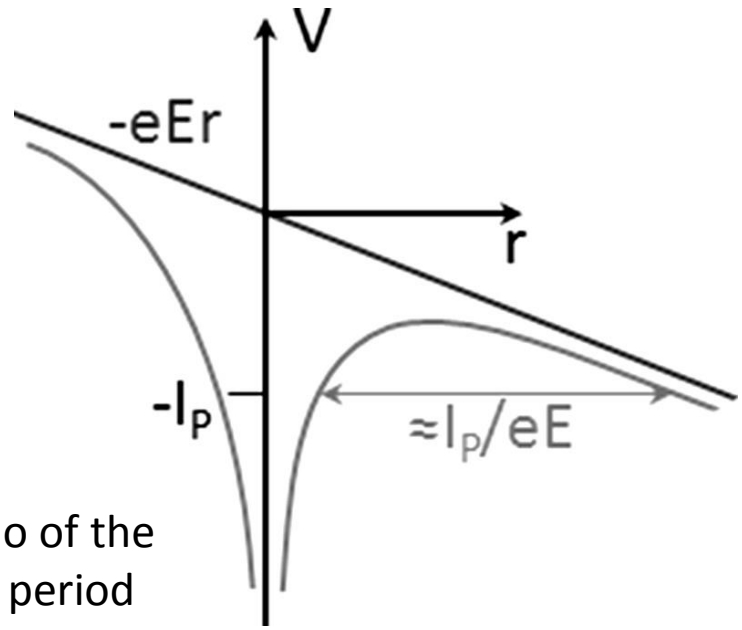
1 a.u. = 3.51x10^{16} W/cm^2

Hydrogen atom (IP=0.5 a.u.) : $I_{laser} = 0.0039$ a.u. = 1.4x10^{14} W/cm^2

Below $I_{laser,OTB}$ the electron can escape the atom by tunneling through the Coulomb + laser electric field potential, provided that the potential is sufficiently quasi-static

This condition is expressed by the Keldysh parameter γ

$$\gamma = \sqrt{\frac{IP}{2U_p}} = \frac{\tau_{tunneling}}{\tau_{laser}} << 1$$



The Keldysh parameter can be interpreted as the ratio of the time it takes the electron to tunnel out and the laser period

Tunneling formulas

Provided suitable approximations are made, the rate of tunnel ionization can be described by simple formulas

Strong field approximation:
Assume that after the ionization process the interaction of the electron with the core is negligible, and that the photoelectron only interacts with the laser electric field

Adiabatic approximation:
Assume that in the presence of the laser field the atom remains in the lowest available state, and that no population is transferred to excited states

Single active electron approximation:
Assume only the most weakly bound electron is ionized

Tunneling formulas

In the adiabatic approximation, the ionization rate at time t, when the electric field equals E(t), is given by $\Gamma_{DC}(E(t))$

Ground state hydrogenic atom:

$$\Gamma_{DC}(E) = \frac{4Z^5}{E} exp\left(-\frac{2Z^3}{3E}\right)$$

Non-hydrogenic atoms in arbitrary states:

$$\kappa = (2IP)^{1/2}$$

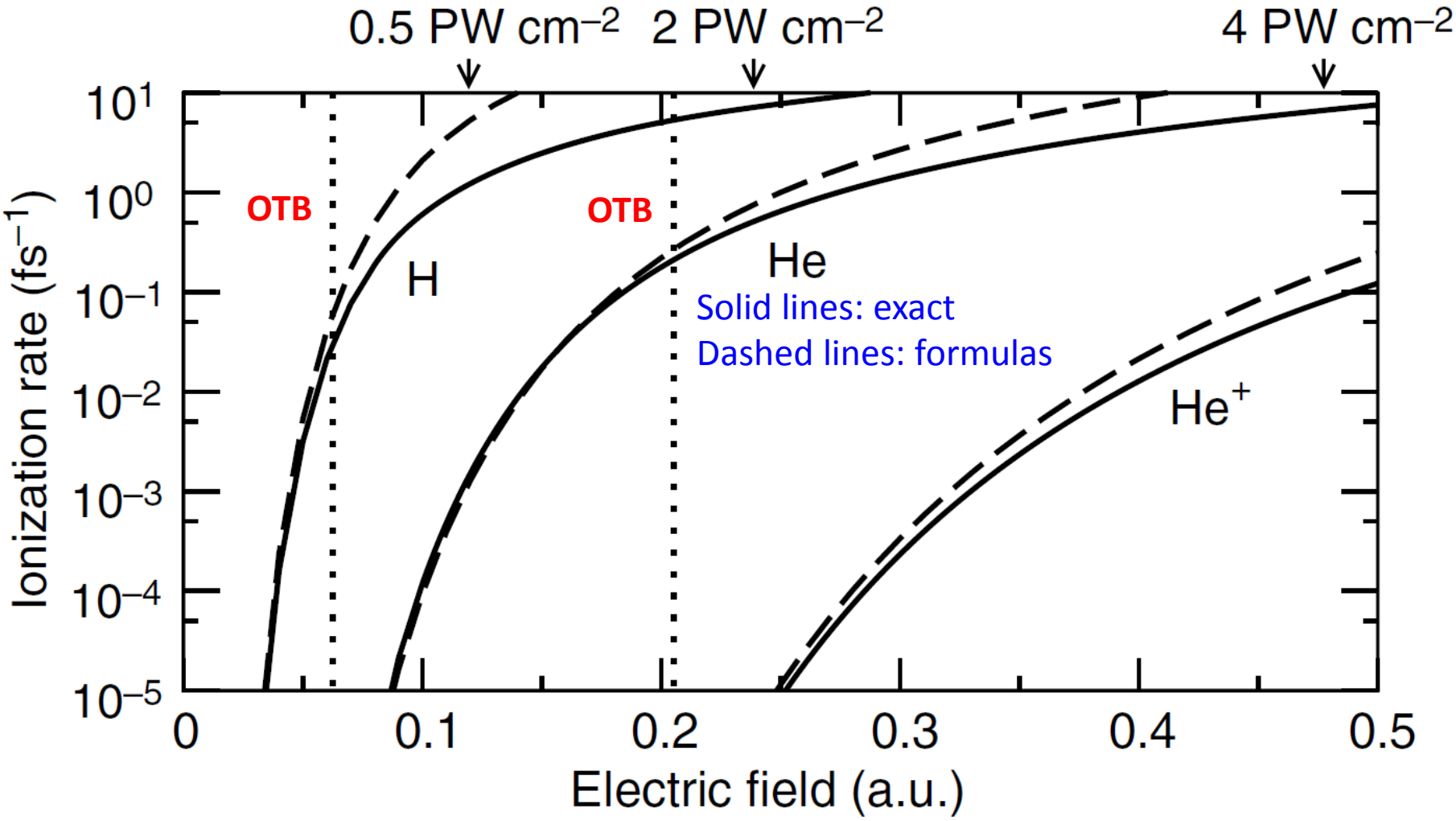
$$\Gamma_{DC}(E) = C_{as}^2 A(l,m) \frac{\kappa^2}{2} \left(\frac{2\kappa^3}{E}\right)^{\frac{2Z_c}{\kappa}-|m|-1} exp\left(-\frac{2\kappa^3}{3E}\right)$$

$$A(l,m) = \frac{2l+1}{2^{|m|}|m|!} \frac{(l+|m|)!}{(l-|m|)!} \qquad C_{as} = \left[\frac{2^{2n^*}}{n^*\Gamma(n^*+l+1)\,\Gamma(n^*-l)}\right]^{1/2}$$

C.J. Joachain, N.J. Kylstra and R.M. Potvliege, Atoms in Intense Laser Fields, (Cambridge University Press, 2012)

NB Simplified to ADK by Ammosov-Delone-Krainov

Tunneling formulas



C.J. Joachain, N.J. Kylstra and R.M. Potvliege, Atoms in Intense Laser Fields, (Cambridge University Press, 2012)

After ionization: Propagation assuming the strong-field approximation (SFA)

Assume that the electron does not feel the ion anymore as soon as it has tunneled out (strong field approximation)
Assume, moreover, that the Coulomb-free motion starts with v=0 at r=0, and that the laser amplitude is constant

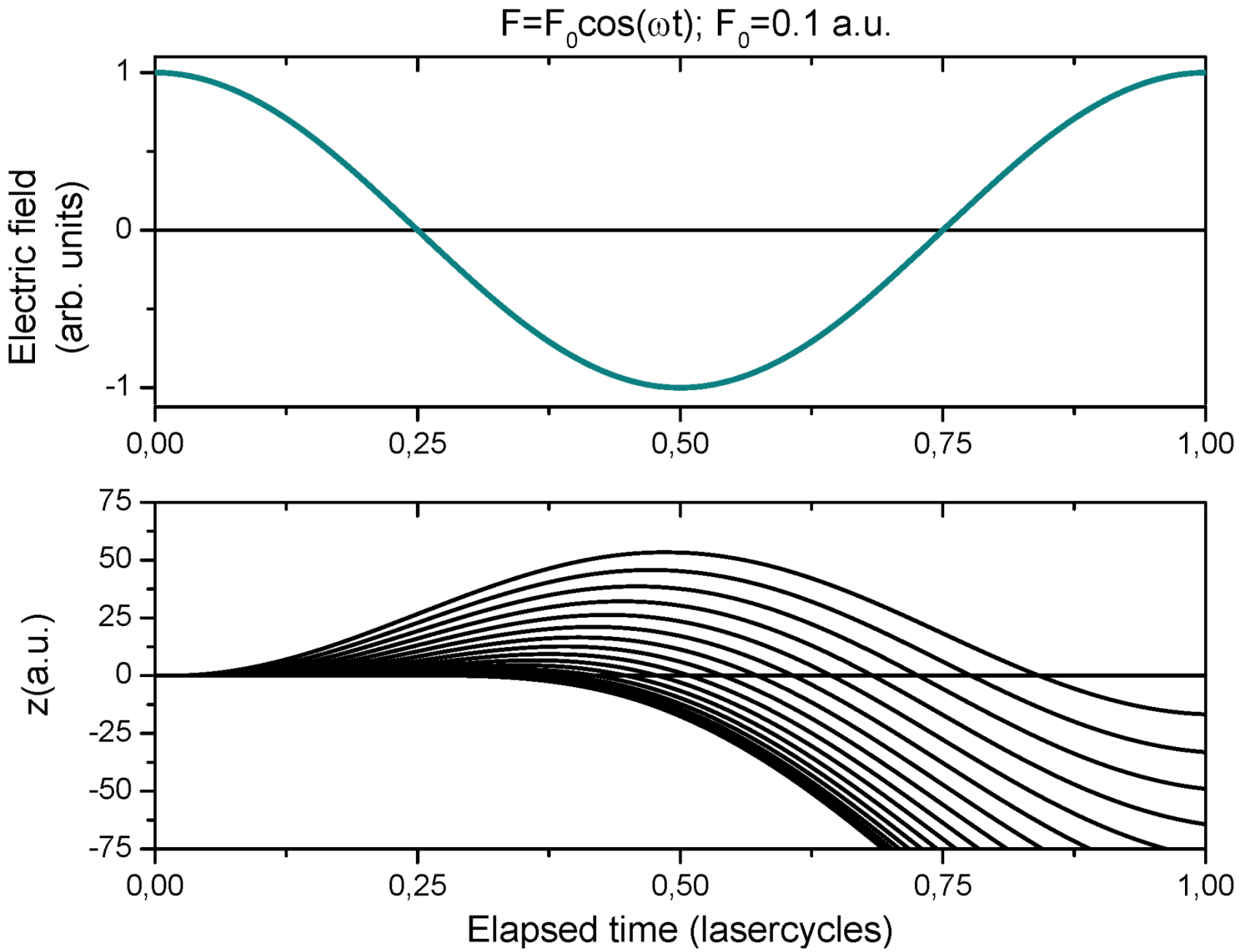
$$a(t) = (qE_0/me)cos\omega t$$

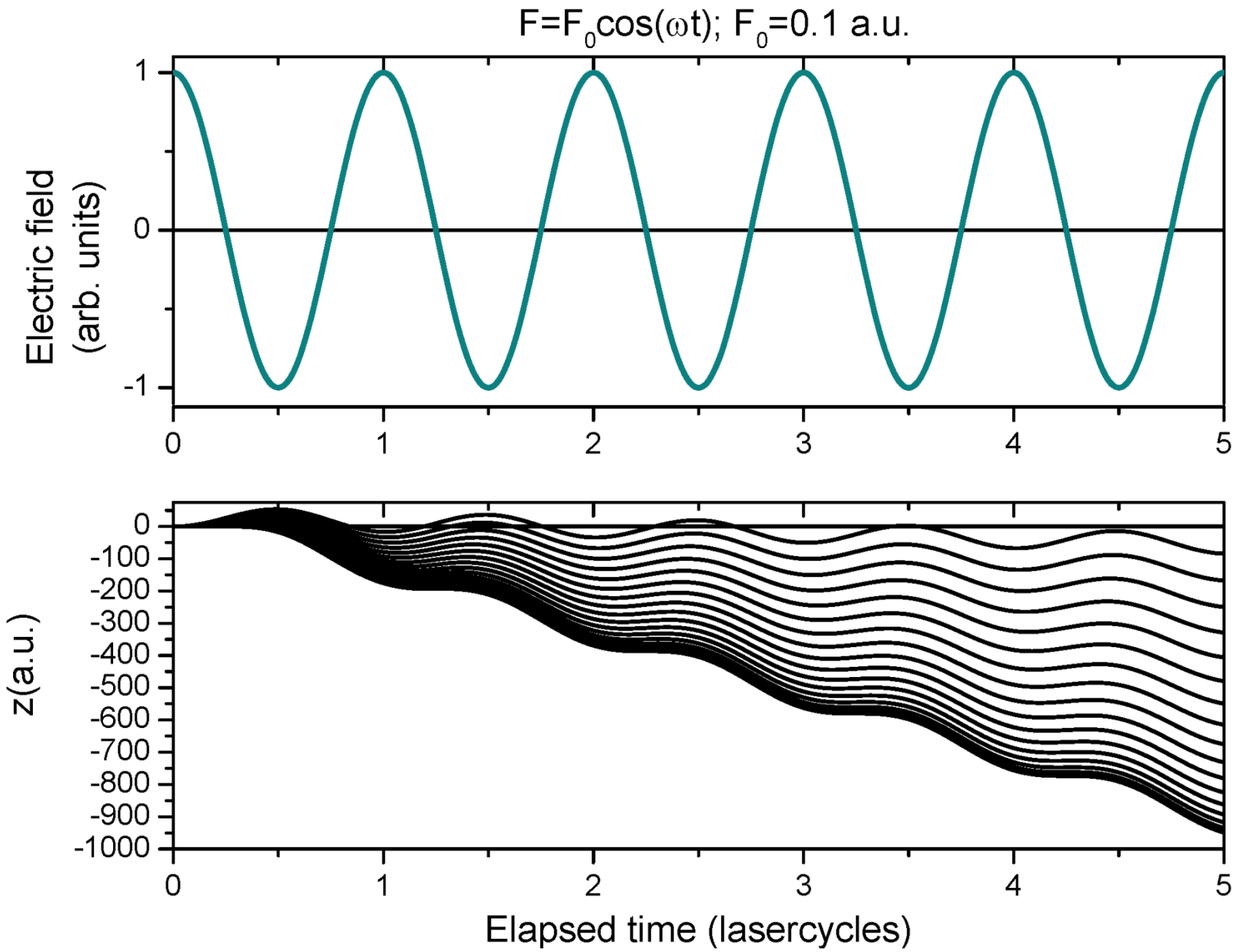
$$v(t) = v_0 sin\omega t + v_{0z} \qquad v_0 = qE_0/m_e\omega$$

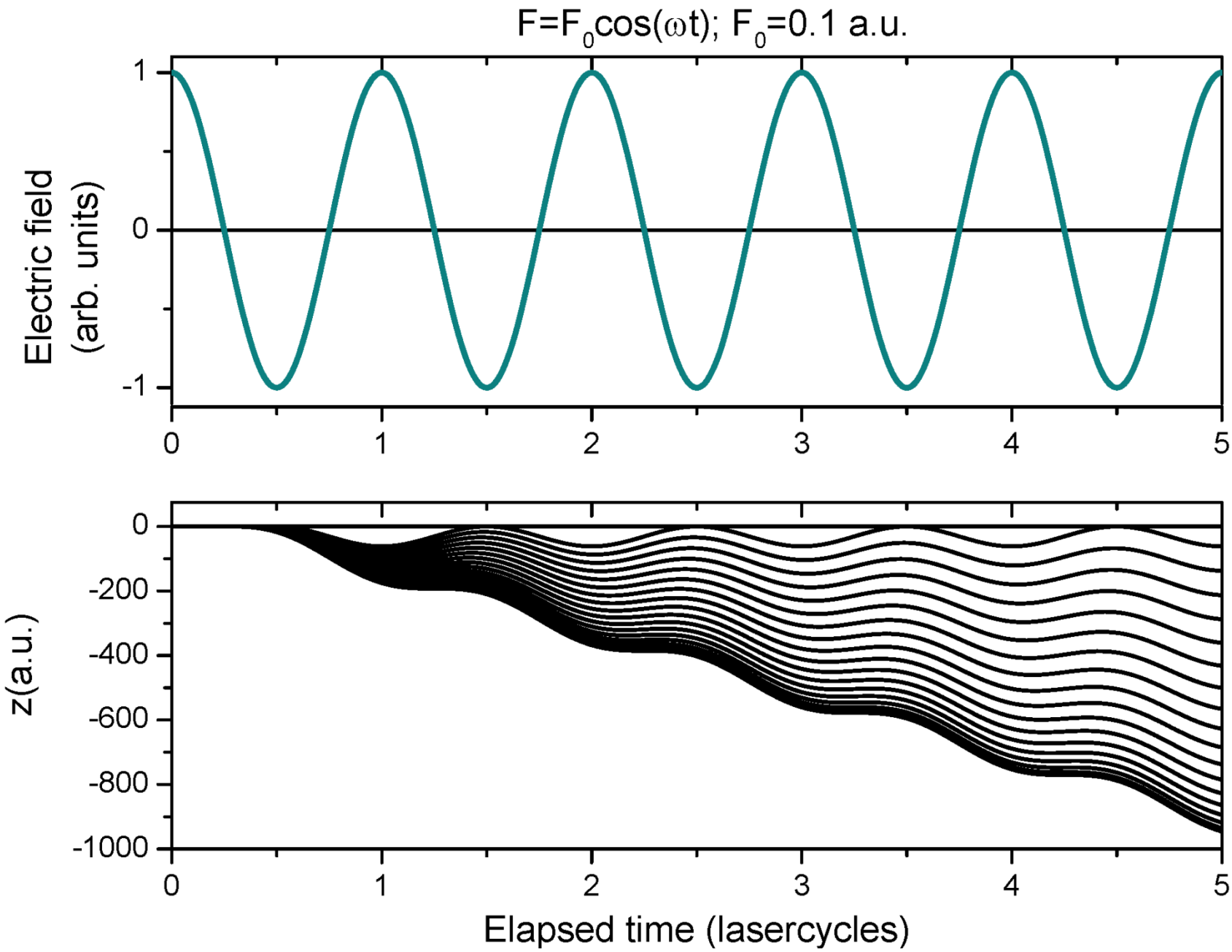
$$z(t) = z_0(-cos\omega t) + v_{0z}t + z_{0z} \qquad z_0 = qE_0/m_e\omega^2$$

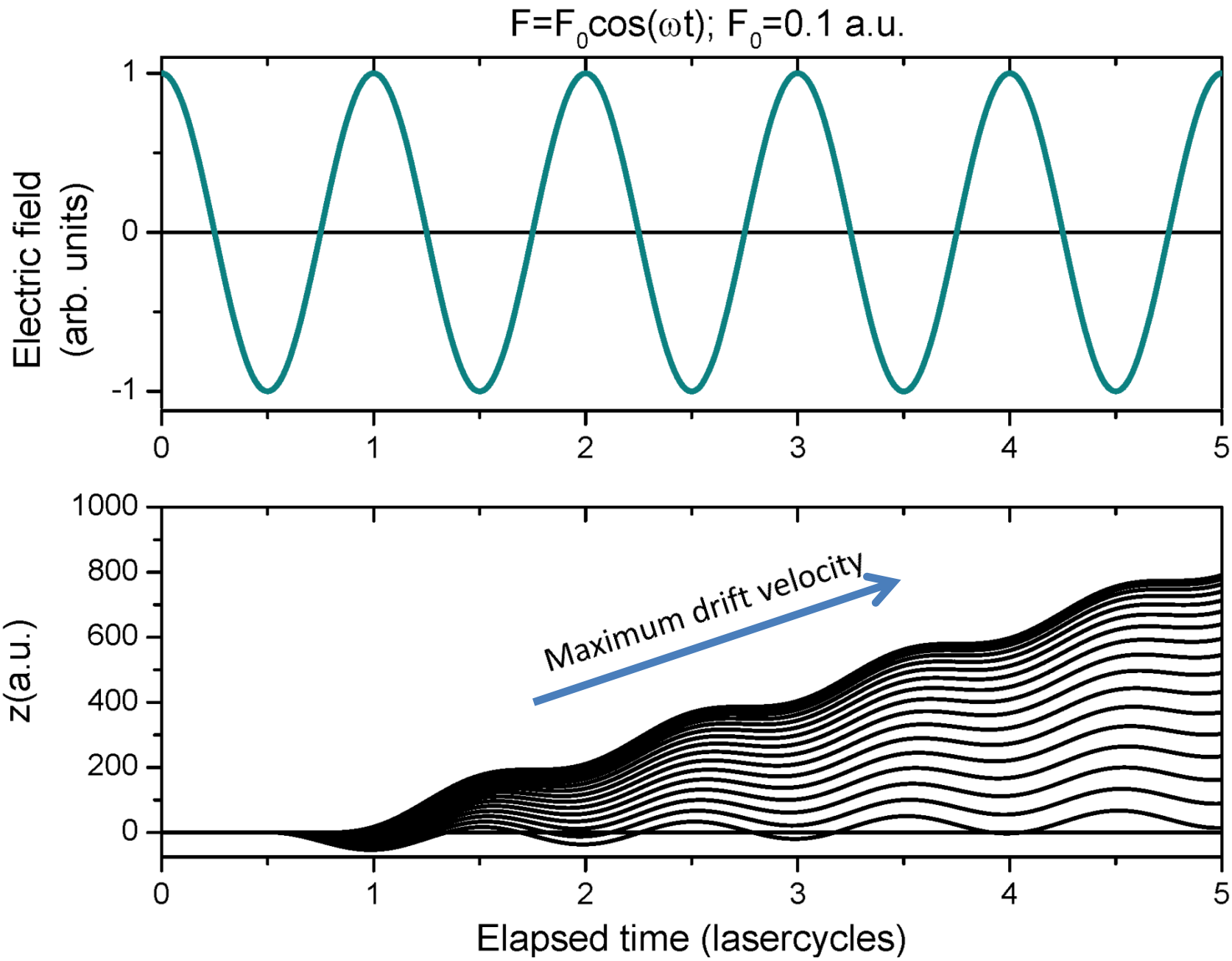
N.B. $E(t) = -dA(t)/dt, i.e. v_0 = qA_0/me$

P. Corkum. Phys. Rev. Lett. 71, 1994 (1993)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0,00
0,25
0,50
0,75
1,00
z(a.u.)
75
50
25
0
-25
-50
-75
0,00
0,25
0,50
0,75
1,00
Elapsed time (lasercycles)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0
1
2
3
4
5
z(a.u.)
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
0
1
2
3
4
5
Elapsed time (lasercycles)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0
1
2
3
4
5
z(a.u.)
0
-200
-400
-600
-800
-1000
Elapsed time (lasercycles)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0
1
2
3
4
5
z(a.u.)
1000
800
600
400
200
0
Maximum drift velocity
Elapsed time (lasercycles)

Maximum drift velocity

$$v_\infty(t_{ionization}) = \int_{t_{ionization}}^{\infty} a(t)dt =$$

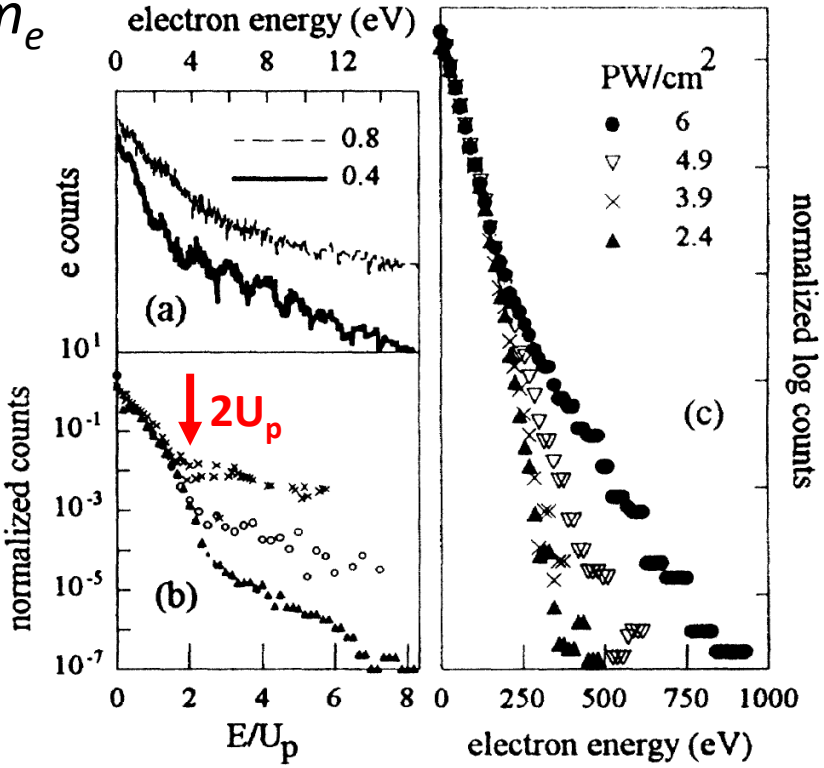
$$\int_{t_{ionization}}^{\infty} dt\left(\frac{qE(t)}{m_e}\right)cos\omega t \sim \frac{qE(t)}{m_e\omega} sin\omega t\Big|_{t_{ionization}}^{\infty} =$$

$$= \frac{-qE_0}{m_e\omega}\sin(\omega t_{ionization}) = qA(t_{ionization})/m_e$$

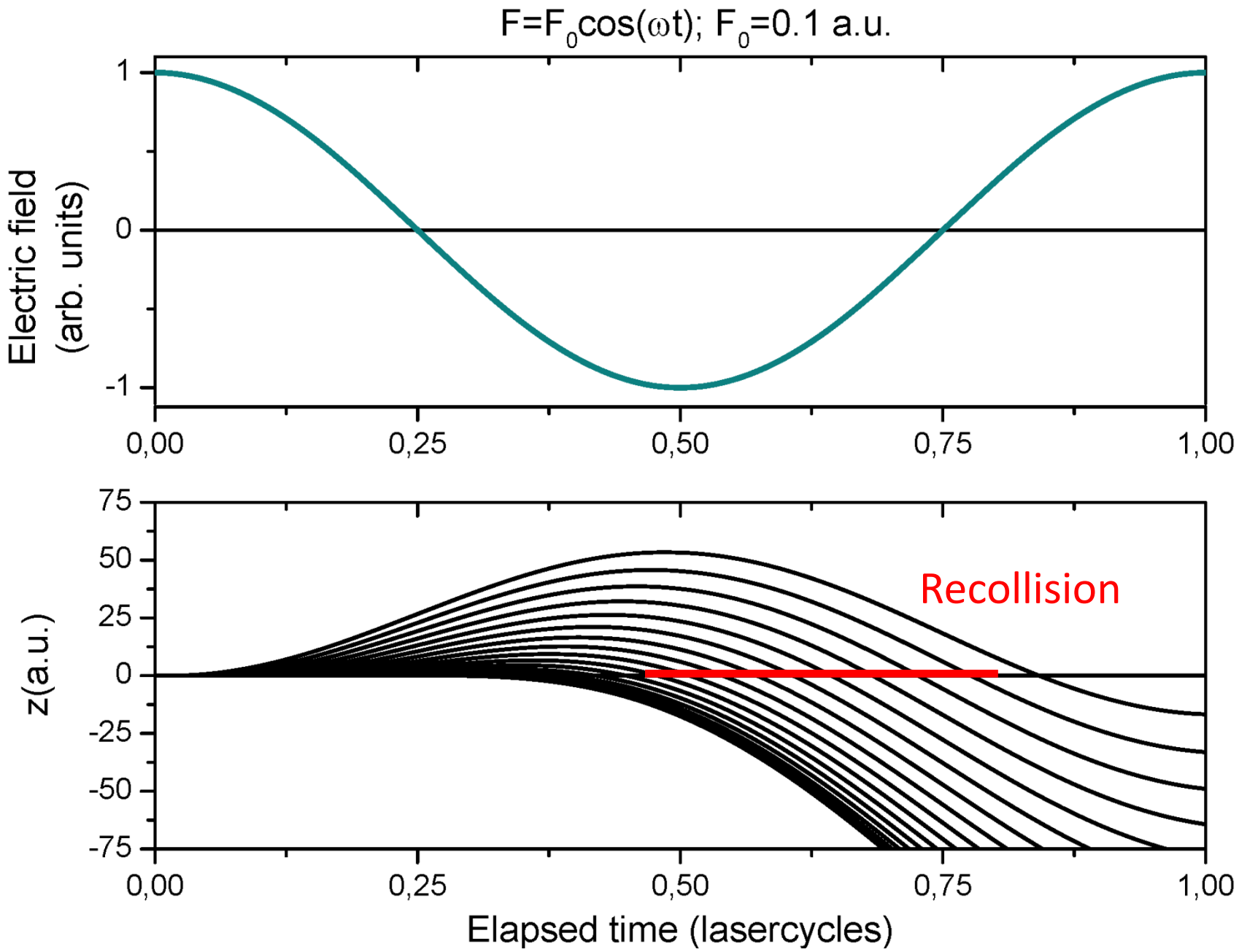
$$E_{k,max} = \frac{1}{2}m_e v_{max}^2 = \frac{q^2E_0^2}{2m_e\omega^2} = \frac{q^2A_0^2}{2m_e}$$

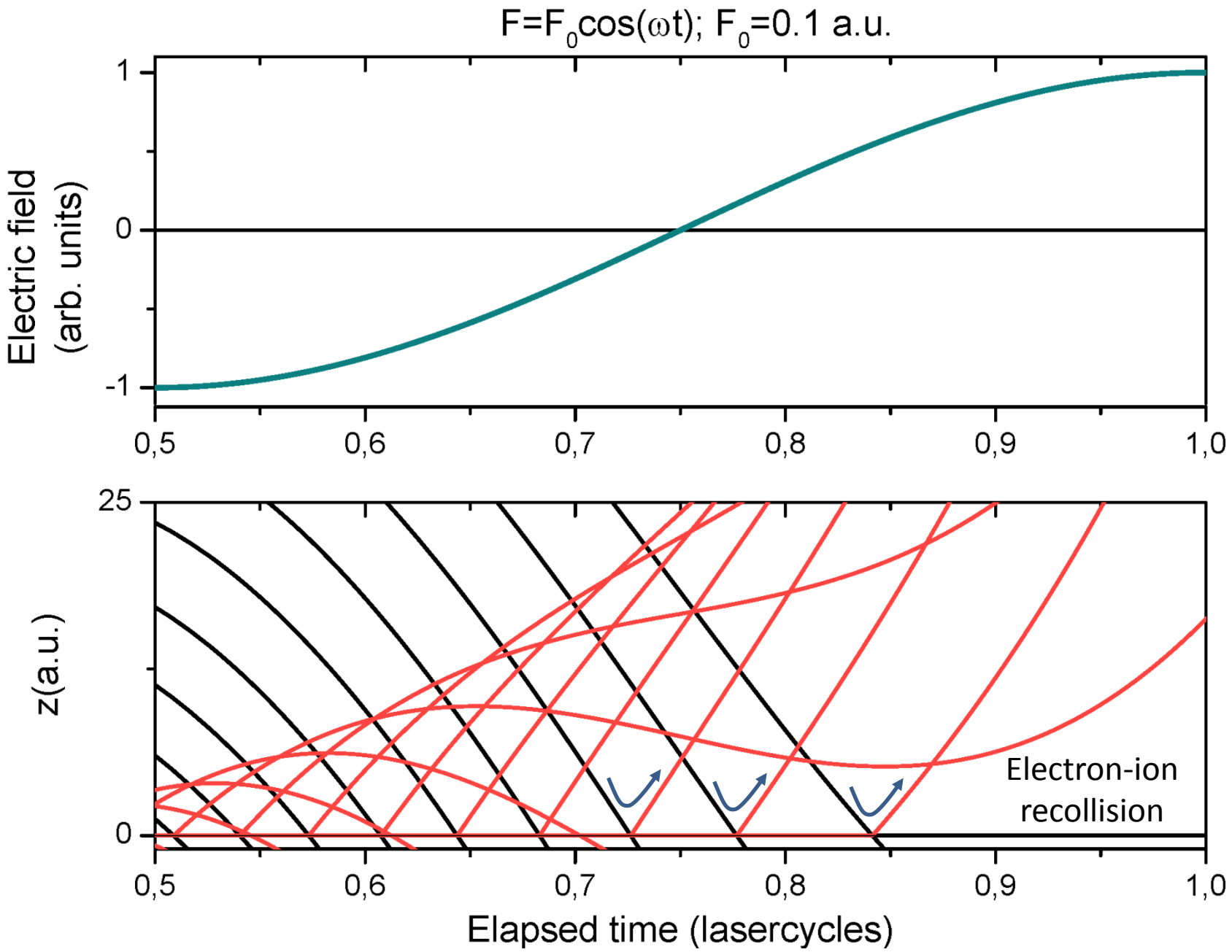
$2U_p$

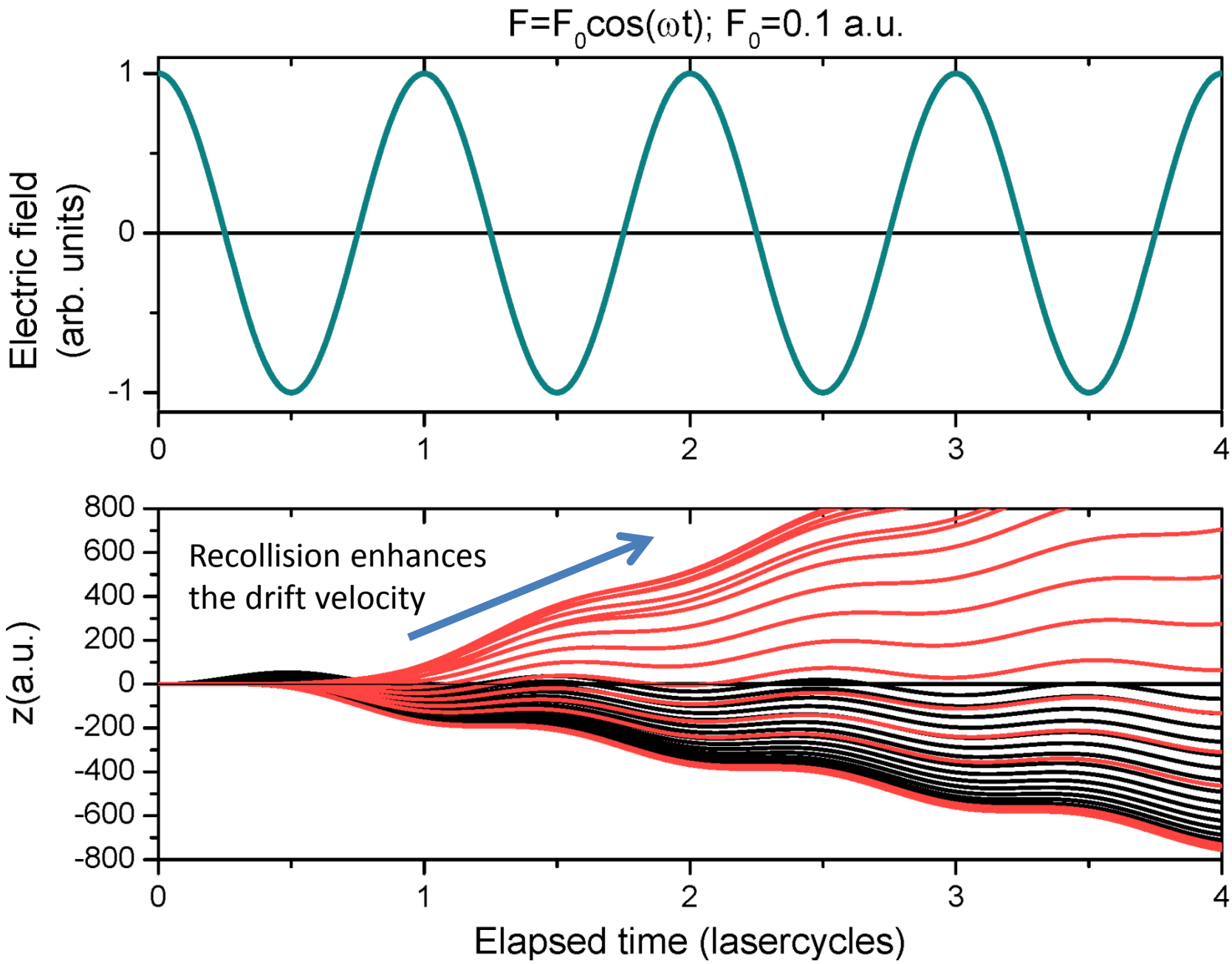
The photoelectron spectrum also contains energies > $2U_p$

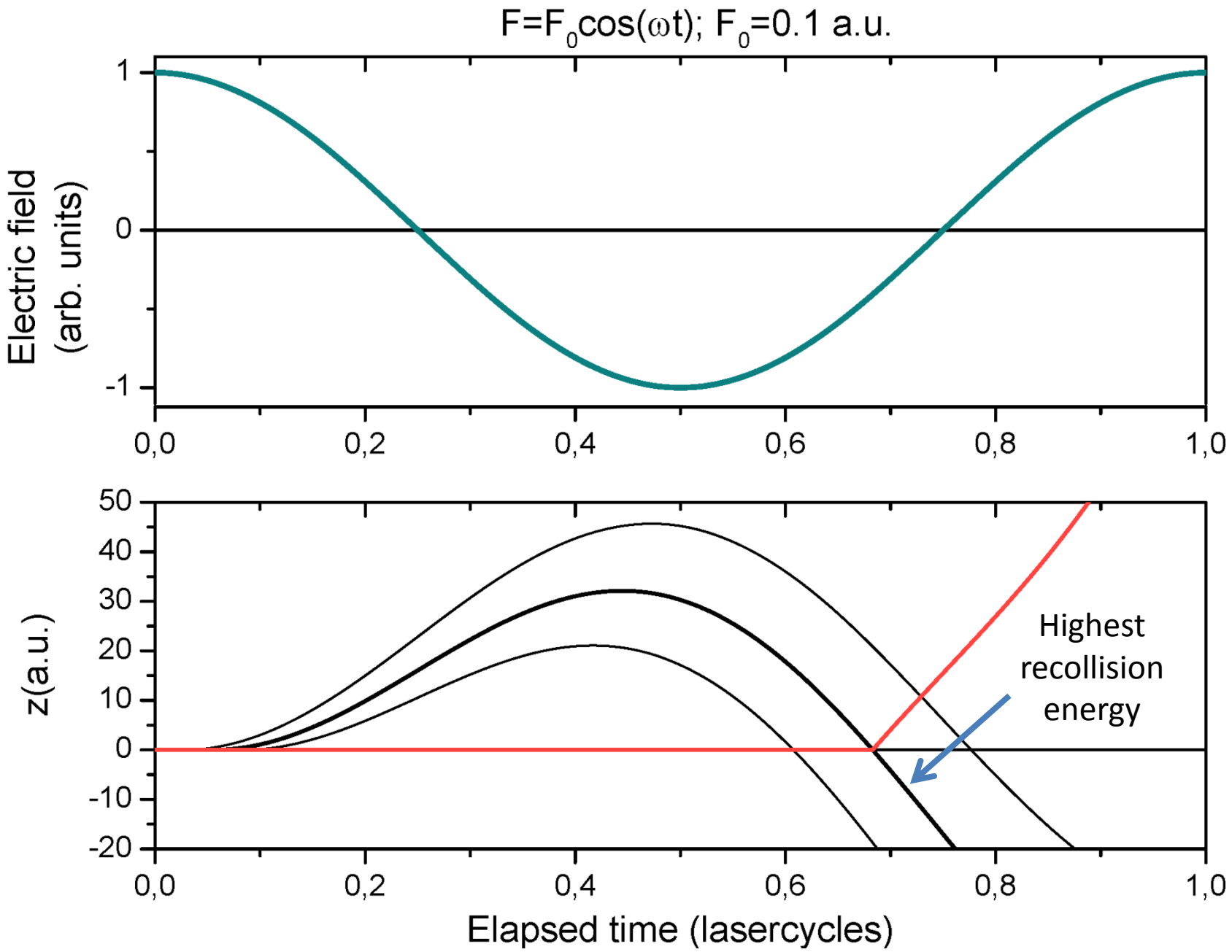


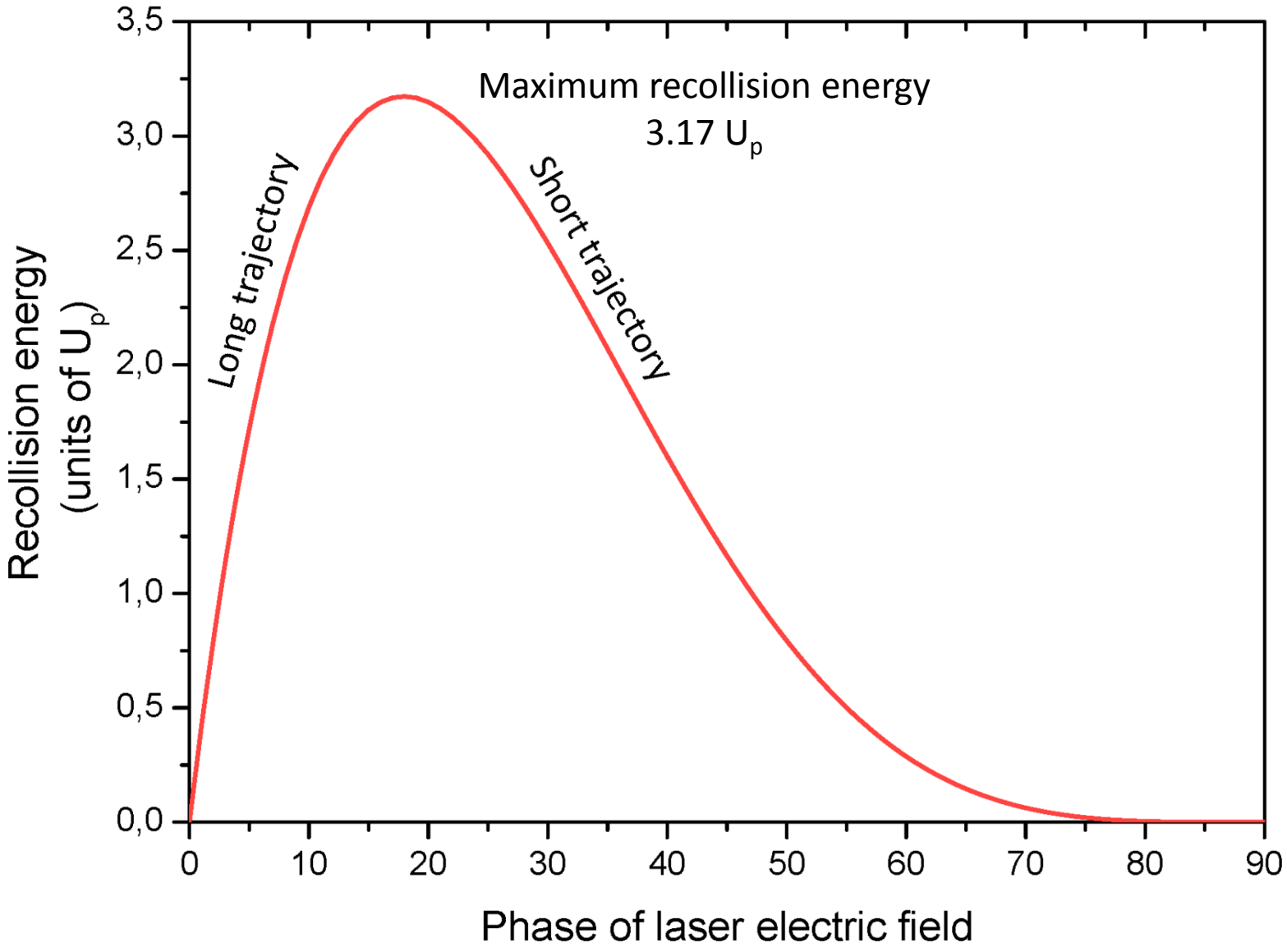
B. Walker et al., Phys. Rev. Lett. 73, 1227 (1994)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0,00
0,25
0,50
0,75
1,00
z(a.u.)
75
50
25
0
-25
-50
-75
Recollision
Elapsed time (lasercycles)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0,5
0,6
0,7
0,8
0,9
1,0
25
z(a.u.)
0
Electron-ion recollision
Elapsed time (lasercycles)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0
1
2
3
4
800
600
400
200
0
-200
-400
-600
-800
z(a.u.)
Recollision enhances the drift velocity
Elapsed time (lasercycles)


F=F0cos(ωt); F0=0.1 a.u.
Electric field (arb. units)
1
0
-1
0,0
0,2
0,4
0,6
0,8
1,0
z(a.u.)
50
40
30
20
10
0
-10
-20
Highest recollision energy
Elapsed time (lasercycles)

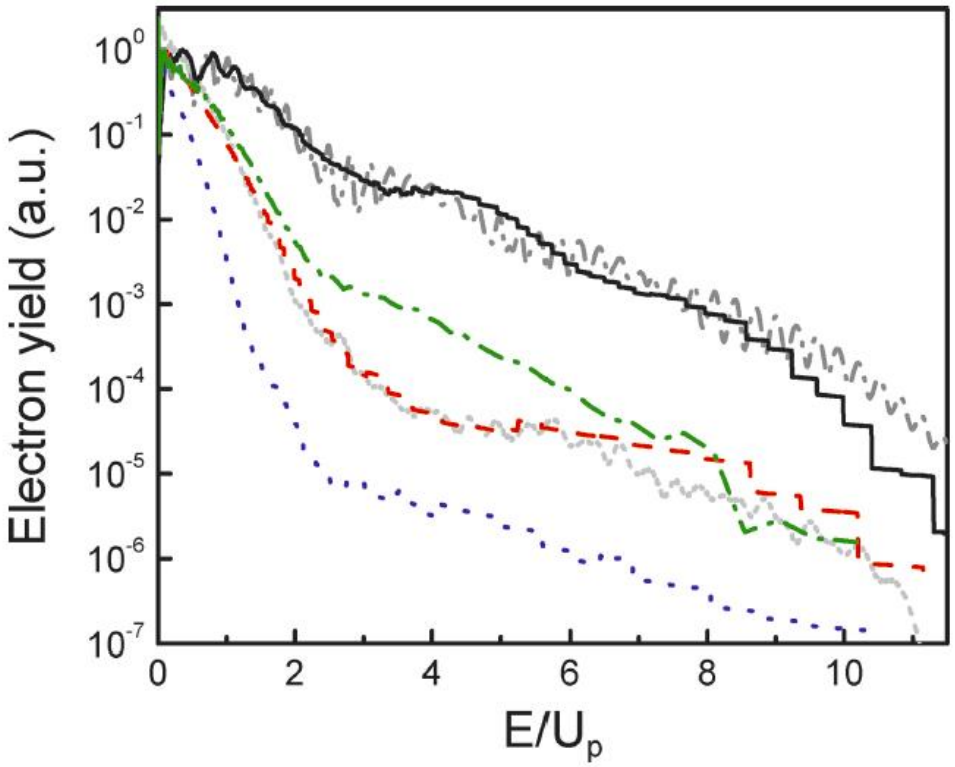

Maximum recollision energy
3.17 U_p
Long trajectory
Short trajectory
Recollision energy
(units of U_p)
Phase of laser electric field
3,5
3,0
2,5
2,0
1,5
1,0
0,5
0,0
0
10
20
30
40
50
60
70
80
90

Recollision trajectories

The highest possible return energy is 3.17 U_p = 0.7925 $q^2A_0^2/m_e$, corresponding to a velocity of 1.259 qA_0/m_e. This recollision occurs near a zero crossing of the field.

When the recollision flips the sign of the velocity, the field increases the velocity to appr. -2.259 qA_0/m_e , corresponding to an energy of 10.2 U_p

ATI of Argon at 0.8 µm (black line), 1.3µm (green line), 2 µm (red line), and 3.6µm (blue line) at an intensity of 0.08 PW/cm2.



Colosimo, P. et al., Nat. Phys., 4, 386 (2008)

Canonical momentum

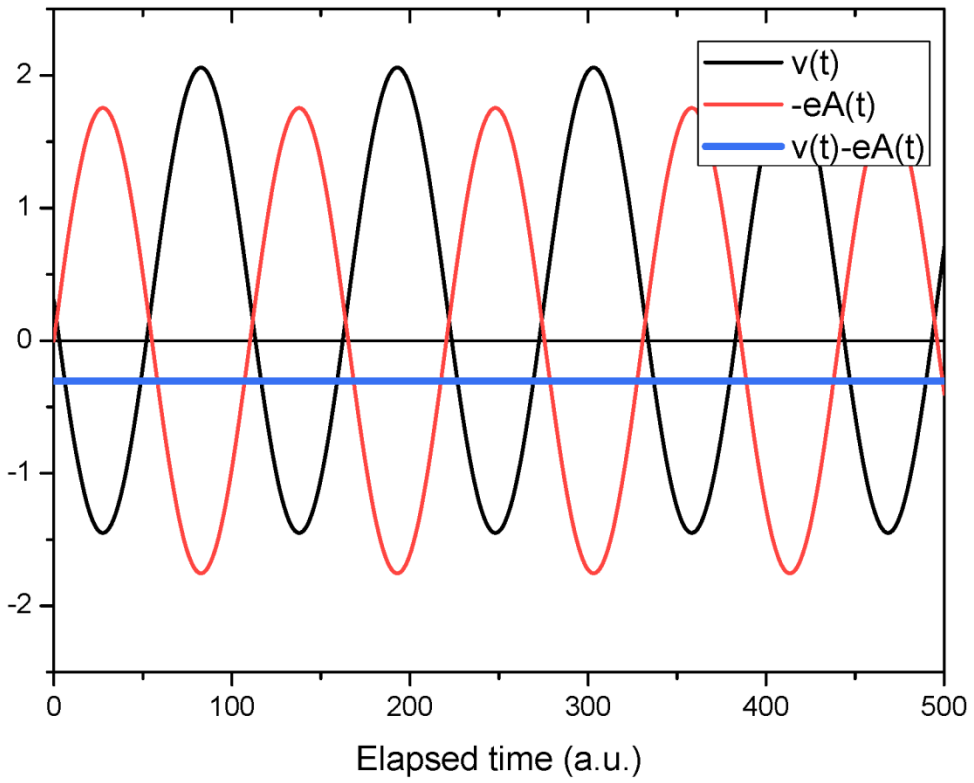
$$E(t) = E_0 \cos(\omega t) = -\frac{dA(t)}{dt} \qquad A(t) = -A_0 \sin(\omega t) + constant \qquad A_0 = \frac{E_0}{\omega}$$

$$v(t) = v_0 + \int_{t_0}^{t} a(t)dt = v_0 + \int_{t_0}^{t} \frac{-eE(t)}{m} dt = v_0 + \frac{e}{m}(A(t) - A(t_0))$$

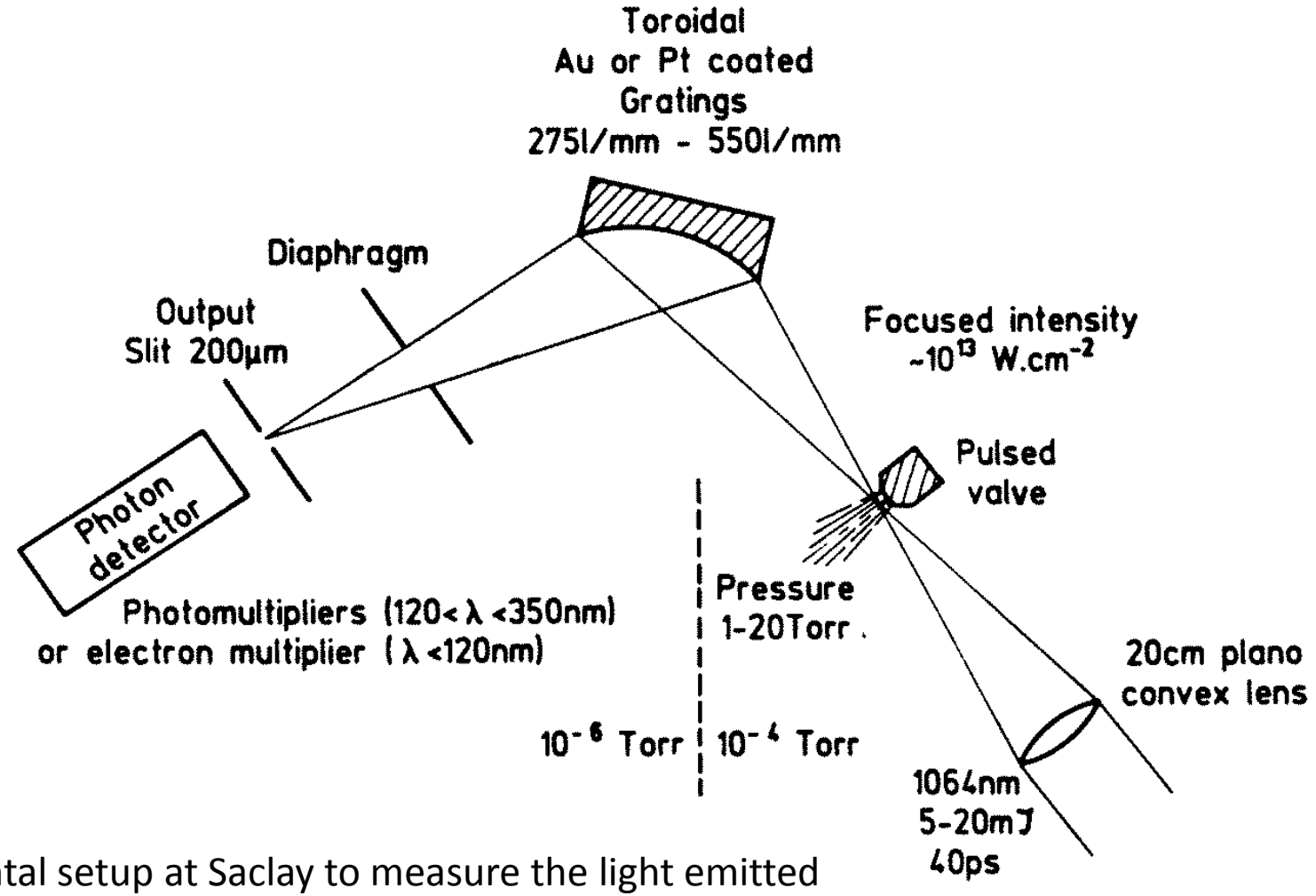
$$v(t) - \frac{e}{m}A(t) = v_0 - \frac{e}{m}A(t_0)$$

In a strong laser field the conserved quantity is the canonical momentum:

p = m**v**(t) – eA(t)



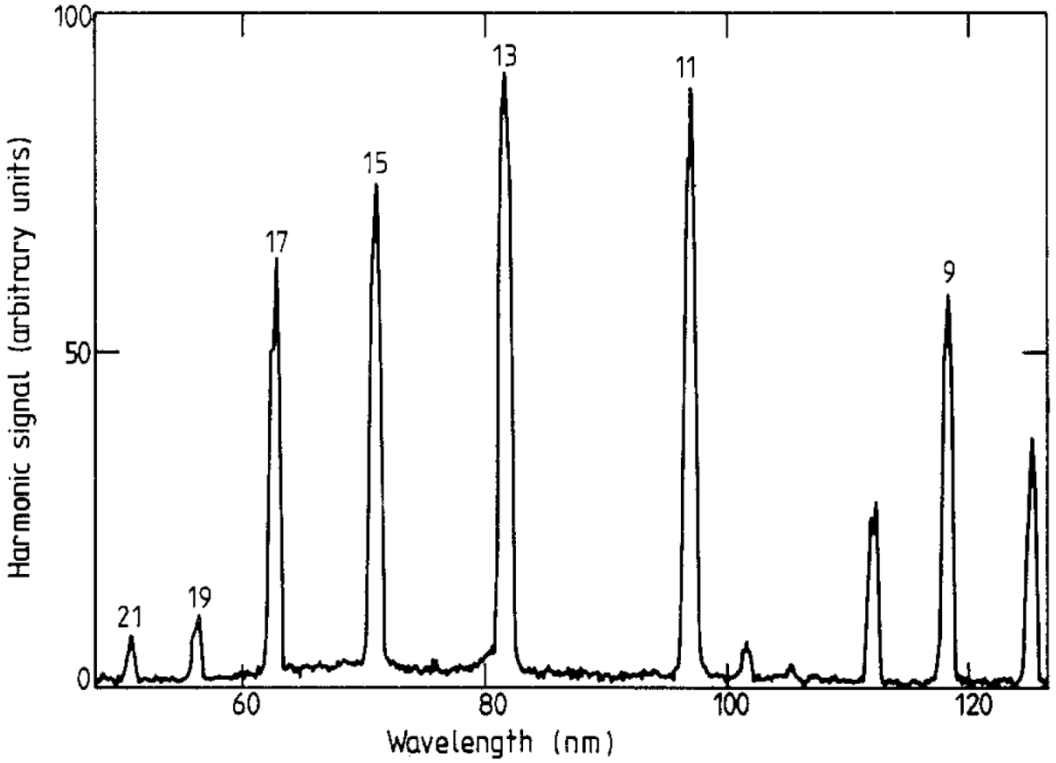
Mid-1980´s: studies of ATI

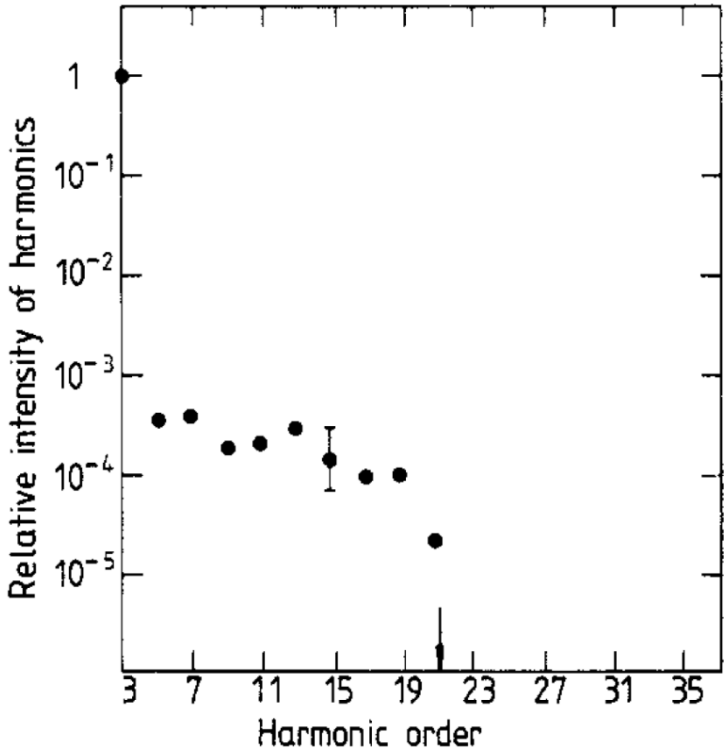


Experimental setup at Saclay to measure the light emitted during above-threshold ionization experiments

A. L´Huillier et al., in 'Atoms in Intense Laser Fields ', edited by Gavrila and Muller, (Academic Press, 1992)

Discovery of High-Harmonic Generation (HHG)



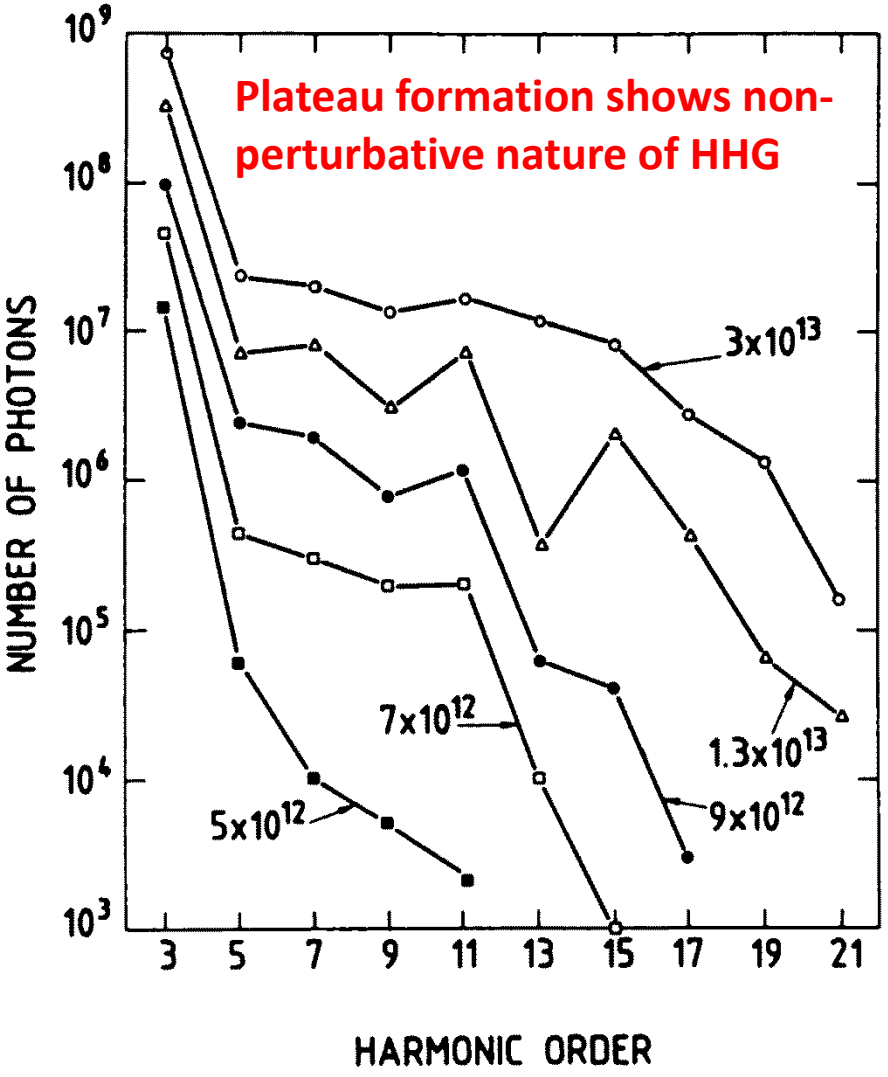


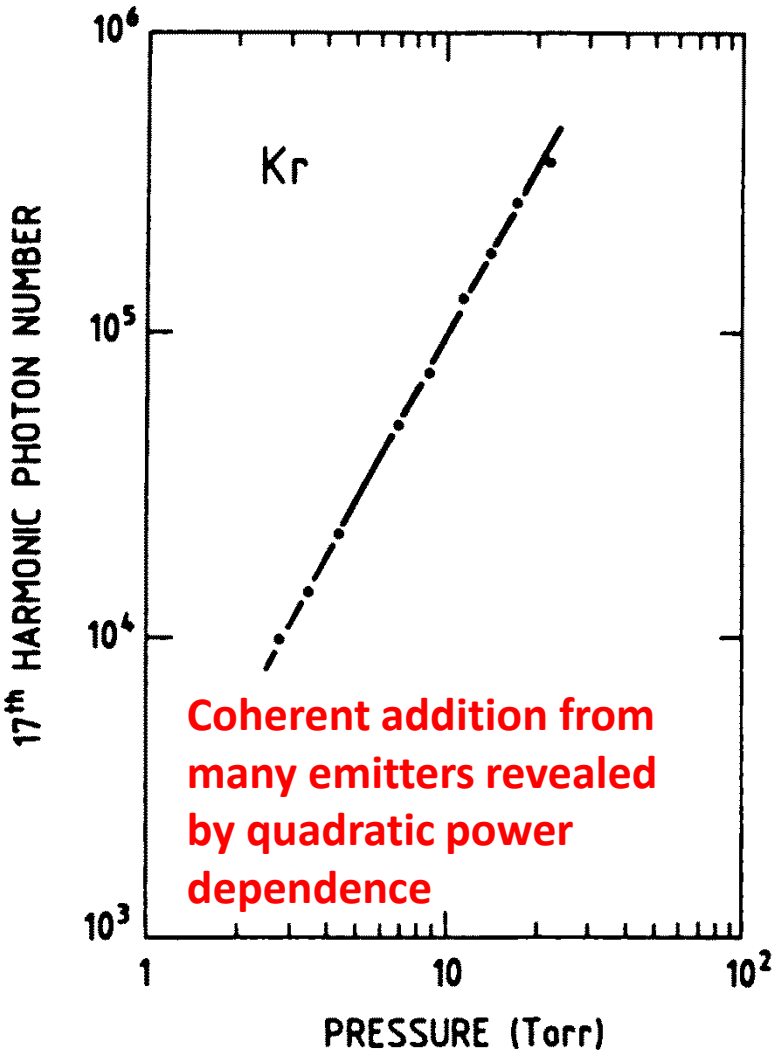
High-harmonic generation in Xe using a 30 ps, 1064 nm laser focused to ca. 10^{13} W/cm^2

M. Ferray et al., J. Phys. B 21 L31 (1988)

+ similar observations around the time in the Rhodes-group using 248 nm driver lasers

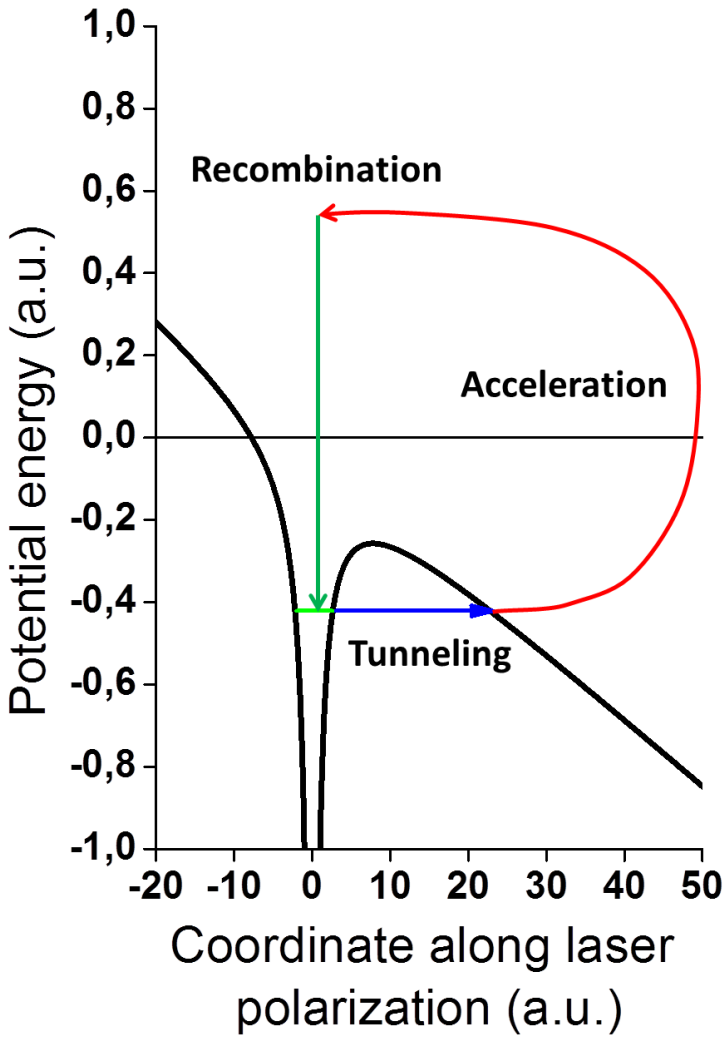
Intensity and pressure dependence

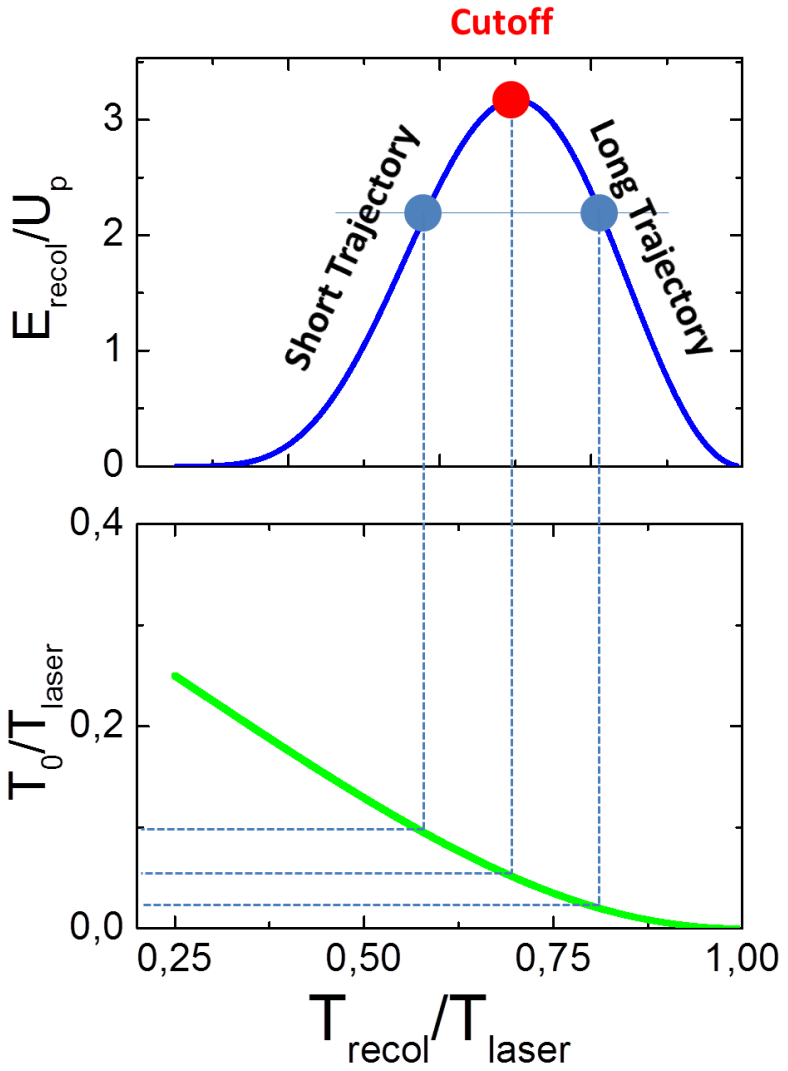




A. L´Huillier et al., in 'Atoms in Intense Laser Fields', edited by Gavrila and Muller, (Academic Press, 1992)

Cut-off law: $E_{cutoff} = IP + 3.17\,U_p$

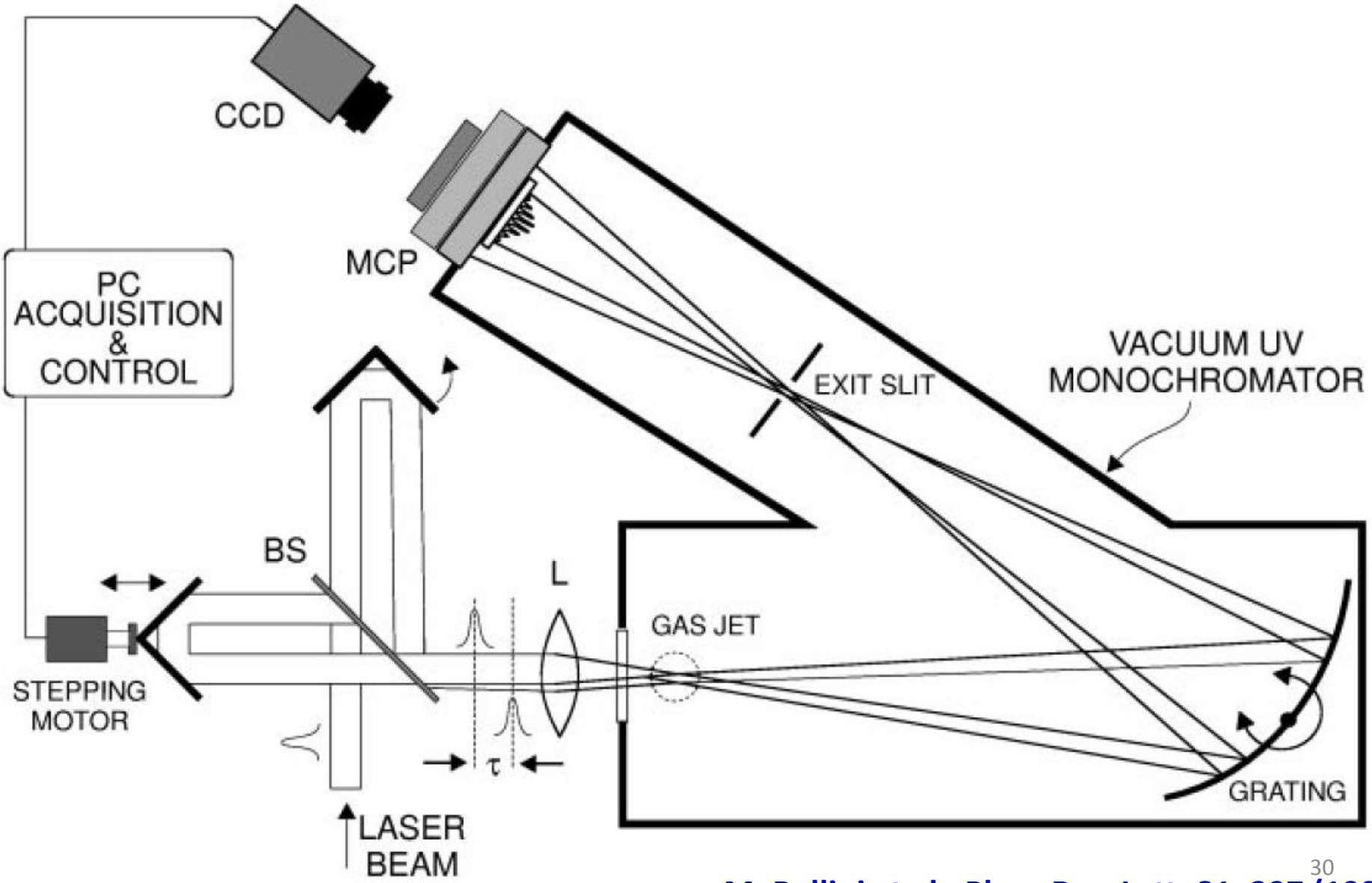




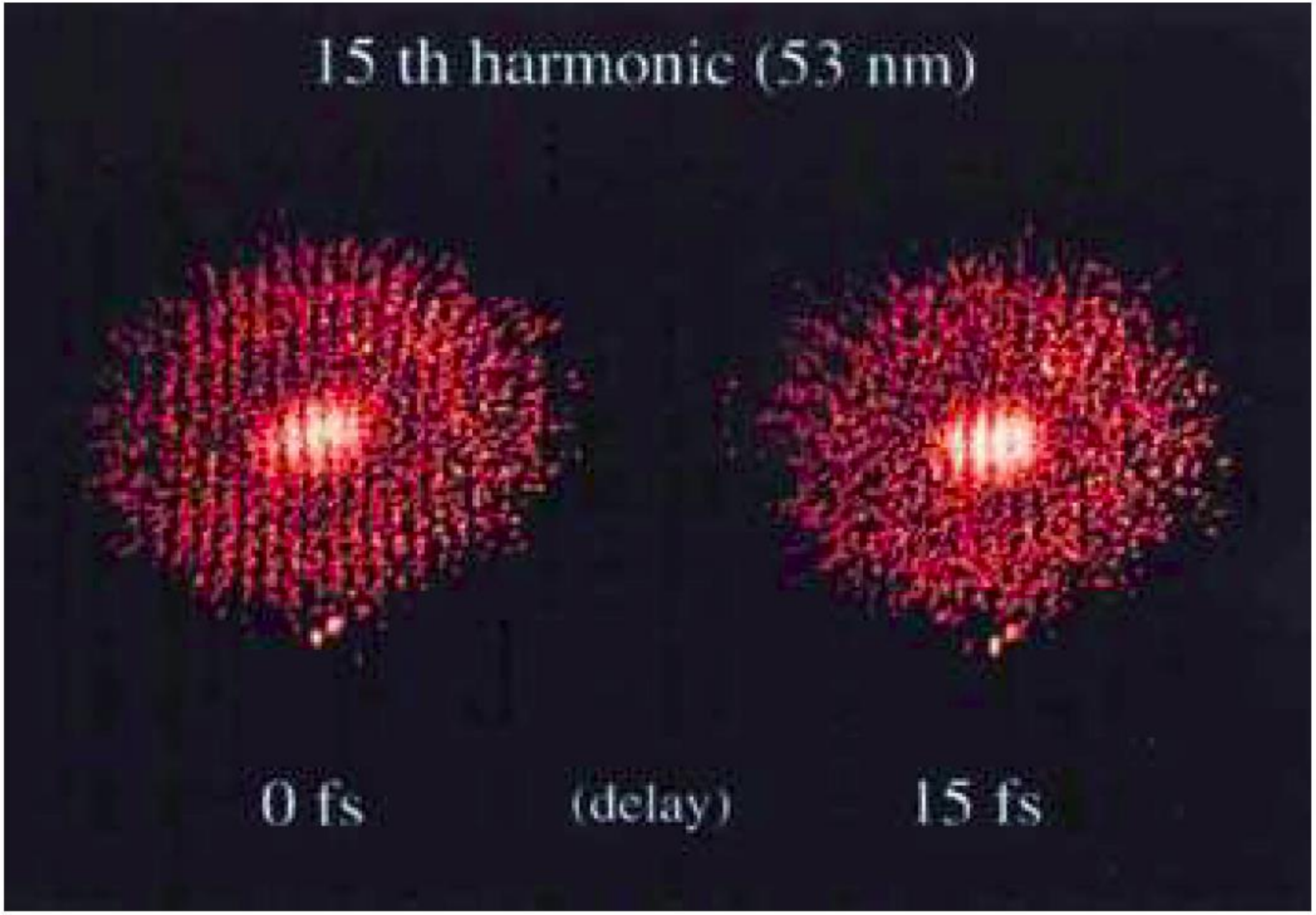
P. Corkum. Phys. Rev. Lett. 71, 1994 (1993)

The main triumph of the three-step model was that it explained the cut-off law

HHG via short and long trajectories



M. Bellini et al., Phys. Rev. Lett. 81, 297 (1998)



M. Bellini et al., Phys. Rev. Lett. 81, 297 (1998)

Phase-matching

In the HHG medium, the driver laser and the generated harmonics move with a different phase velocity

$$v_{phase} = \lambda\nu = \frac{\lambda\omega}{2\pi} = \frac{\omega}{k}$$

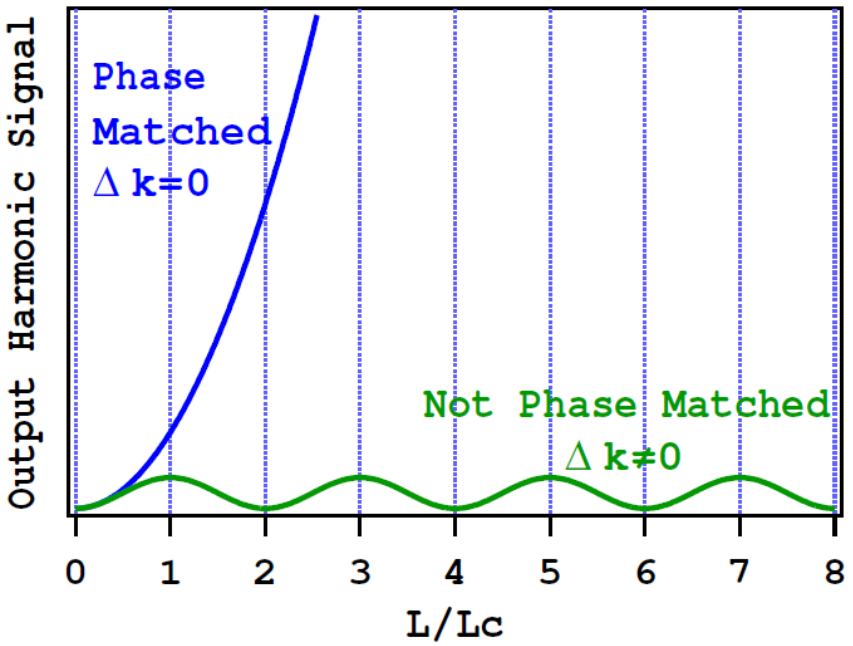
ω laser frequency

k laser wavevector

$$v_1 = \frac{\omega}{k_1} \qquad v_q = \frac{q\omega}{k_q}$$

Phase matching: $\Delta k_q = k_q - qk_1 = 0$

Coherence length: $L_c = \frac{\pi}{\Delta k}$



Thesis Amy Lytle, JILA 2008

Phase-matching

~pressure

$$\Delta k = \Delta k_a + \Delta k_{fe} + \Delta k_{foc} + \Delta k_{traj}$$

~intensity

In the HHG medium, phase matching is affected by

(i) The density of neutral gas $\Delta k_a = \frac{q\omega}{2\varepsilon_0 c} N\left[\alpha_{pol}(q\omega) - \alpha_{pol}(\omega)\right]$

(ii) The density of free electrons $\Delta k_{fe} = \frac{qe^2}{2\varepsilon_0 cm\omega} N_e$

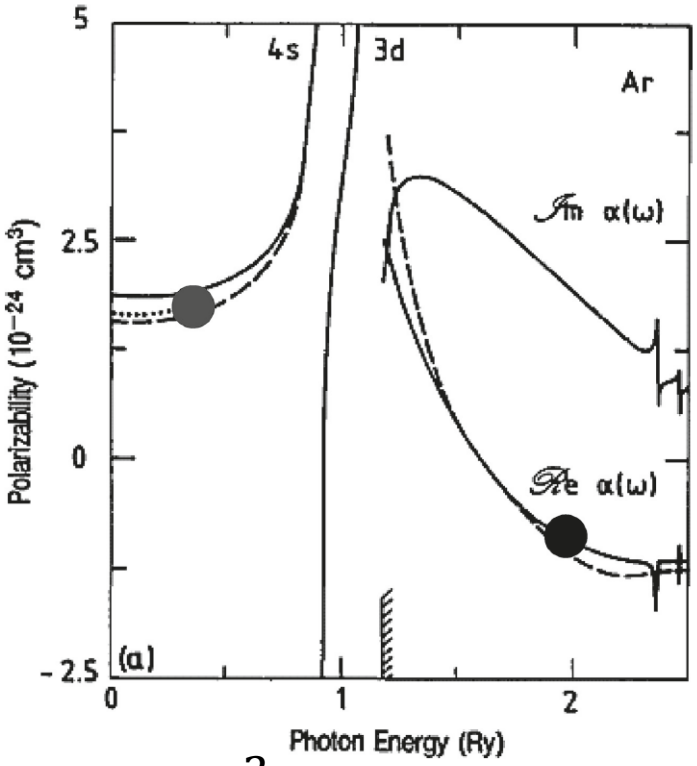
(iii) The laser focusing (no waveguiding assumed) $\Delta k_{foc} \sim \frac{q}{z_0}$

(iv) The electron trajectories $\Delta k_{traj} = \alpha_{traj} \frac{\partial I}{\partial z}$

Serendipity in Phase-matching

$$\Delta k_a = \frac{q\omega}{2\varepsilon_0 c} N\left[\alpha_{pol}(q\omega) - \alpha_{pol}(\omega)\right]$$

<0

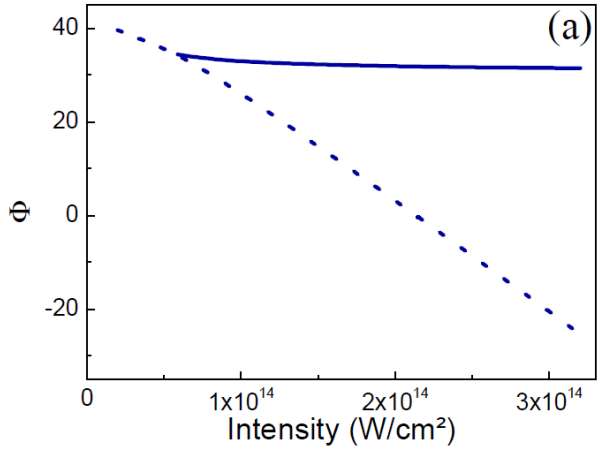


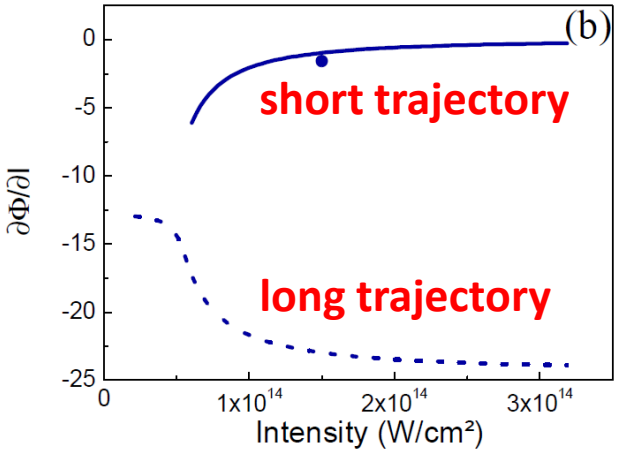
$$\Delta k_{fe} = \frac{qe^2}{2\varepsilon_0 cm\omega} N_e$$ >0

L'Huillier et al., JOSA B 7, 529 (1990)

$$\Delta k_{traj} = \alpha_{traj} \frac{\partial I}{\partial z}$$

$$\alpha_{traj} = -\frac{\partial \Phi}{\partial I} > 0$$



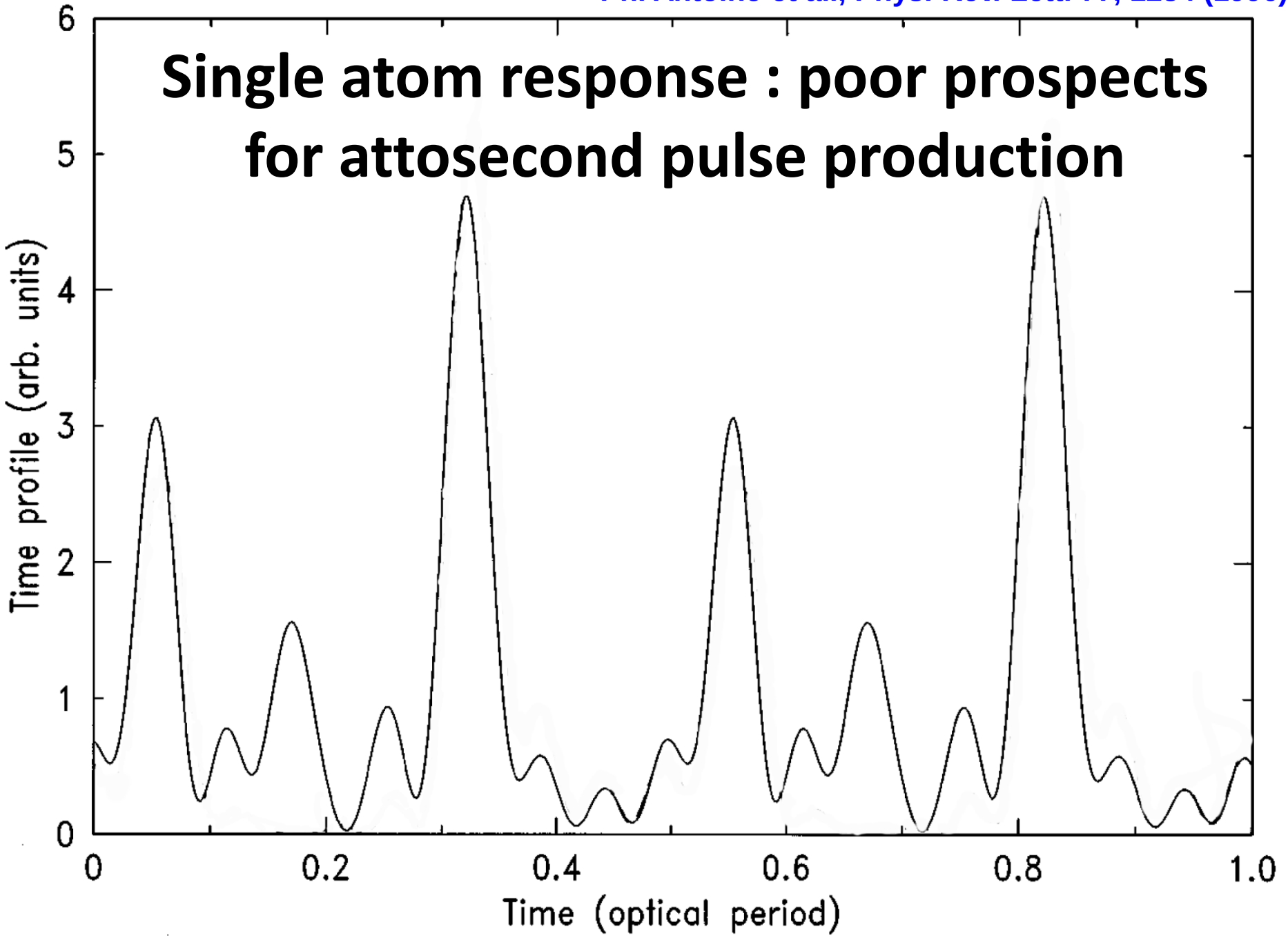


Short and long trajectory have different phase-matching conditions!

Varju et al., J. Mod. Opt. 2, 379 (2004)

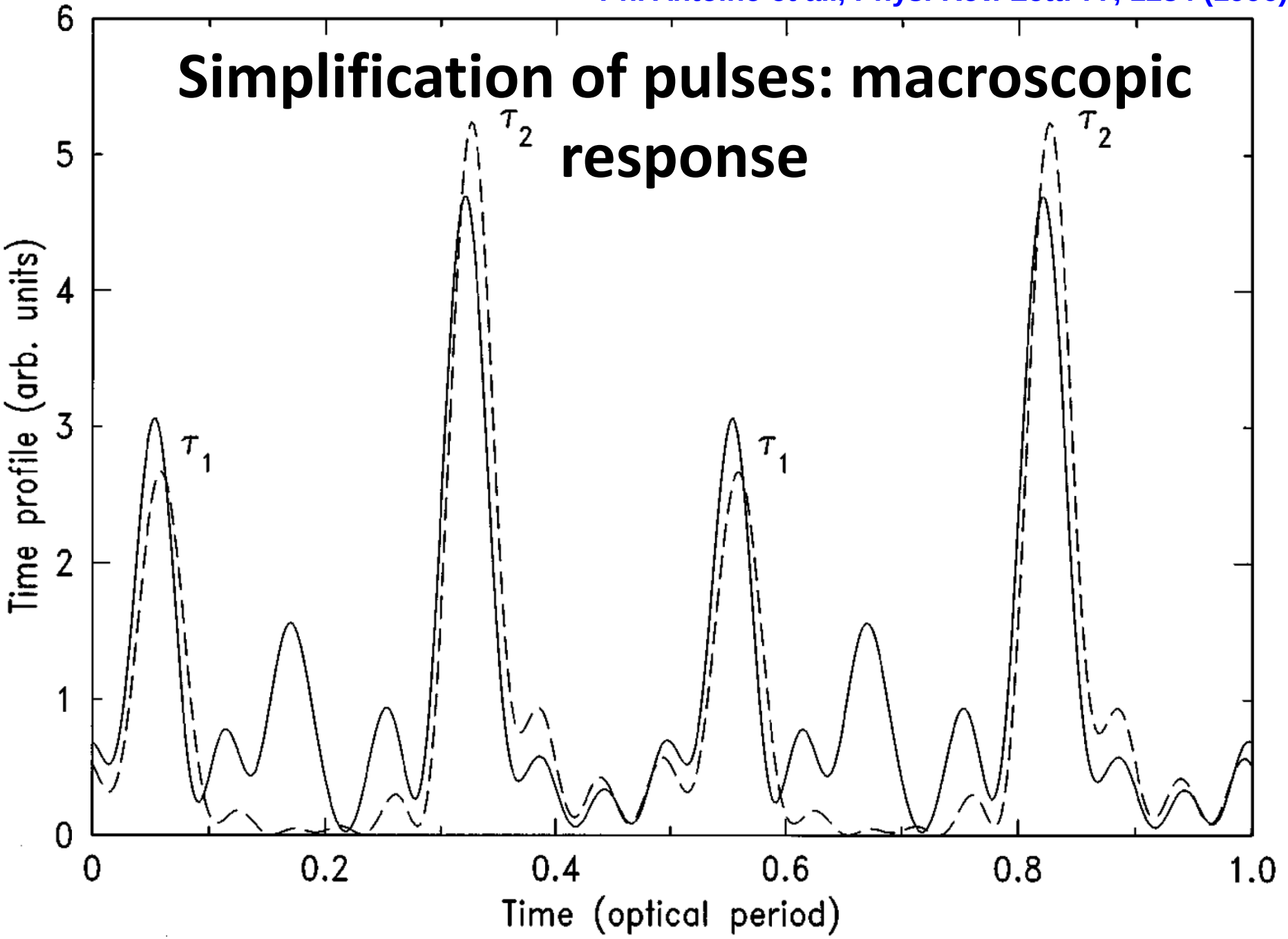
Ph. Antoine et al., Phys. Rev. Lett. 77, 1234 (1996)

Single atom response : poor prospects for attosecond pulse production



Ph. Antoine et al., Phys. Rev. Lett. 77, 1234 (1996)

Simplification of pulses: macroscopic response



Generation of attosecond pulses by HHG

Science **292**, 1689 (2001);
DOI: 10.1126/science.1059413

P. M. Paul,[1] E. S. Toma,[2] P. Breger,[1] G. Mullot,[3] F. Augé,[3]
Ph. Balcou,[3] H. G. Muller,[2]* P. Agostini[1]

In principle, the temporal beating of superposed high harmonics obtained by focusing a femtosecond laser pulse in a gas jet can produce a train of very short intensity spikes, depending on the relative phases of the harmonics. We present a method to measure such phases through two-photon, two-color photoionization. We found that the harmonics are locked in phase and form a train of 250-attosecond pulses in the time domain. Harmonic generation may be a promising source for attosecond time-resolved measurements.

Attosecond metrology

M. Hentschel*†, R. Kienberger*†, Ch. Spielmann*, G. A. Reider*, N. Milosevic*, T. Brabec*, P. Corkum‡, U. Heinzmann§, M. Drescher§ & F. Krausz*

The generation of ultrashort pulses is a key to exploring the dynamic behaviour of matter on ever-shorter timescales. Recent developments have pushed the duration of laser pulses close to its natural limit—the wave cycle, which lasts somewhat longer than one femtosecond (1 fs = 10^{-15} s) in the visible spectral range. Time-resolved measurements with these pulses are able to trace dynamics of molecular structure, but fail to capture electronic processes occurring on an attosecond (1 as = 10^{-18} s) timescale. Here we trace electronic dynamics with a time resolution of $\leq$ 150 as by using a subfemtosecond soft-X-ray pulse and a few-cycle visible light pulse. Our measurement indicates an attosecond response of the atomic system, a soft-X-ray pulse duration of 650 $\pm$ 150 as and an attosecond synchronism of the soft-X-ray pulse with the light field. The demonstrated experimental tools and techniques open the door to attosecond spectroscopy of bound electrons.

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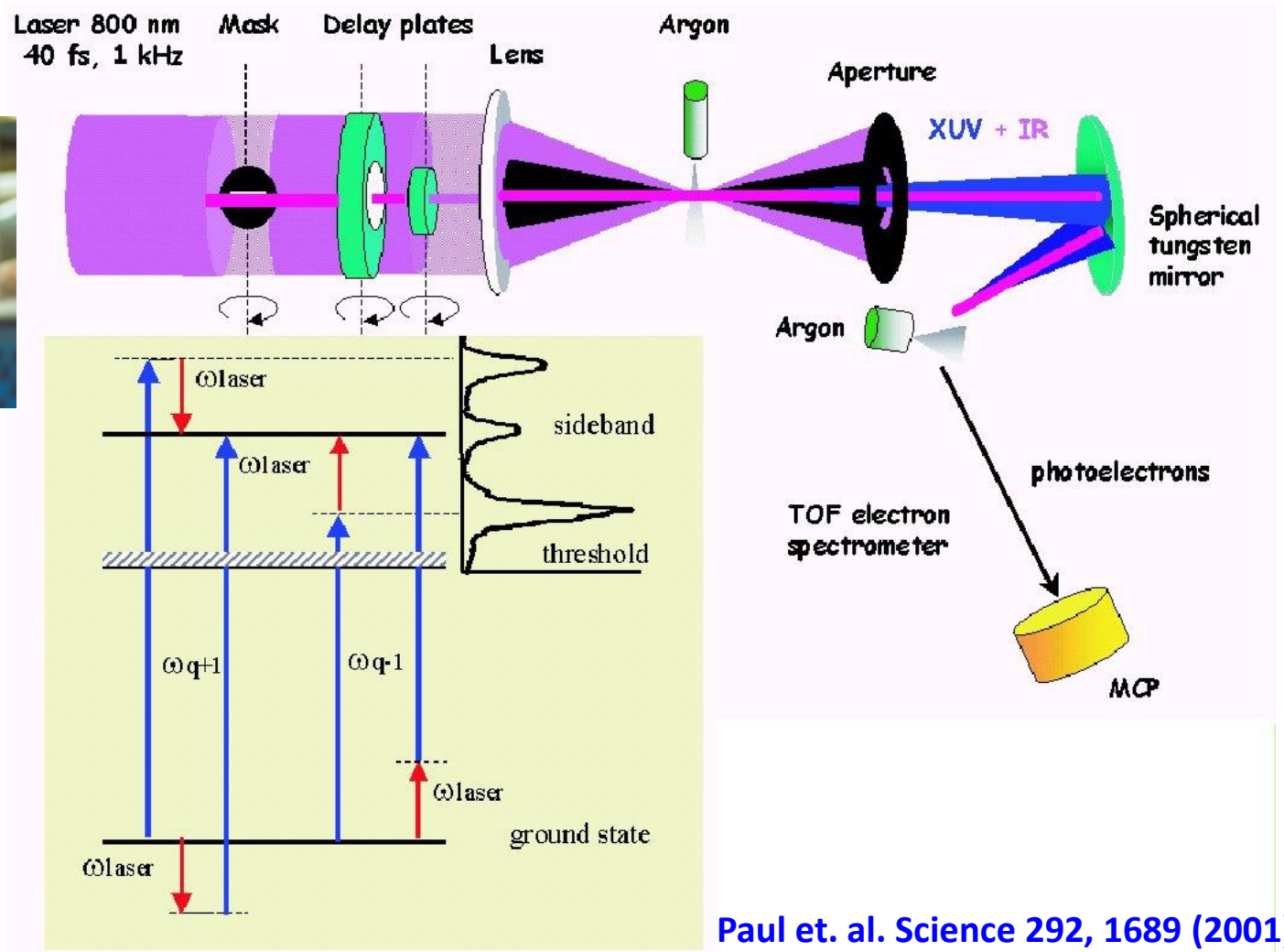
RABBITT

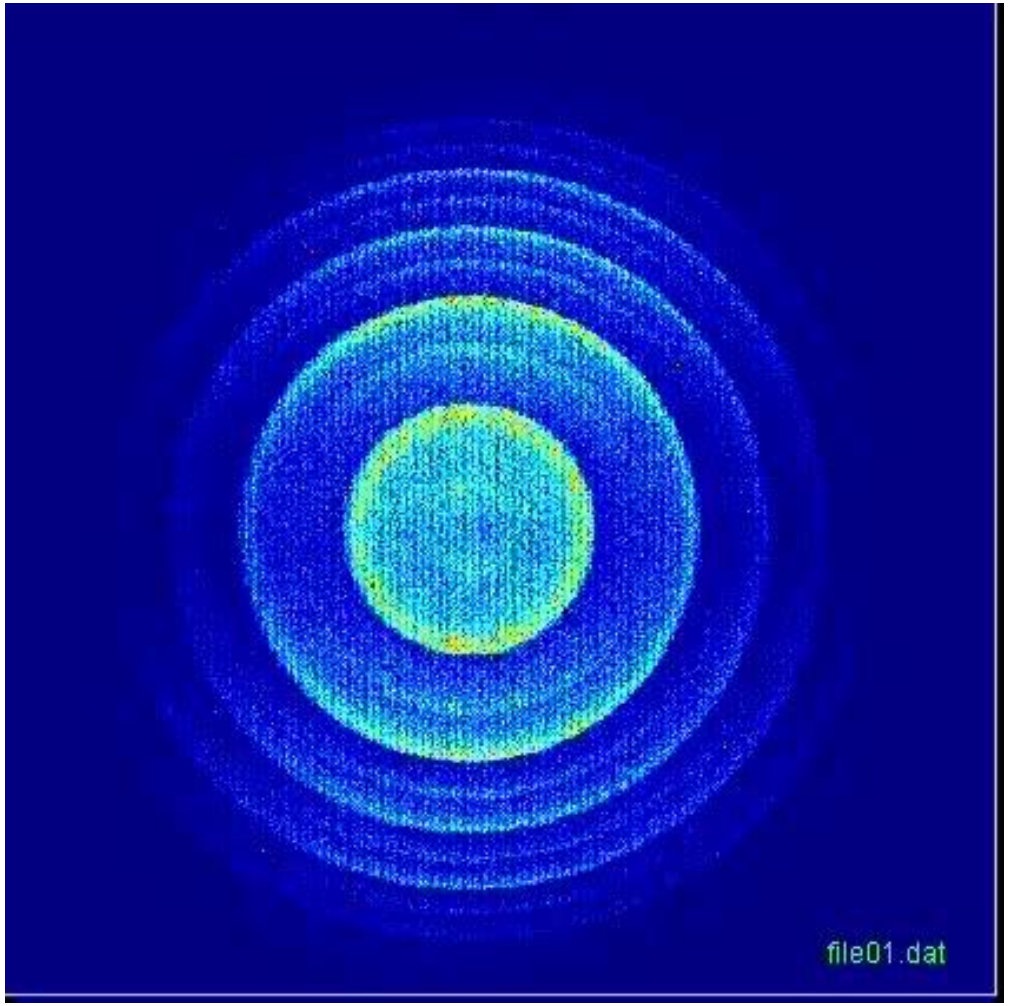
Reconstruction of Attosecond harmonic Beating By Interference of Two-photon Transitions

Harm-Geert Muller



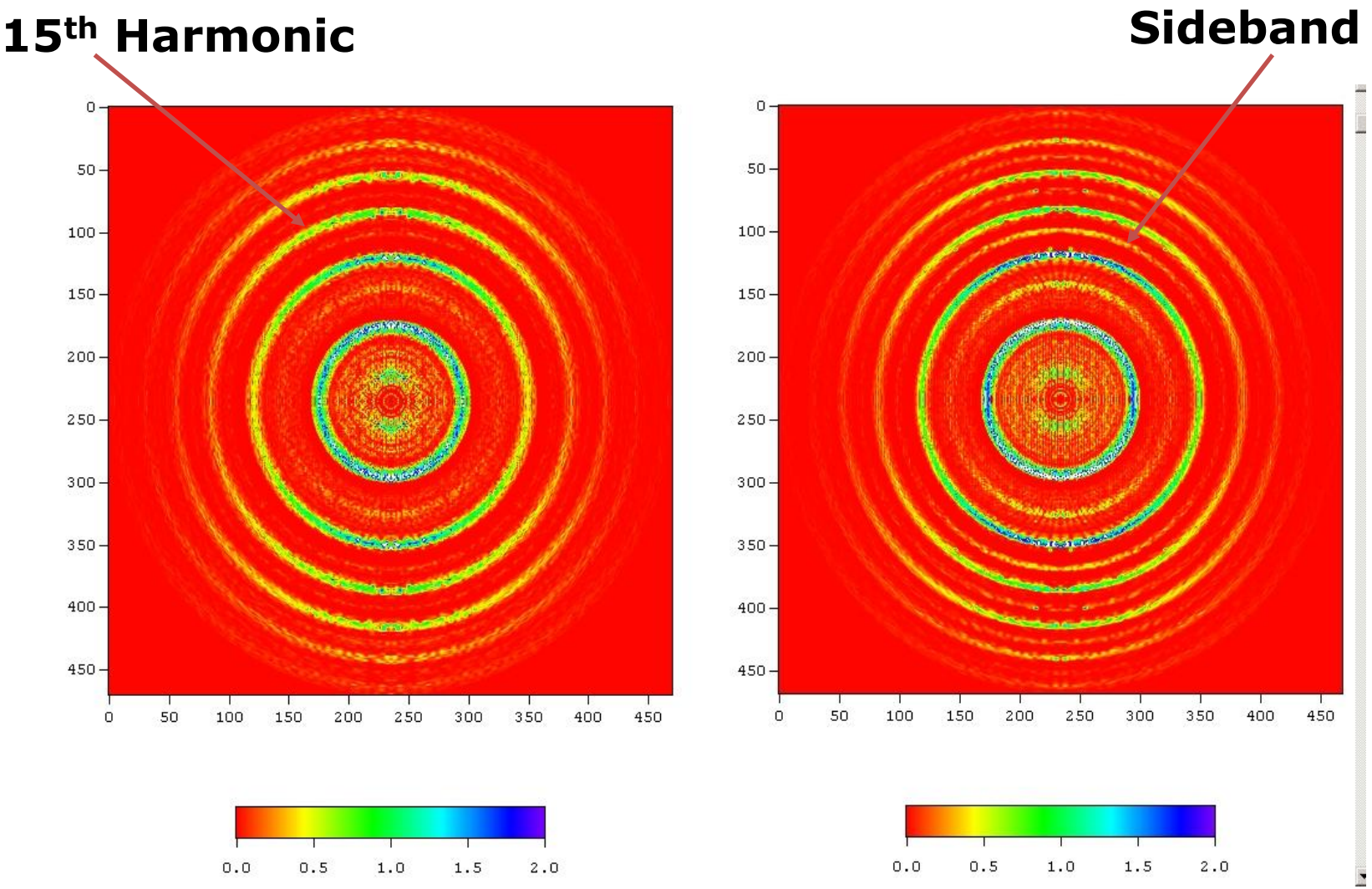
Paul et. al. Science 292, 1689 (2001)

Raw Photoelectron Images vs Time-delay



Aseyev et.al., Phys. Rev. Lett. 91, 223902 (2003)

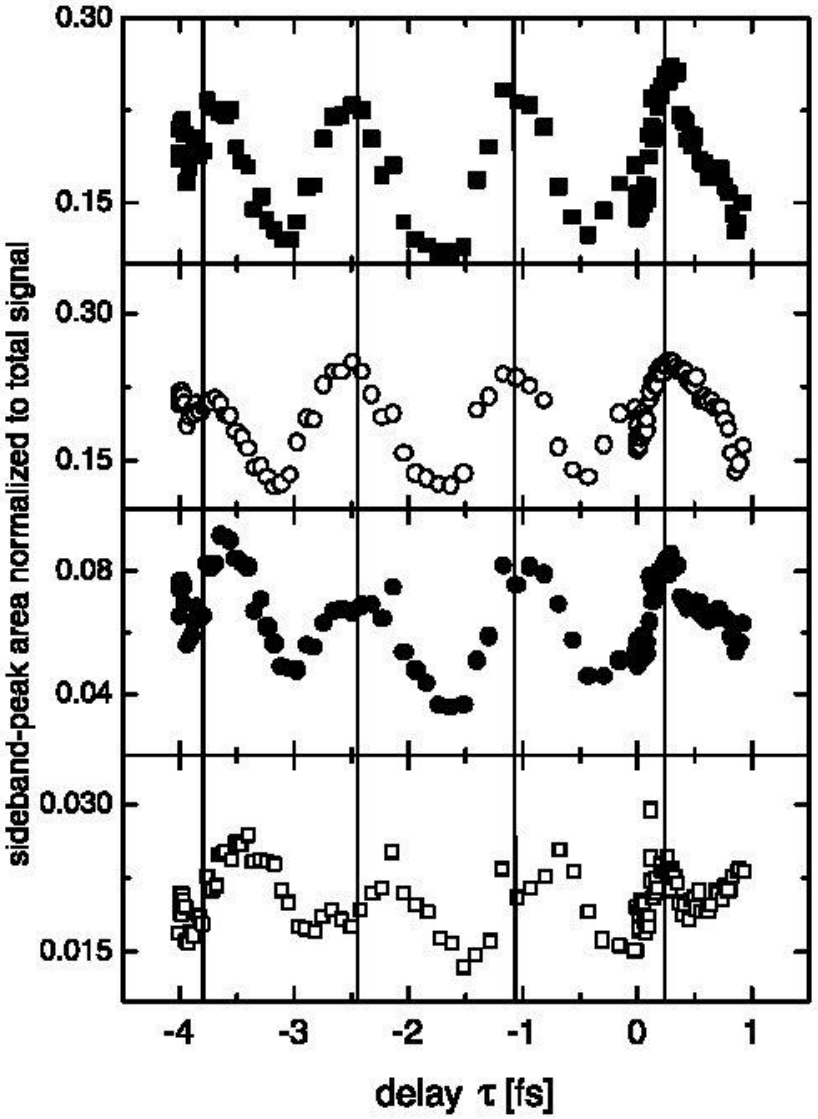
Inverted Photoelectron Image

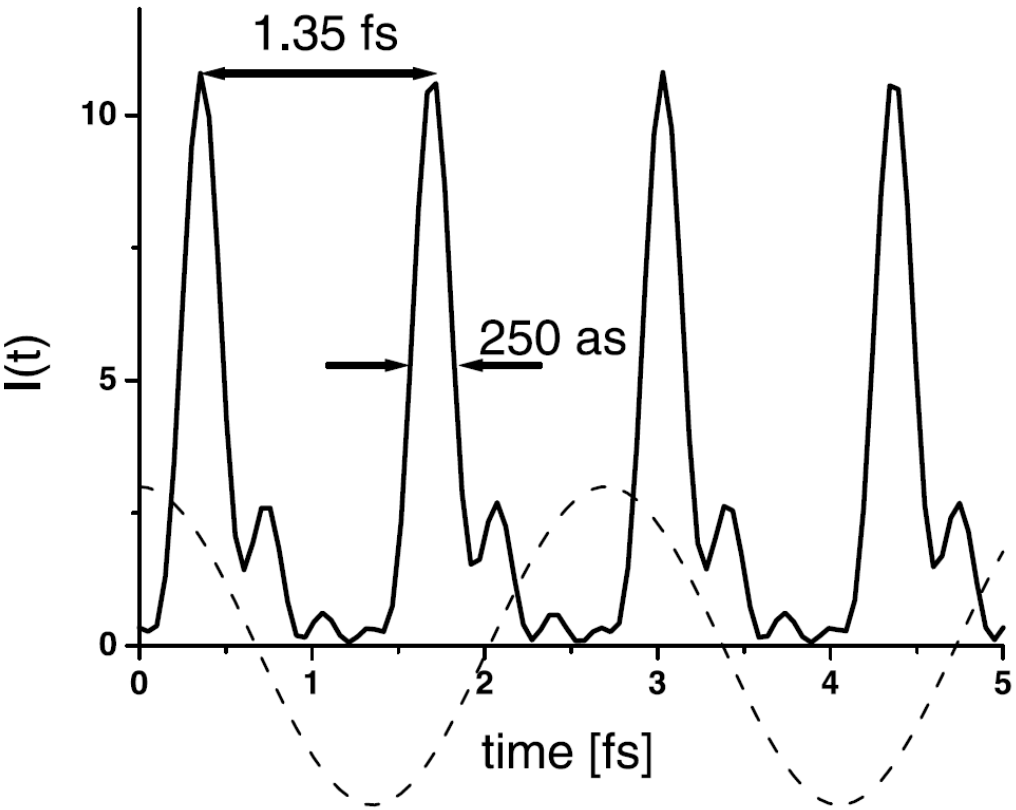


Aseyev et.al., Phys. Rev. Lett. 91, 223902 (2003)

Sideband intensity

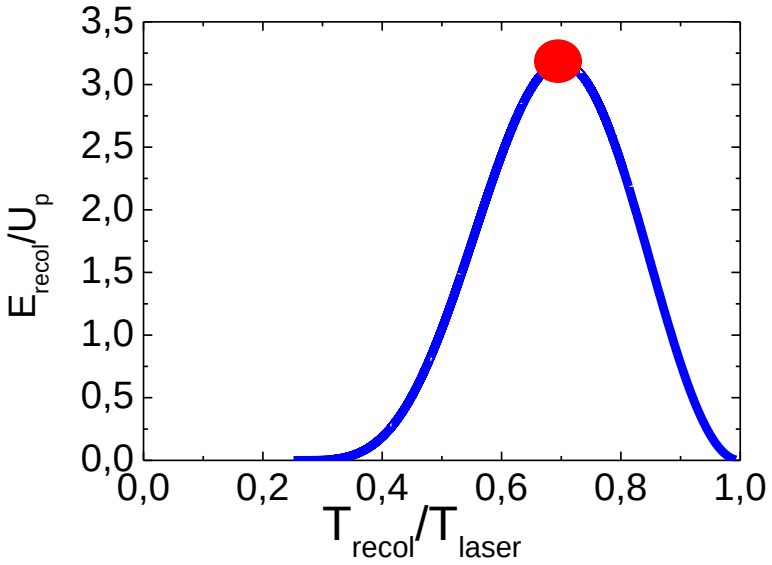
$$S_f(\Delta t) \sim A_f cos\left[2\omega_{IR}\Delta t + \varphi_{q-1} - \varphi_{q+1} - \Delta\varphi^f_{atomic}\right]$$



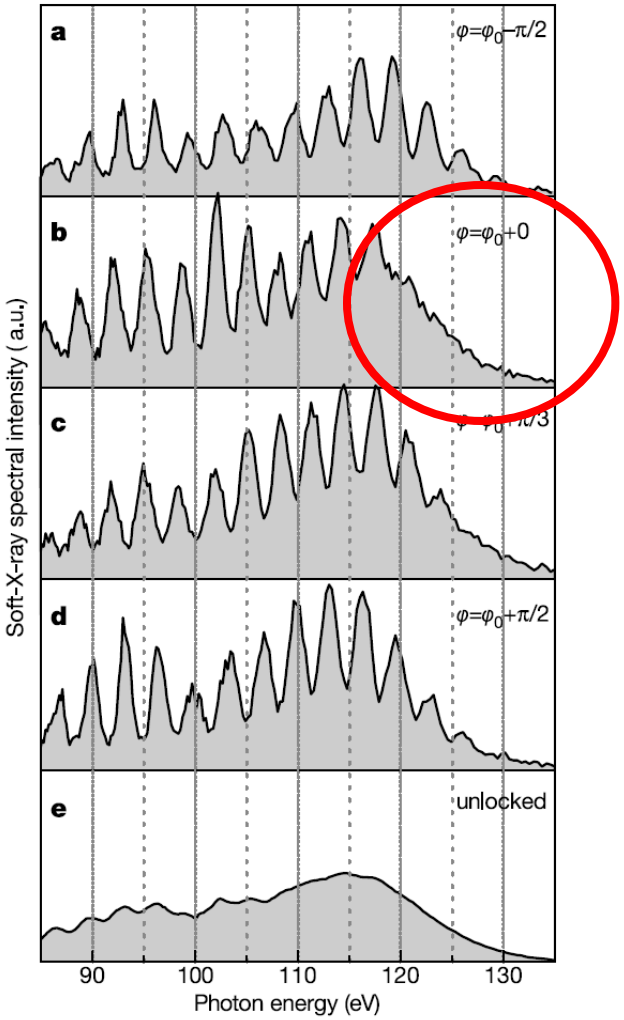


Paul et. al. Science 292, 1689 (2001)

Isolated Attosecond Pulse (IAP) from an Attosecond Pulse Train (APT)



Method 1: use cut-off harmonics



A. Baltuska *et al.*, *Nature* 421, 611 (2003).