Models for Time-Dependent Phenomena

I. Laser-matter interaction: atoms

II. Laser-matter interaction: molecules

III. Model systems and TDDFT

Manfred Lein

Leibniz Universität Hannover

quest

Outline

Laser-matter interaction: molecules

- Molecules, Born-Oppenheimer approximation
- Bond softening, enhanced ionization, Coulomb explosion
- High-harmonic generation in molecules, tomographic imaging of orbitals

Molecules

Set of nuclear and electronic coordinates $\mathbf{R}_j$ and $\mathbf{r}_k$.

Hamiltonian:

$$H_0 = \sum_j \frac{P_j^2}{2M_j} + \sum_k \frac{p_k^2}{2} + \sum_{j,k} w_{j,\mathrm{e}}(\mathbf{R}_j, \mathbf{r}_k) + \sum_{j_1 \neq j_2} w_{j_1,j_2}(\mathbf{R}_{j_1}, \mathbf{R}_{j_2}) + \sum_{k_1 \neq k_2} w_{\mathrm{ee}}(\mathbf{r}_{k_1}, \mathbf{r}_{k_2})$$

with w_{j_1,j_2} nucleus-nucleus interaction, $w_{j,\mathrm{e}}$ nucleus-electron interaction, and w_{ee} electron-electron interaction.

Light-molecule interaction:

$$H(t) = H_0 - \mathbf{D} \cdot \mathbf{E}(t)$$

with dipole moment $\mathbf{D} = (\sum_j Z_j \mathbf{R}_j) - (\sum_k \mathbf{r}_k)$

Born-Oppenheimer approximation

Separation of time scales for nuclear and electronic motion due to great mass difference

$\rightarrow$ Electrons adjust “instantaneously” to nuclear positions.

Born-Oppenheimer (BO) Ansatz for wave function:

$$\boxed{\Psi(\mathbf{R},\mathbf{r},t) = \sum_m \chi_m(\mathbf{R},t)\,\Phi_m(\mathbf{R},\mathbf{r}),}$$

$\Phi_m(\mathbf{R},\mathbf{r}) =$ electronic eigenstates at fixed nuclear positions.

Inserting into the field-free TDSE yields

$$i\frac{\partial}{\partial t}\chi_m(\mathbf{R},t) = \left[T_\mathrm{n} + V_m^\mathrm{BO}(\mathbf{R})\right]\chi_m \qquad \leftarrow \textbf{BO approximation}$$

$$+\sum_{m'}\langle\Phi_m|T_\mathrm{n}|\Phi_{m'}\rangle\chi_{m'} \qquad \leftarrow \text{nonadiabatic couplings}$$

(T_n acting on both $\Phi_{m'}$ and $\chi_{m'}$)

Born-Oppenheimer approximation

Including the laser-molecule interaction, the BO TDSE becomes:

$$\boxed{i\frac{\partial}{\partial t}\chi_m(\mathbf{R},t) = \left[T_{\mathrm{n}} + V_m^{\mathrm{BO}}(\mathbf{R})\right]\chi_m(\mathbf{R},t) \ - \ \mathbf{E}\cdot\sum_{m'}\langle\Phi_m|\mathbf{D}|\Phi_{m'}\rangle\chi_{m'}}$$

$\rightarrow$ Functions χ_m coupled only by the dipole matrix elements.

BO approximation breaks down for highly excited electrons:

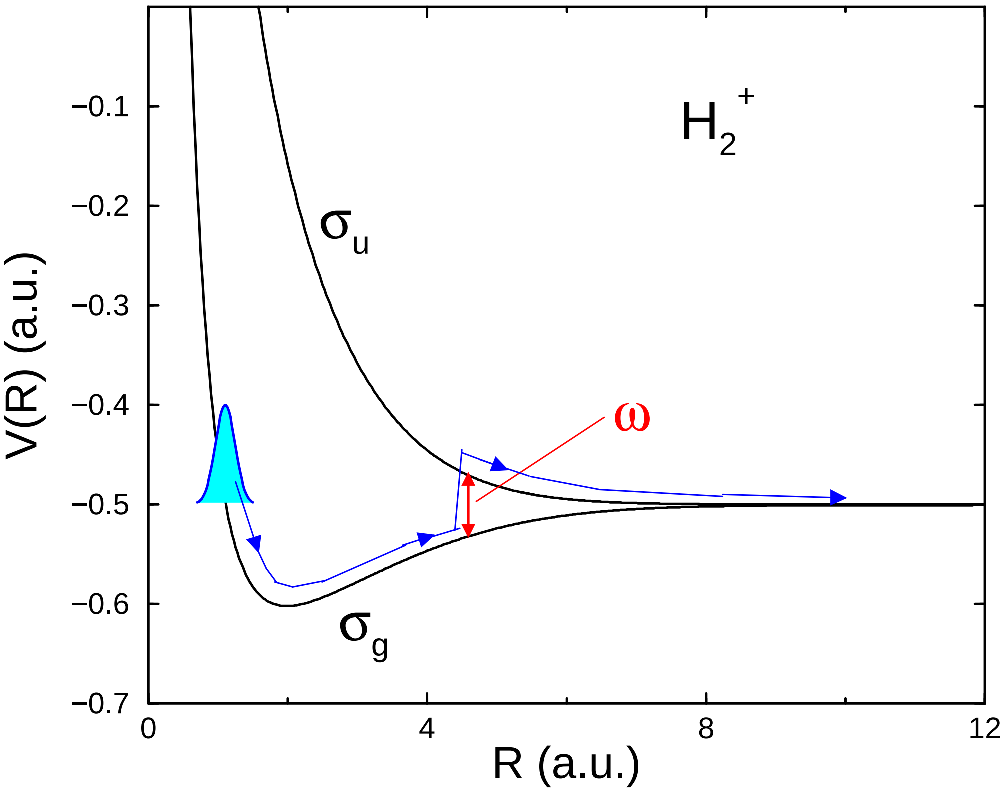
- Rydberg molecules
- Electrons in the continuum

Fragmentation mechanisms in H_2^+

- Bond softening
- “Above-threshold” dissociation
- Charge resonance enhanced ionization
- Coulomb explosion

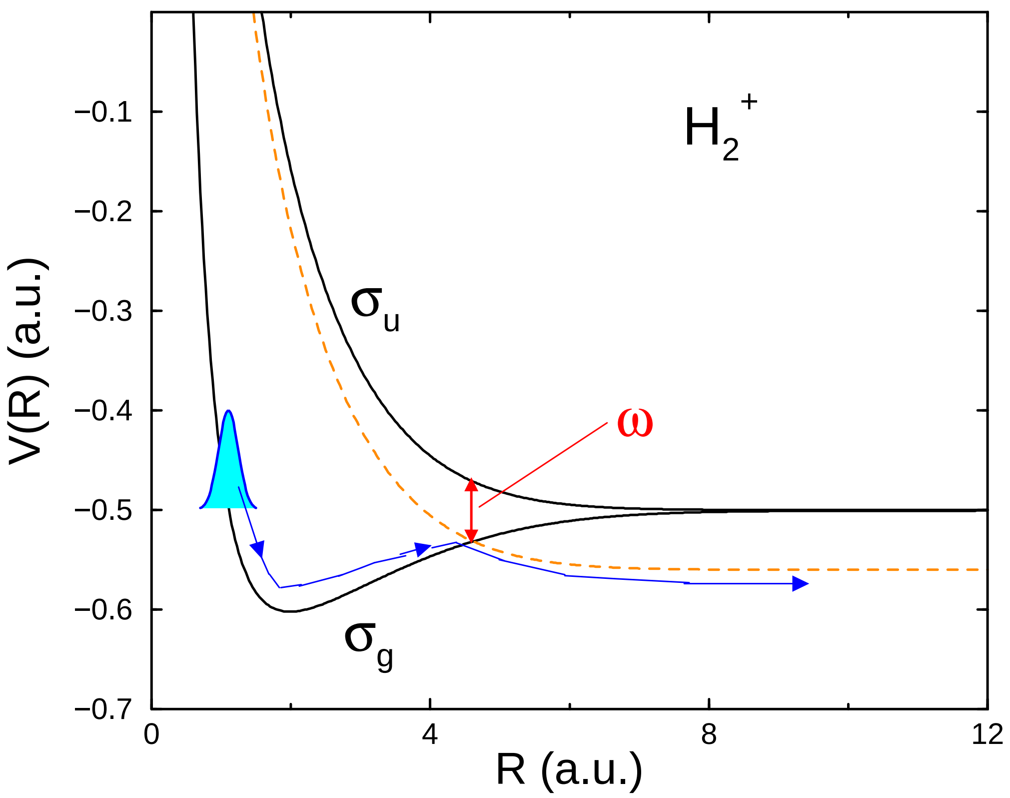
Bond softening

Transitions between BO states occur at nuclear positions where photon energy is resonant.



Bond softening

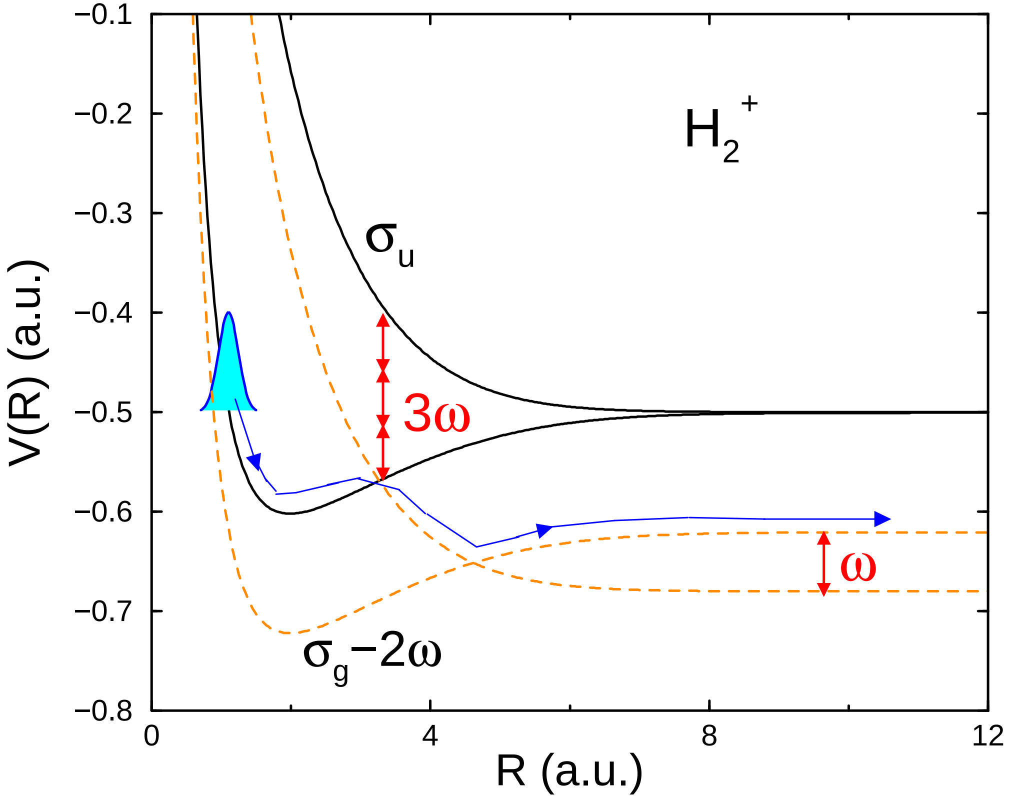
Alternative picture: potential surfaces shifted by multiples of the photon energy (→ **diabatic potentials**)



Lowering of dissociation threshold = **bond softening**

"Above-threshold" dissociation

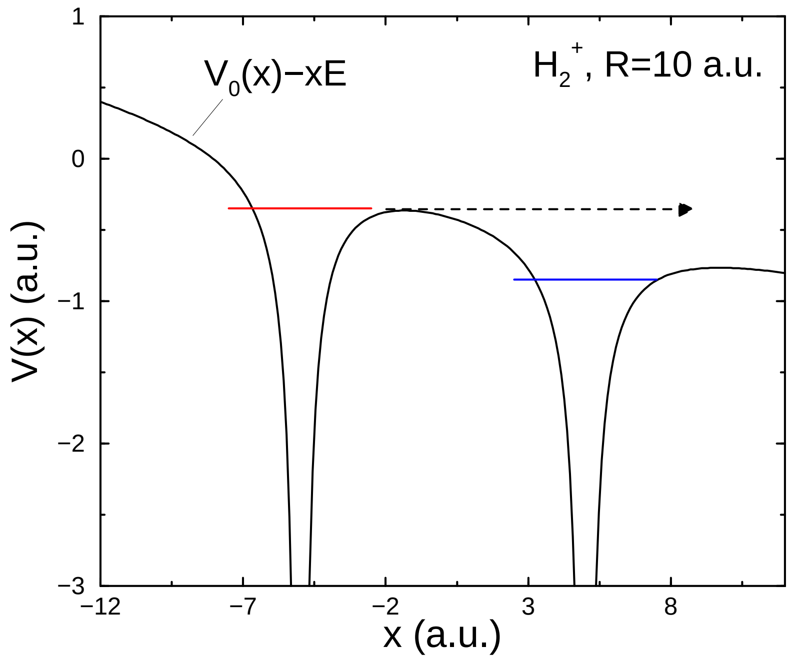
3-photon absorption + 1-photon emission
= effective 2-photon absorption



Charge-resonance enhanced ionization

At a range of internuclear distances, the tunneling barrier is suppressed by the presence of the second center.

$\rightarrow$ **enhancement of ionization**

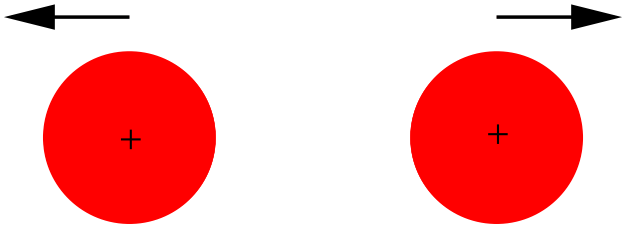


Seideman, Ivanov, Corkum, PRL **75**, 2819 (1995),

Zuo, Bandrauk, PRA **52**, R 2511 (1995).

Coulomb explosion

Ionization of H_2^+ and other molecular ions can create two charged centers $\rightarrow$ rapid fragmentation due to Coulomb repulsion.



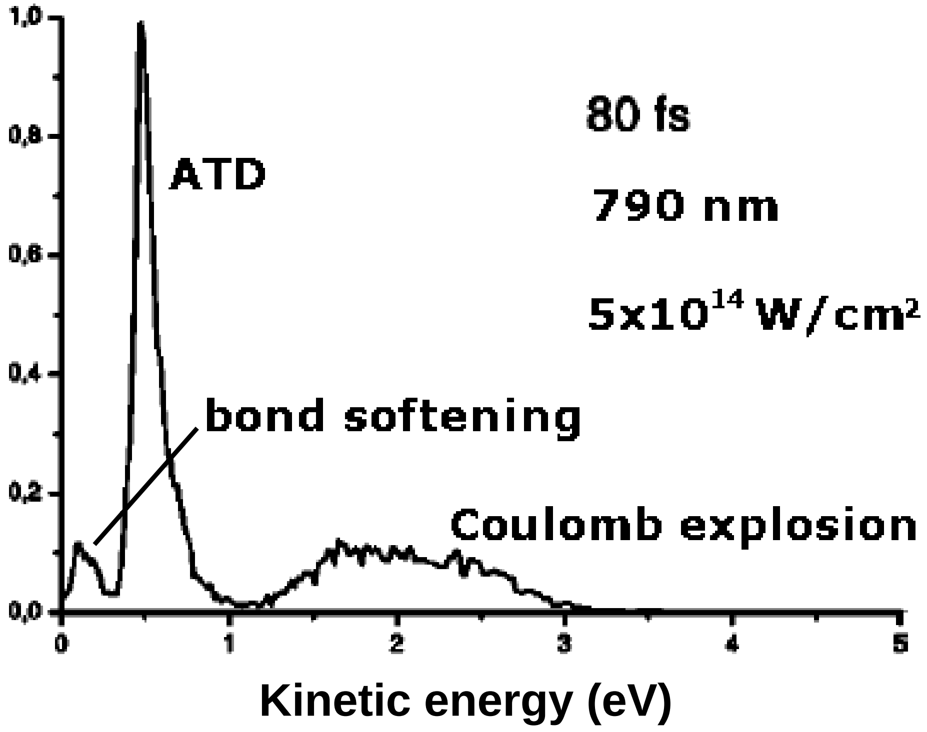
Kinetic energy release indicates initial internuclear distance by energy conservation:

$$E_{\mathrm{kin}} \approx 1/R_{\mathrm{initial}}$$

$\rightarrow$ **Coulomb explosion imaging**

Typical fragment spectrum

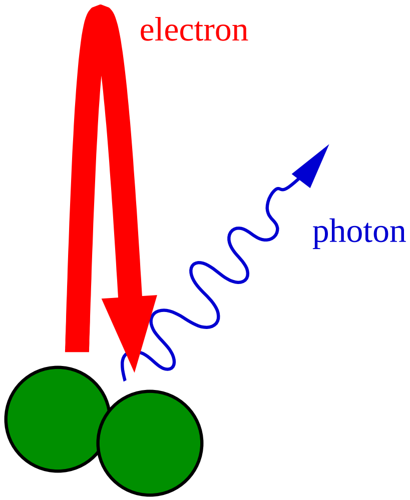
Energies of D^+ ions from D_2 in a strong pulse



[Trump et al. PRA **62**, 063402 (2000)]

High-harmonic generation in molecules

For small molecules: electron excursion $>>$ molecular size



Atom-like mechanism

Influence of molecular properties on ionization and recombination

$\rightarrow$ *Probing of molecular structure / dynamics*

Calculation of emission spectra

Calculation of the time-dependent dipole acceleration

$$\boxed{\mathbf{a}(t) = \langle \psi(t) | \nabla V_0 + \mathbf{E}(t) | \psi(t) \rangle}$$

and Fourier transform

$$\boxed{\mathbf{a}(\Omega) = \int \mathbf{a}(t) e^{i\omega t}}$$

gives emission spectrum

$$\boxed{S(\Omega) \sim |\mathbf{a}(\Omega)|^2}$$

In practice: time integration over pulse duration T,

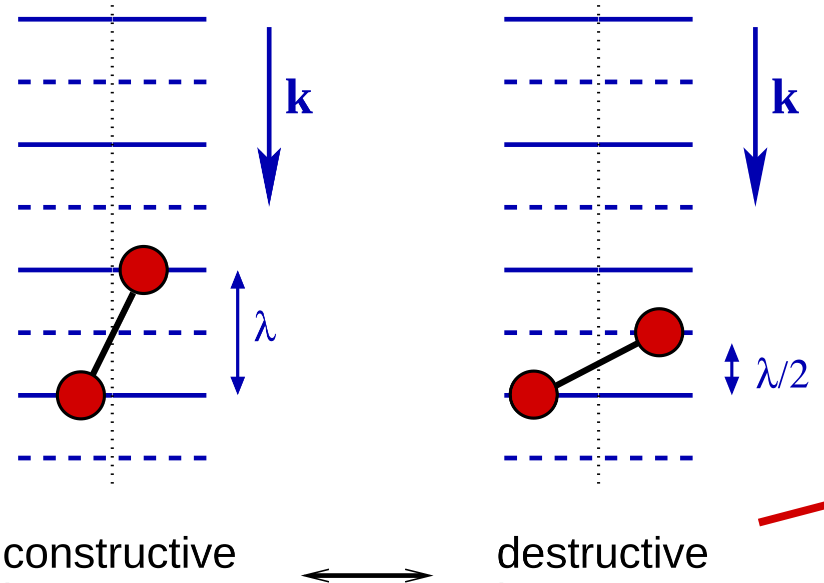
$$\boxed{\mathbf{a}(\Omega) = \int_0^T \mathbf{a}(t) f(t) e^{i\omega t}}$$

with some window function $f(t)$.

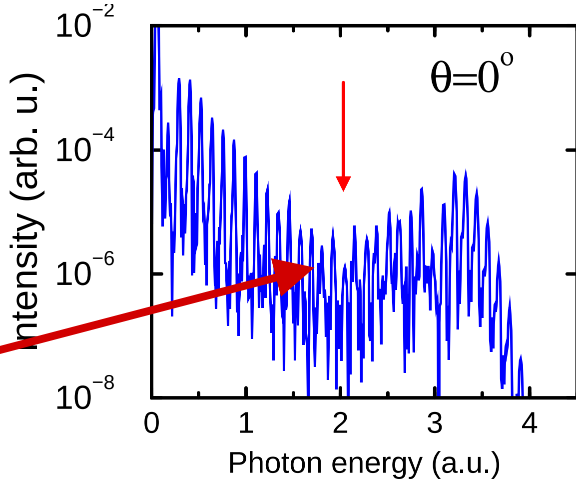
Alternatively: $\mathbf{a}(t) = \ddot{\mathbf{D}}(t)$ from time-dependent dipole moment $\mathbf{D}(t)$
or: $\mathbf{a}(t) = \dot{\mathbf{v}}(t)$ from time-dependent dipole velocity $\mathbf{v}(t)$

Two-center interference

Recolliding electron with wave vector $\mathbf{k}$ in H_2 or H_2^+



constructive interference ⟷ destructive interference



M.L., N. Hay, R. Velotta, J.P. Marangos, P.L. Knight, PRL **88**, 183903 (2002)]

Minimum occurs when $R\cos\theta = \lambda/2$ with $\lambda = 2\pi/k$ = electron wavelength

More precisely:

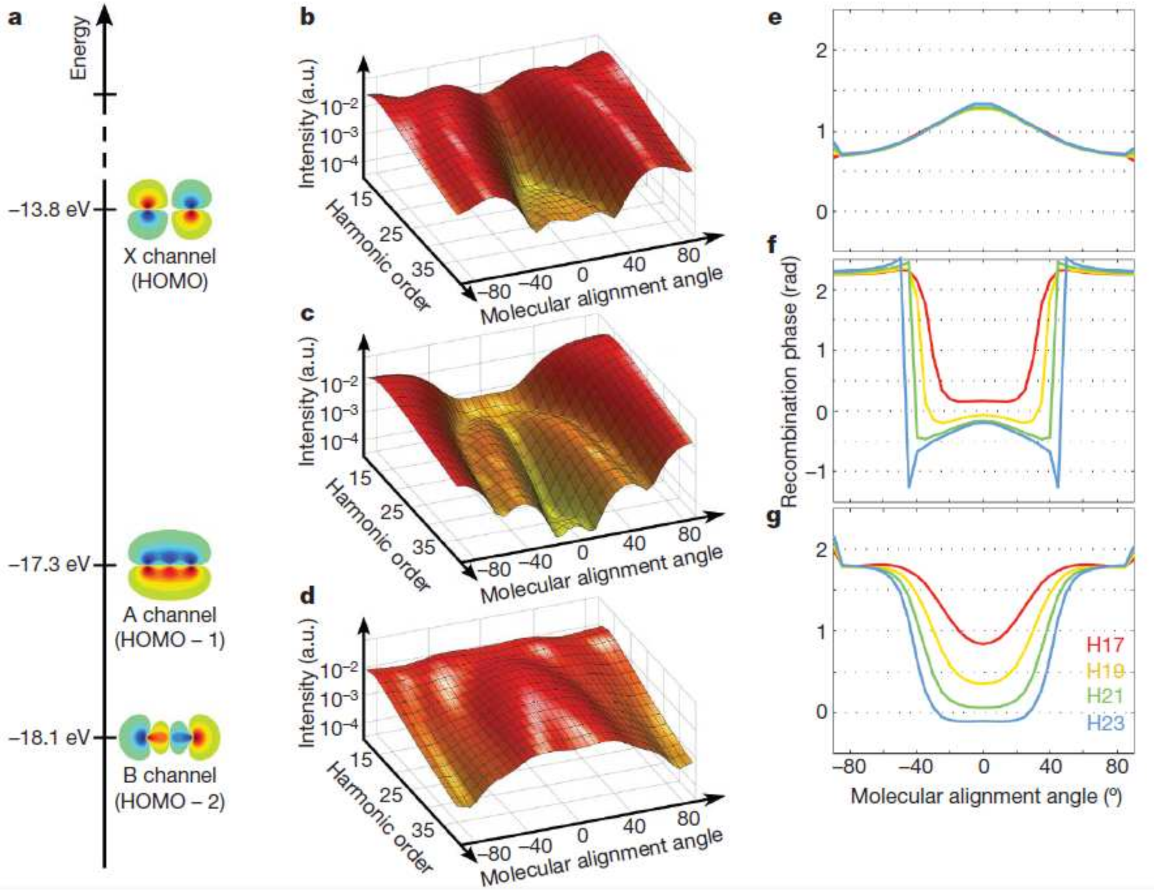
recombination probability is proportional to the square of the *bound-continuum transition dipole* $d = \langle \mathbf{k}|\hat{D}|\Phi\rangle$.

Multielectron dynamics in HHG

Not only the highest occupied molecular orbital (HOMO), but also lower-lying orbitals participate in harmonic generation when HOMO contribution is suppressed by symmetry.

Example: CO_2

O. Smirnova et al.,
Nature **460**, 972 (2009)



Strong-field approximation for high-harmonic generation

(also known as Lewenstein model)

$$\boxed{\mathbf{D}(t) = i \int_0^t dt' E(t') \int d^3p \, \langle \mathbf{p}+\mathbf{A}(t')|x|0\rangle\langle 0|\mathbf{r}|\mathbf{p}+\mathbf{A}(t)\rangle \exp(-iS) \ + \mathrm{c.c.}}$$

where $S(\mathbf{p},t,t') = \int\limits_{t'}^{t} dt'' \left[\frac{(\mathbf{p}+\mathbf{A}(t''))^2}{2} + I_\mathrm{p} \right]$

(length-gauge form) [Lewenstein et al., Phys. Rev. A **49**, 2117 (1994)]

Strong-field approximation for high-harmonic generation

(also known as Lewenstein model)

$$\boxed{\mathbf{D}(t) = i \int_0^t dt' E(t') \int d^3p \, \langle \mathbf{p}+\mathbf{A}(t')|x|0\rangle\langle 0|\mathbf{r}|\mathbf{p}+\mathbf{A}(t)\rangle \exp(-iS) \; + \mathrm{c.c.}}$$

where $S(\mathbf{p},t,t') = \int_{t'}^{t} dt'' \left[\frac{(\mathbf{p}+\mathbf{A}(t''))^2}{2} + I_\mathrm{p}\right]$

(length-gauge form) [Lewenstein et al., Phys. Rev. A **49**, 2117 (1994)]

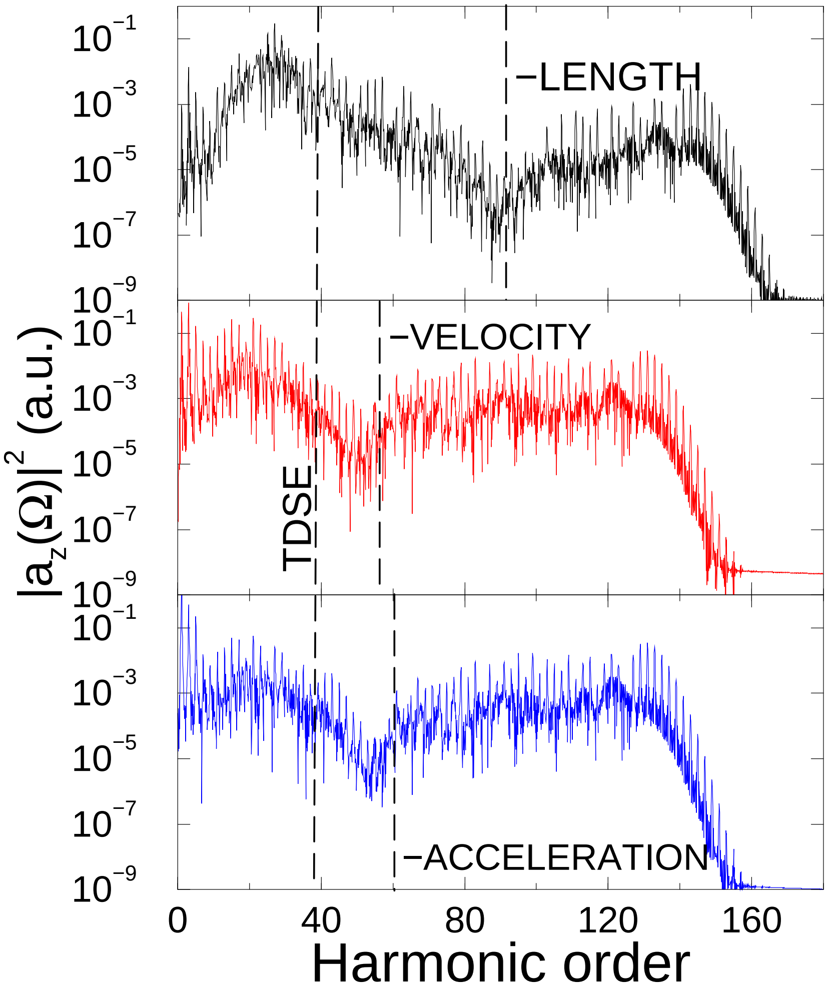
In addition to the gauge problem, there is a ***choice of recombination operator***:

velocity (or acceleration) form preferable to length form

[A. Gordon, F.X. Kärtner, PRL **95**, 223901 (2005),

C.C. Chirilă, M.L., J. Mod. Opt. **54**, 1039 (2007)]

Results for harmonic generation in H_2^+



$\theta = 40^{\mathrm{o}}$

curves: full SFA results

dashed lines: minima from
- TDSE
- recombination elements only

SFA for harmonics in vibrating molecules

Assume

- Born-Oppenheimer motion of core electrons,
- transition matrix element independent of internuclear distance

  (sufficient is $d(\mathbf{k}, R) = f(\mathbf{k})\, g(R)$)

$\rightarrow$ Creation of a nuclear wave packet χ that evolves on the BO potential surface of the ion between t' and t.

SFA for harmonics in vibrating molecules

Assume

- Born-Oppenheimer motion of core electrons,
- transition matrix element independent of internuclear distance

  (sufficient is $d(\mathbf{k}, R) = f(\mathbf{k})\, g(R)$)

$\rightarrow$ Creation of a nuclear wave packet χ that evolves on the BO potential surface of the ion between t' and t.

$$\rightarrow \mathbf{P}(t) = 2 \int_0^t dt'\, E(t') \int dR\, \chi(R,0)^* \chi(R, t-t') \times \int d^3p\, \langle \mathbf{p}+\mathbf{A}(t')|x|0\rangle \, \langle 0|\nabla|\mathbf{p}+\mathbf{A}(t)\rangle \exp[-iS(\mathbf{p}, t, t')] \; + \; \mathrm{c.c}$$

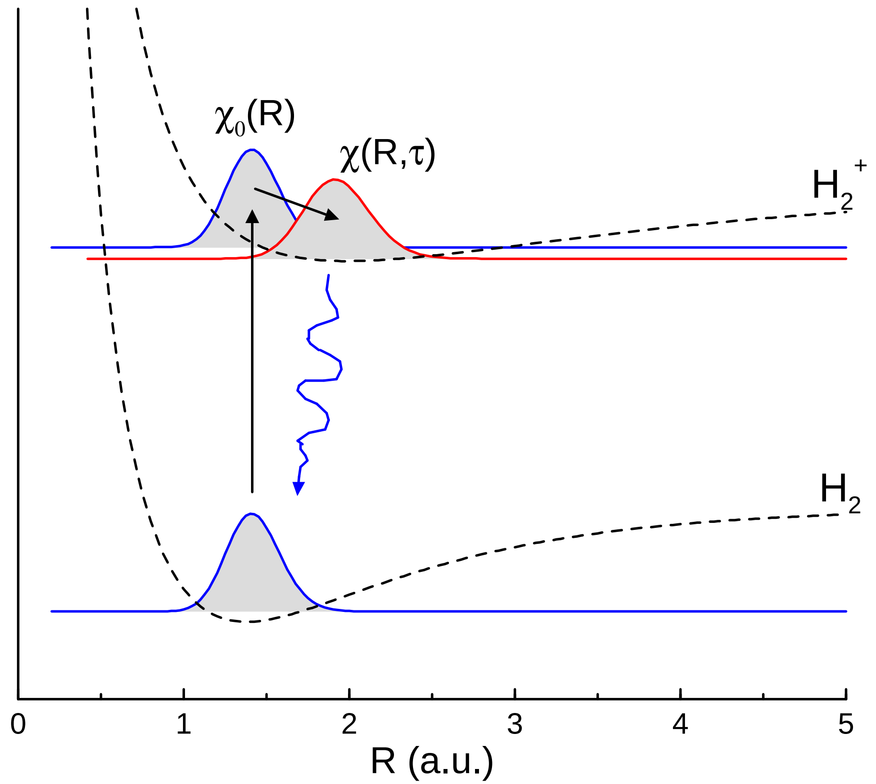
with vibrational wave packet $\chi(R, \tau)$.

$\rightarrow$ Harmonics are sensitive to the vibrational autocorrelation function

$$C(\tau) = \int dR\, \chi(R,0)^* \chi(R, \tau)$$

Vibrational autocorrelation function

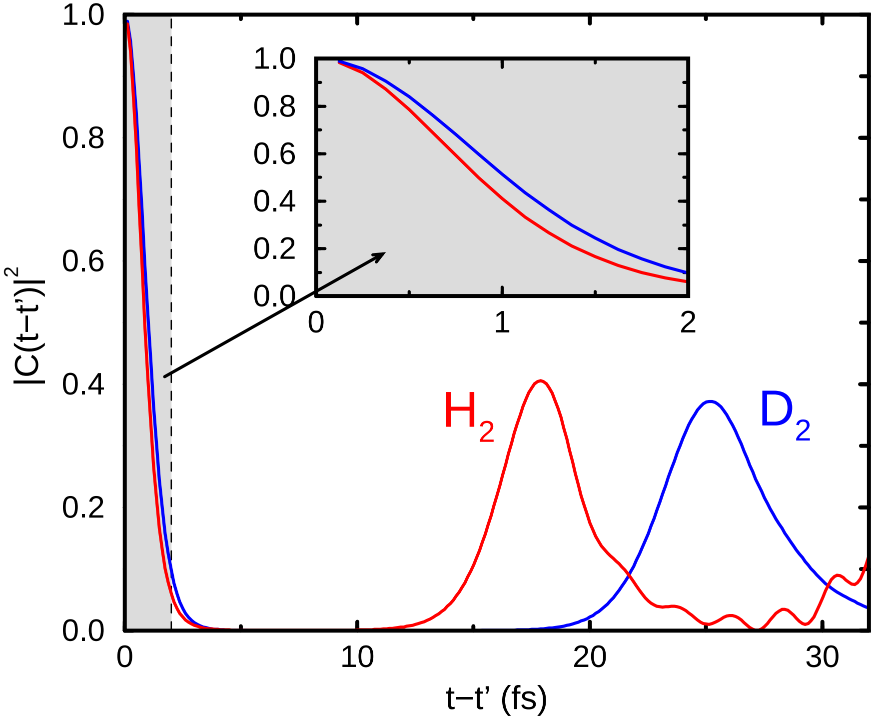
Illustration of physical mechanism:



Vibrational autocorrelation function

Calculate field-free evolution of a vibrational wave packet in the BO potential of H_2^+/D_2^+,

$$i\frac{\partial\chi(R,t)}{\partial t} = \left[-\frac{\partial_R^2}{M} + V_{\rm BO}^+(R)\right]\chi(R,t), \quad \chi(R,0) = \chi_0^{\rm H_2}(R)$$

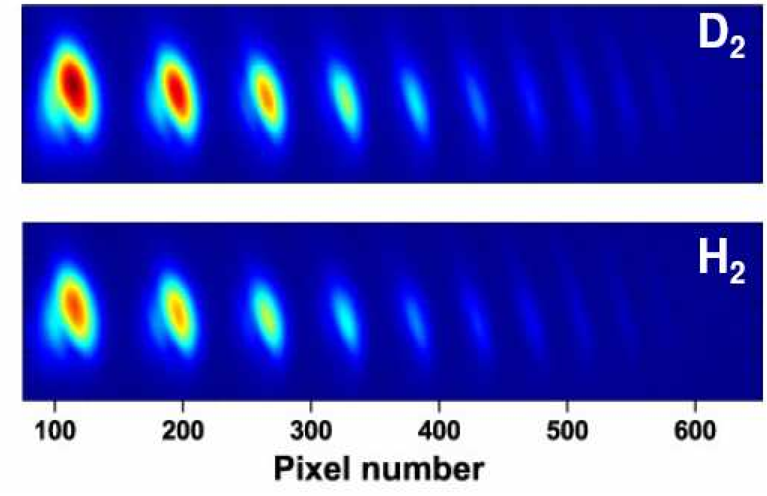


→ More intense harmonics in heavier isotope D_2.

Comparison with experiment

8 fs pulses, wavelength 775 nm, intensity 2×10^{14} W/cm^2

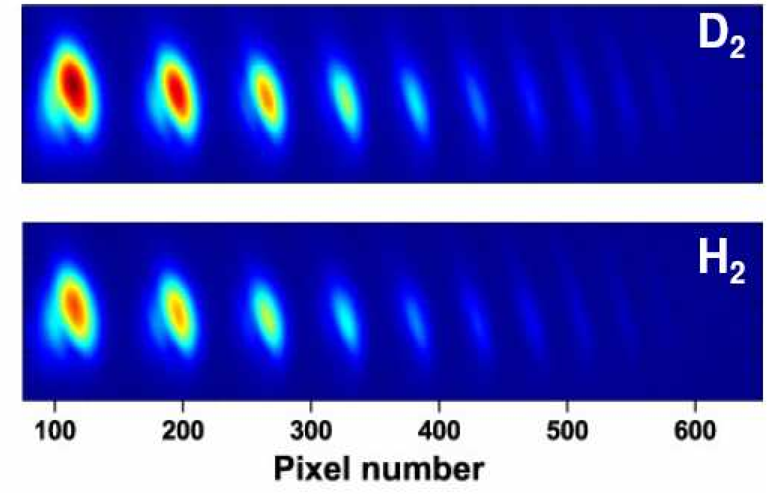
Raw data of harmonics in D_2 and H_2



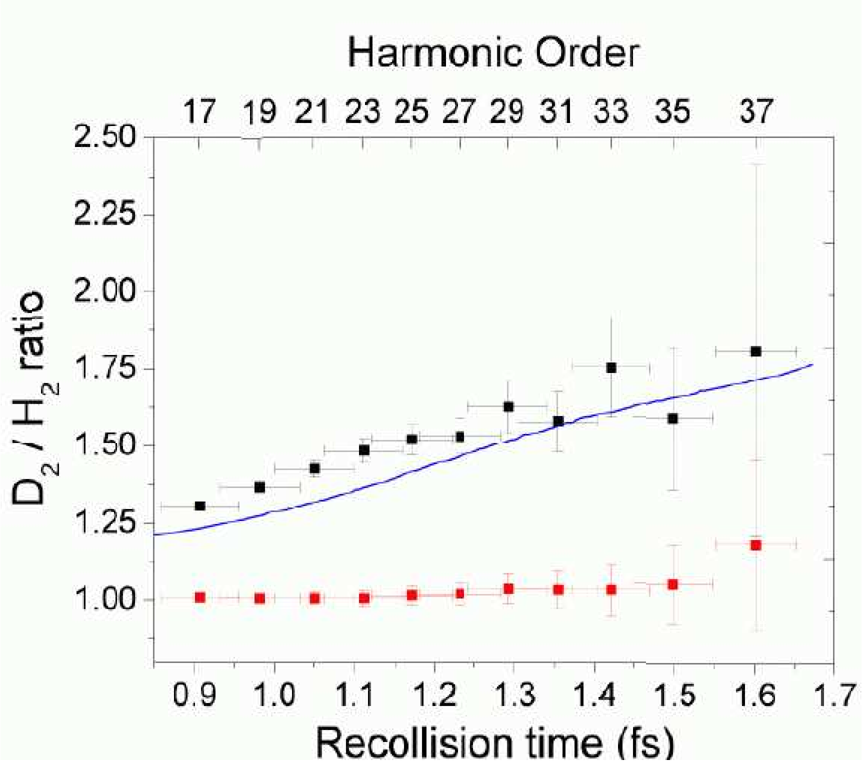
Comparison with experiment

8 fs pulses, wavelength 775 nm, intensity 2×10^{14} W/cm^2

Raw data of harmonics in D_2 and H_2



Ratio D_2/H_2

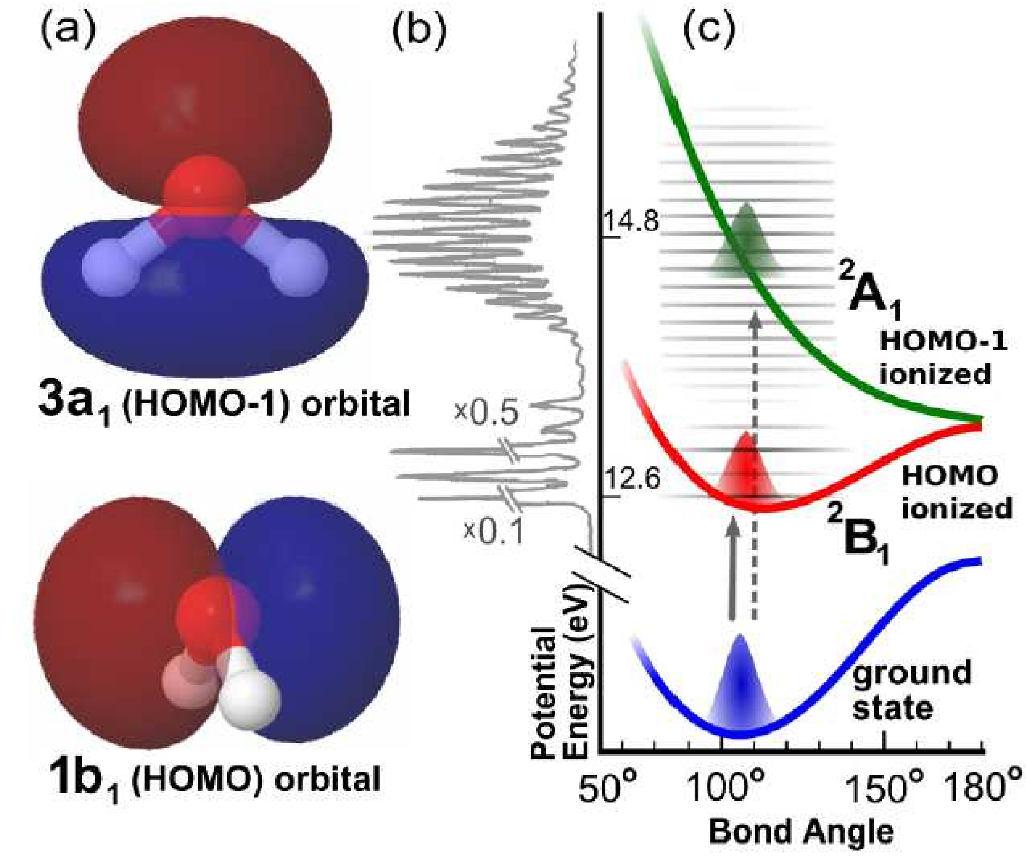


Blue: theory

Baker et al. Science **312**,424 (2006)

Isotope effects in water molecules

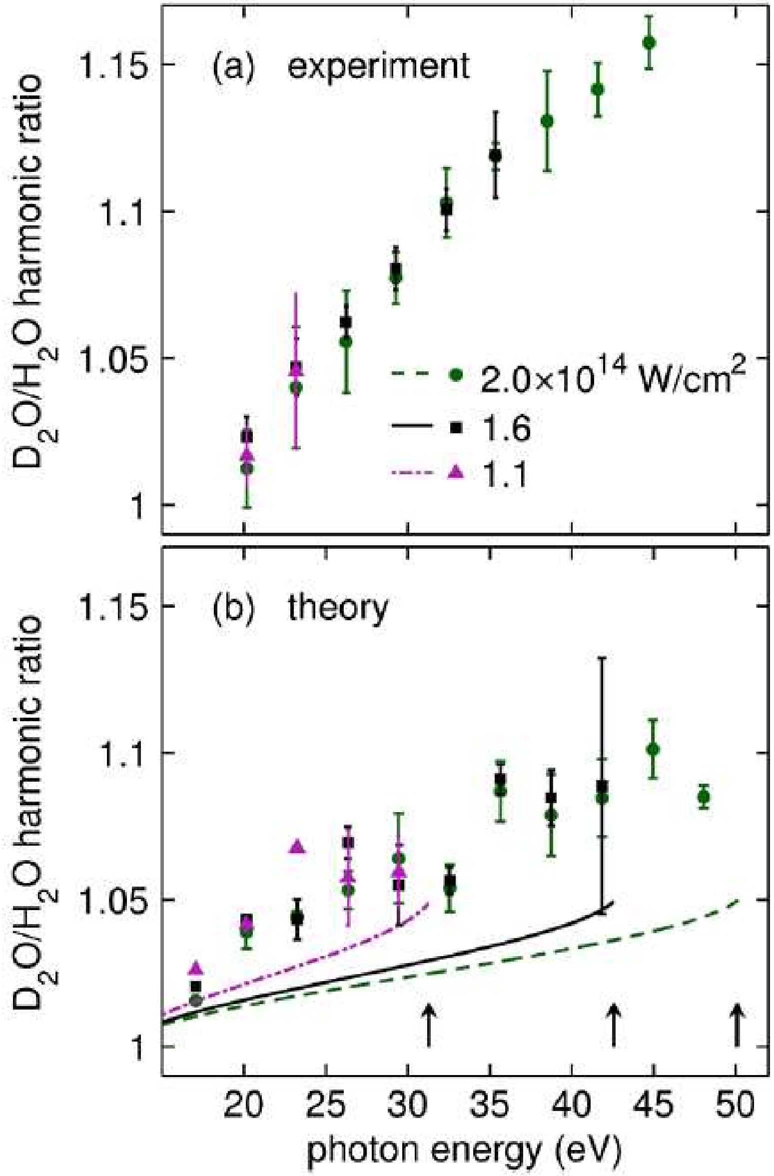
HHG in water proceeds from HOMO or HOMO-1:



Farrell et al., PRL **107**, 083001 (2011)

Isotope effects in water molecules

Ratio of harmonics D_2O / H_2O:



Farrell et al., PRL **107**, 083001 (2011)

Tomographic imaging of molecular orbitals

Idea: factorize measured harmonic amplitude into “recollision wave packet” $a(\omega)$ and recombination dipole $d(\omega)$:

$$D(\omega) = a(\omega)d(\omega)$$

Compare to measured amplitude for a reference system with known orbitals (i.e. known recombination dipole) and the same recollision amplitude:

$$D^{\mathrm{ref}}(\omega) = a(\omega)d^{\mathrm{ref}}(\omega)$$

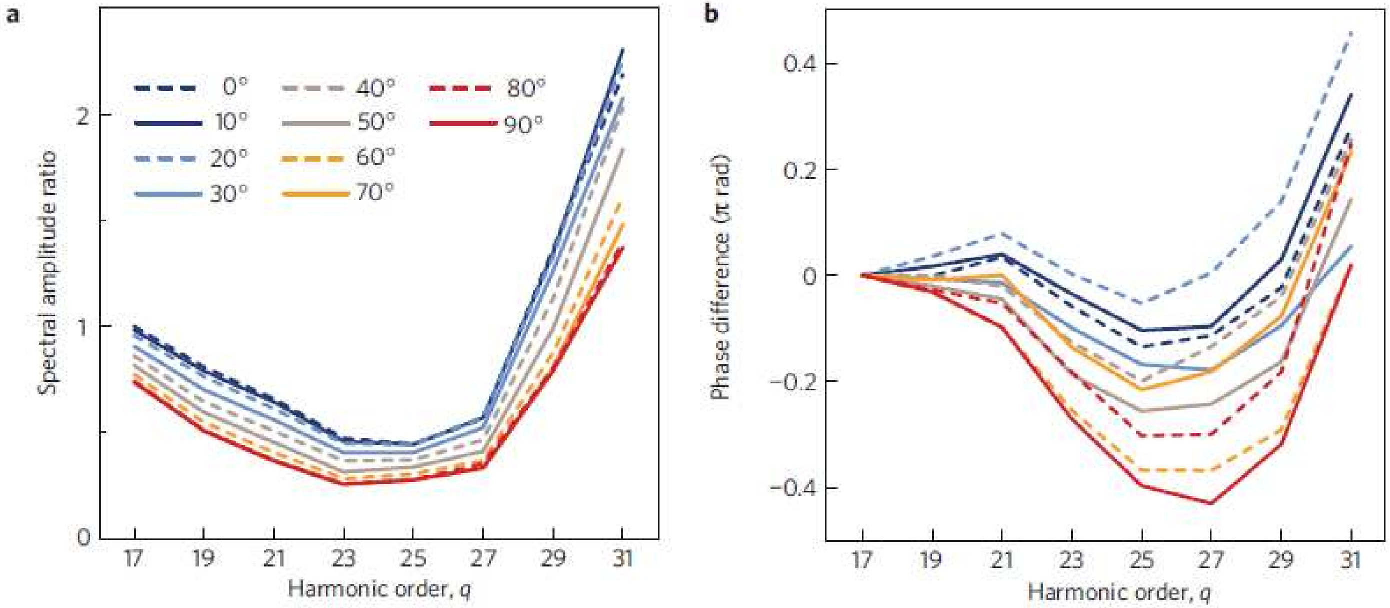
$\rightarrow$ leads to measurement of $d = \frac{D}{D^{\mathrm{red}}}d^{\mathrm{ref}}$.

In the plane-wave approximation, $d(\omega) = \langle \exp(i\mathbf{k}\cdot\mathbf{r}|\hat{D}|\Phi\rangle$,
$\rightarrow$ Fourier transform retrieves orbital Φ.

Itatani et al., Nature **432**, 867 (2004)

Tomographic imaging of molecular orbitals

Measured recombination dipole amplitude and phase for N_2

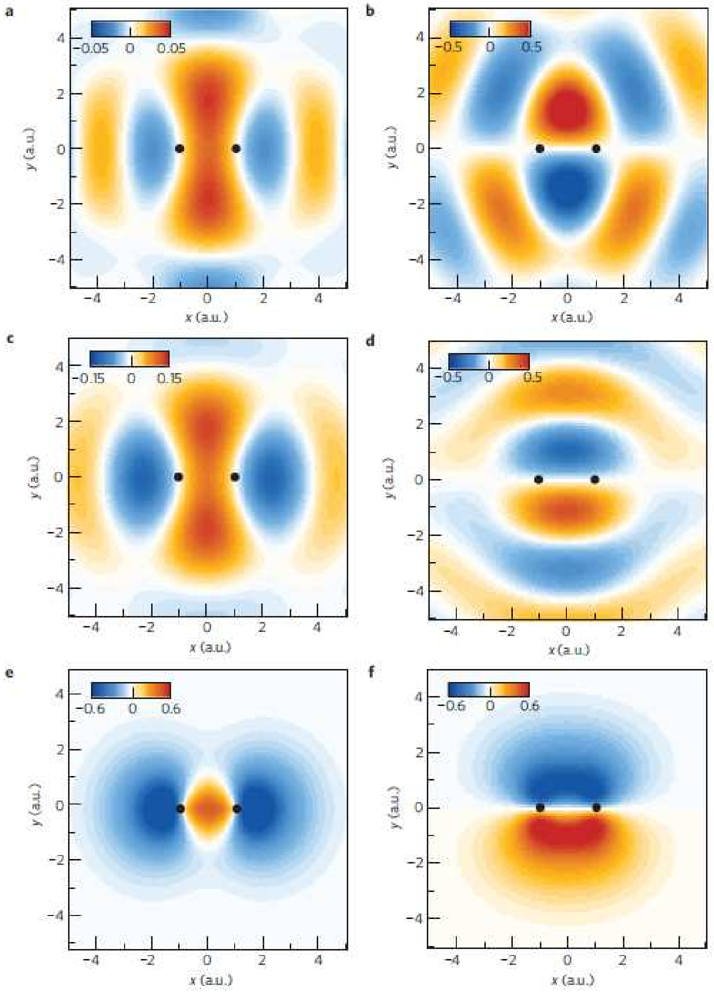


Haessler et al., Nat. Phys. **6**, 200 (2010)

Note the *orientation-independent* minimum at harmonic 25.

Tomographic imaging of molecular orbitals

Retrieved HOMO and HOMO-1 for N_2



experimental

simulated
(filtered ab-initio orbitals)

ab-initio orbitals

Haessler et al., Nat. Phys. **6**, 200 (2010)

Conclusions

- Great importance of multi-orbital dynamics in intense-laser-molecule interactions
- Need for combining strong-field methods with quantum-chemical calculations
- It is desirable to combine nuclear motion with TDDFT

Next part:

- Learning about TDDFT and physical mechanisms from model systems