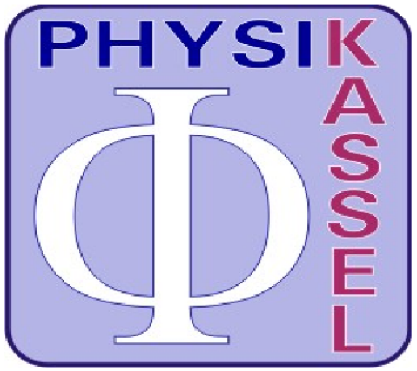
High-harmonic generation in small molecules: influence of vibration and laser dressing

Ciprian C. Chirilă and Manfred Lein



Theoretical physics,
University of Kassel, Germany

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WORKSHOP: "Extreme Light Infrastructure"
Măgurele, România

Outline

- Introduction.

- Harmonic generation in molecules:
  - molecular vibrational motion;
  - laser dressing.

- Results.

Atomic units are used.

Motivation

- To be able to describe accurately the harmonic generation in molecular systems (taking into account the effect of the molecular vibration, laser dressing, etc…).

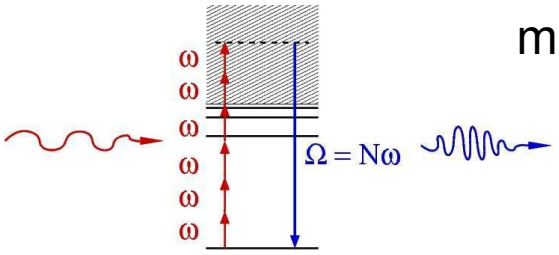
- To be able to understand in simple physical terms the relevant aspects of the harmonic generation dynamics, opening the way to its control.

- Availability of new infrared laser sources (~ 1-2 μm), e.g. Advanced Laser Light Source (ALLS) in Canada.

Introduction

Harmonic Generation –
definition and applications.

Harmonic generation: an atom/molecule irradiated by a laser with frequency ω emits radiation at frequencies Nω, multiples of the laser frequency.



In contrast to atoms, in molecules additional effects influence the HG process:

✓ the interference effect: the harmonic radiation emitted from each of the atomic sites interfere;

✓ the effect of nuclear vibration, greater importance of laser dressing, …

Applications of harmonic generation:

- generate extremely short (attosecond) light pulses;
- coherent X-ray spectroscopy;
- imaging molecular orbitals (molecular tomography);
- resolve molecular dynamics.

The single-atom/molecule dipole moment (SFA)

NEW[2]: ***Insert here the propagator from t' to t for the nuclear motion in the molecular ion (1, or 2 BO-potentials with laser coupling)***

STRONG FIELD APPROXIMATION[1]:

Dipole momentum: $\mathbf{P}(t) = -2\,Im$

$$\int_0^t dt' \,\langle \text{Initial molec. state}(t) \,|-i\vec{\nabla}\,|\, \text{Volkov propagator}(t,t') \times$$

$$\times\, \text{Interaction Hamiltonian}(t') \,|\, \text{Initial molecular state}(t')\rangle$$

recombination matrix element

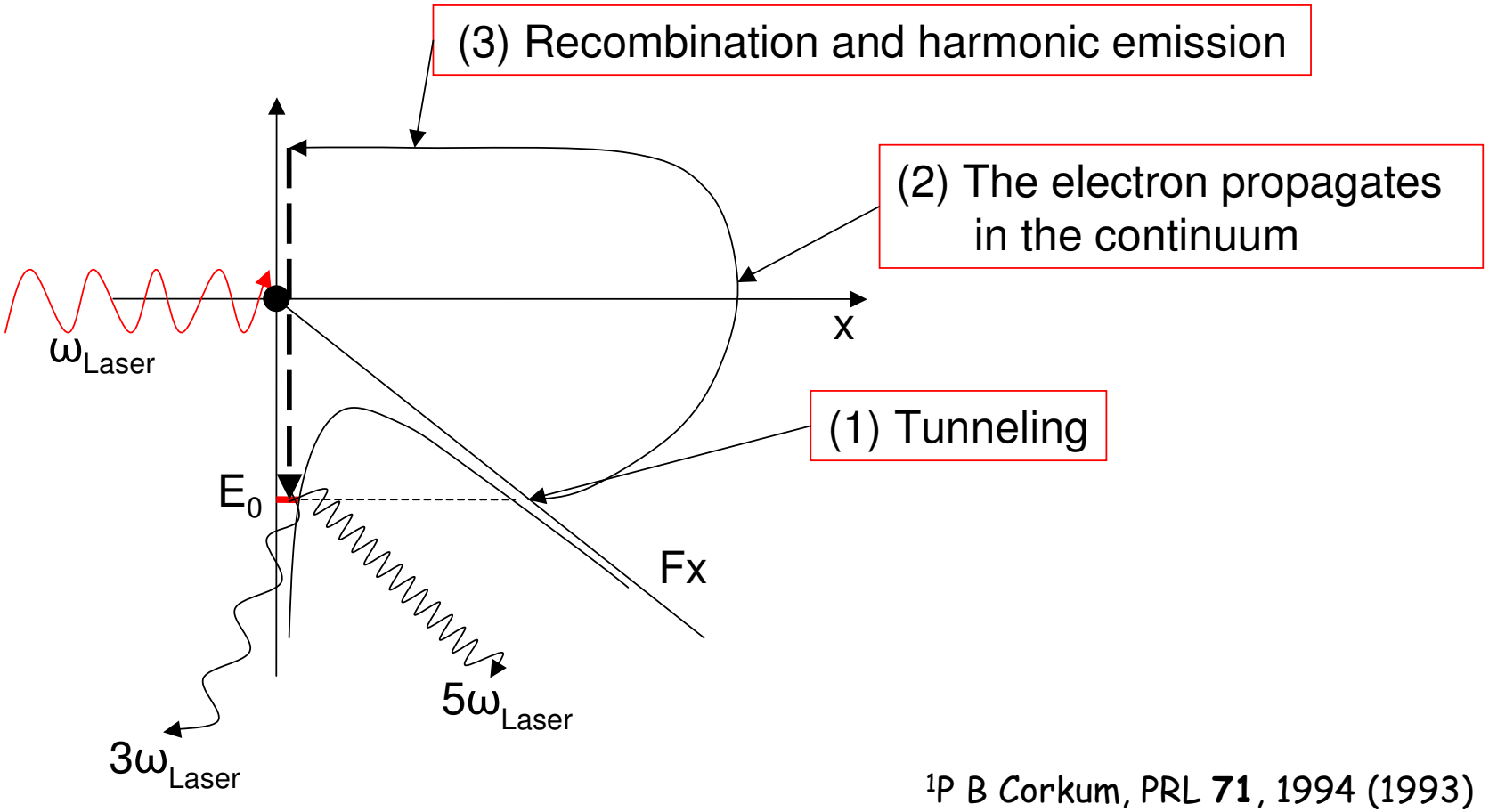
the free-electron propagator in the laser field

ionization matrix element

[1]Lewenstein, Balcou, Ivanov, L'Huillier and Corkum;
[2]C C Chirilă and M Lein, J. Phys. B **39**, S437 (2006).

The simple-man's (3-step) model[1]

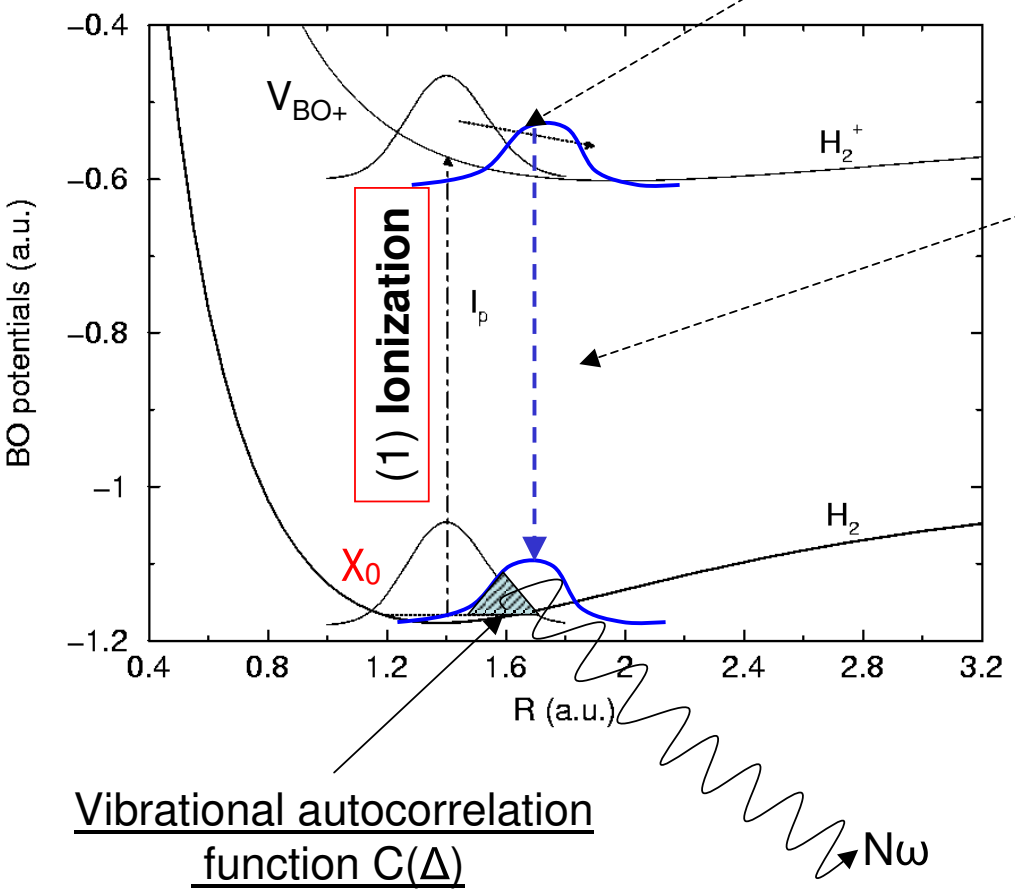
HG can be understood as a *sequence* of the following *three steps* for the electron:



[1]P B Corkum, PRL **71**, 1994 (1993)

The effect of vibration on HG: motion in one level (1L)

(2) **Field acceleration** of the active electron & evolution of the vibrational wave packet in the BO potential of the molecular ion



Vibrational autocorrelation function C(Δ)

(3) **Recombination**

Autocorrelation function:

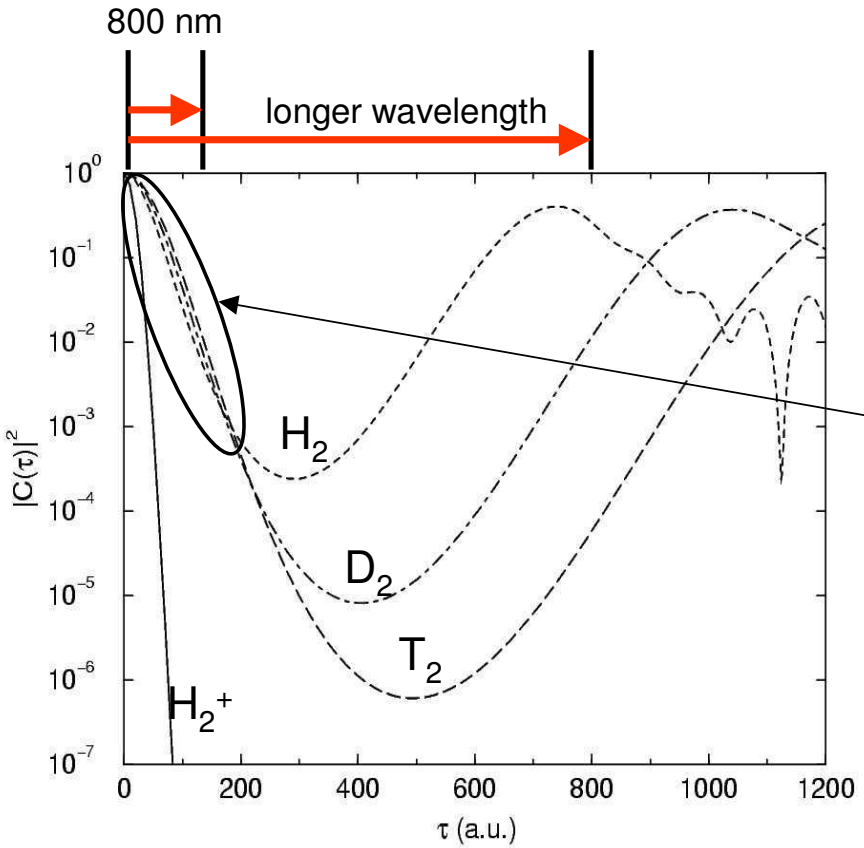
$$C(\Delta) = \int_0^\infty dR\, \chi_0(R) \exp(-i \hat{H}_R \Delta)\, \chi_0(R),$$

where $\chi_0(R)$ is the vibrational part of the molecular ground-state and $\hat{H}_R$ is the vibrational Hamiltonian of the molecular ion (*after* ionization):

$$\hat{H}_R = -1/M\ \partial^2/\partial R^2 + V_{BO+}(R).$$

(M is the mass of one nucleus.)

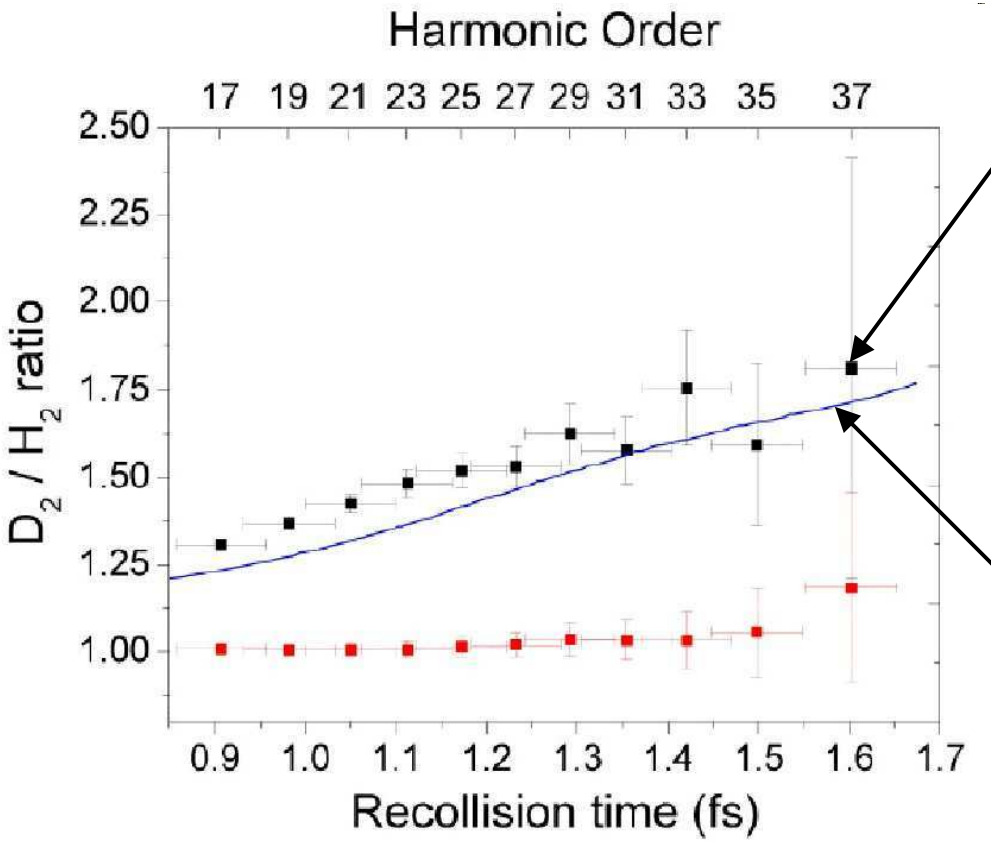
The autocorrelation function (1L): the isotope effect



The vibrational autocorrelation function for different molecular isotopes.

The effect of vibration is <u>smaller</u> for <u>heavier isotopes</u>!

Ratio D_2/H_2 of HG yields: experiment vs. theory



[1]Experiment

[2,3]Theory

The ratios were measured experimentally[1] and the theoretical predictions[2,3] were confirmed.

[1]S Baker, J Robinson, C A Haworth, H Teng, R A Smith, C C Chirilă , M Lein, J W G Tisch, and J P Marangos, Science **312**, 424 (2006);

[2]M Lein, PRL **94**, 053004 (2005);

[3]C C Chirilă and M Lein, J. Phys. B **39** , S437 (2006).

The molecular dipole momentum (SFA)

The electronic dipole momentum along the laser polarization direction reads:

ground vibrational state of the molecule

semiclassical action

$$P_x = -4\,\mathrm{Im}\int_0^t dt' \int_0^\infty dR\; \chi_0(R)\left[\frac{2\pi}{i(t-t')+1}\right]^{3/2} \exp[-i\,S(t',t)]\times$$

first two electronic states of the molecular ion

the unbound active electron

ground electronic state of the molecule

$$\left\langle \Psi_0(\vec{r}_1,\vec{r}_2)\middle|\hat{P}_{x1}\middle|Volkov\ (t,\vec{r}_1)\right\rangle \times [\left|\Psi_g^+(\vec{r}_2)\right\rangle, \left|\Psi_u^+(\vec{r}_2)\right\rangle]\times$$

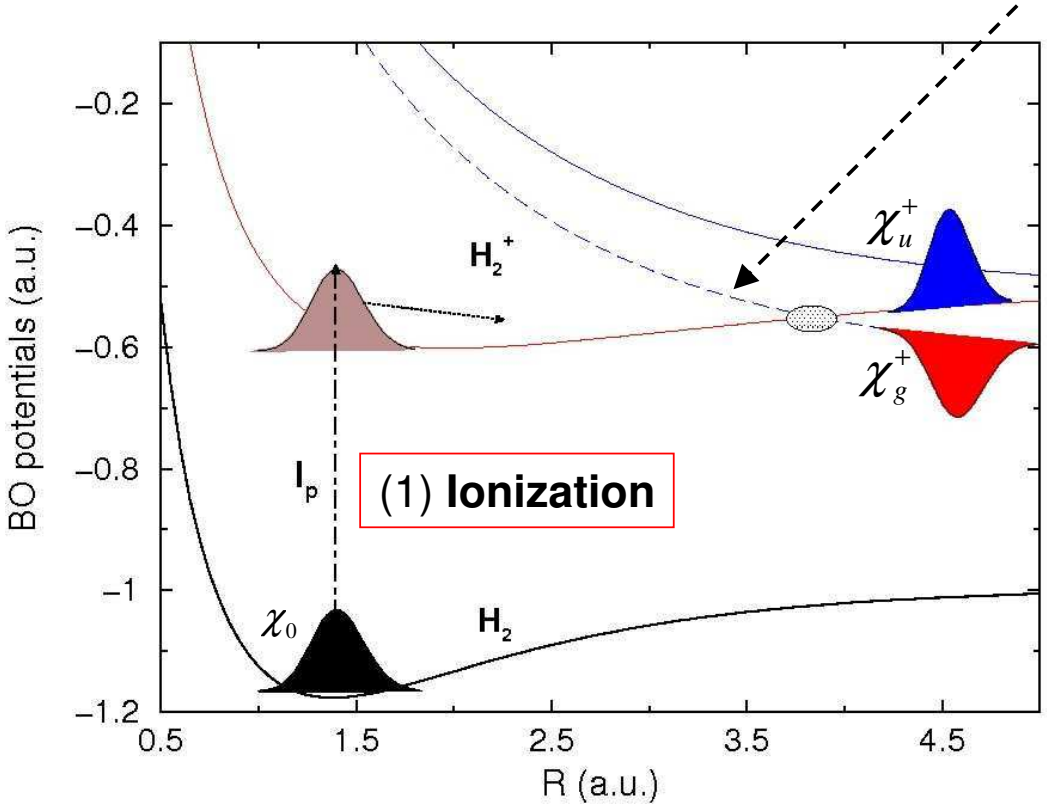
$$\hat{\mathrm{U}}_{\mathrm{R}}(t,t') \begin{bmatrix} \left\langle \Psi_g^+(\vec{r}_2)\right| \\ \left\langle \Psi_u^+(\vec{r}_2)\right| \end{bmatrix} Volkov\ \ (t',\vec{r}_1)\middle|E(t')\,x_1\middle|\Psi_0(\vec{r}_1,\vec{r}_2)\right\rangle \chi_0(R)$$

dipole coupling between the BO levels of the molecular ion

$$i\frac{d}{dt}\begin{bmatrix}\chi_g(R,t)\\ \chi_u(R,t)\end{bmatrix} = \begin{pmatrix} \hat{H}_{0g}^+ & \vec{E}(t)\cdot\vec{D}(R) \\ \vec{E}(t)\cdot\vec{D}(R) & \hat{H}_{0u}^+ \end{pmatrix}\begin{bmatrix}\chi_g(R,t)\\ \chi_u(R,t)\end{bmatrix}$$

The effect of vibration on HG: motion in two laser-dressed levels (2L)

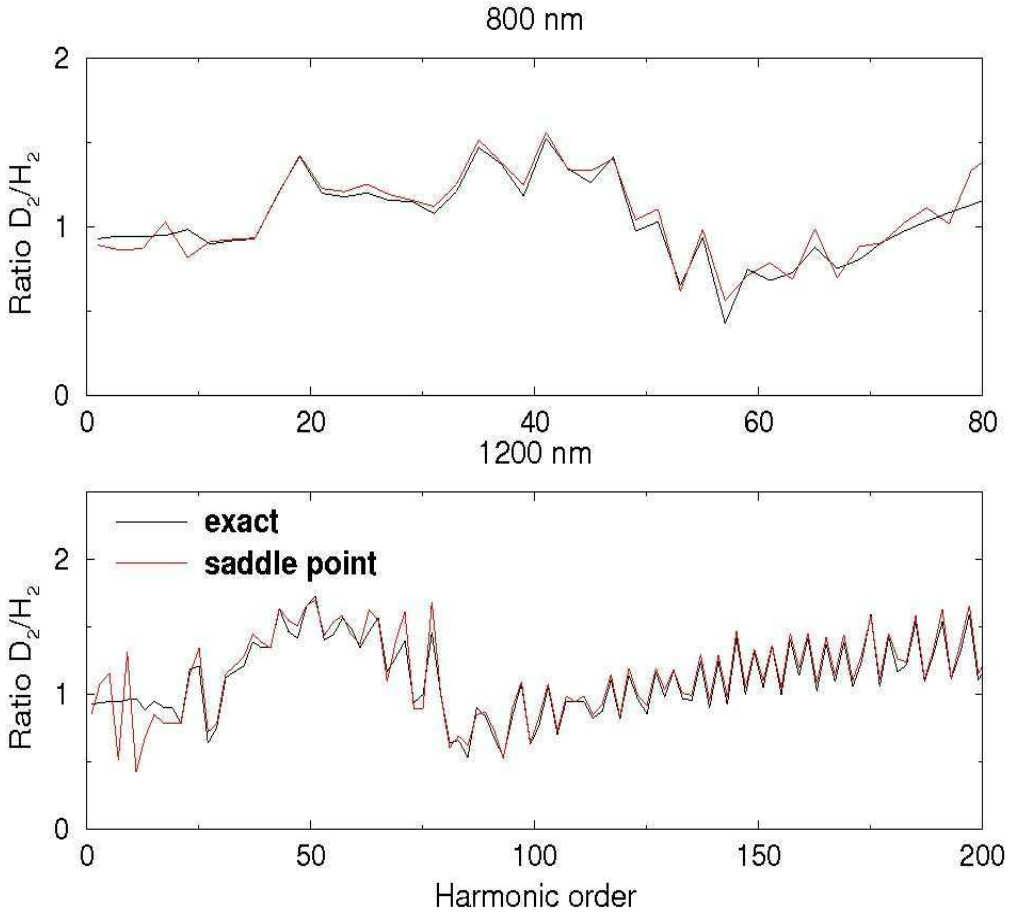
(2) **Field acceleration** of the active electron & evolution of the vibrational wave packet in the BO potential of the molecular ion



✓ After ionization, the vibrational wave packet is launched on the two lowest-laying Born-Oppenheimer potentials in the molecular ion.

✓ These two lowest-laying Born-Oppenheimer potentials in the molecular ion are dressed by the laser field.

Numerical aspects: the saddle-point method*



Ratio of the harmonic intensities in H_2 and D_2, aligned parallel $(\theta = 0)$ to the laser electric field.

The laser intensity is 5×10^{14} W/cm^2, the pulse is trapezoidal, with four optical cycles of constant amplitude.

Typical execution times:

(1) exact SFA calculation ≈ 1 week;

(2) saddle point method ≈ 1day.

*saddle point approximation for the integration over the ionization time.

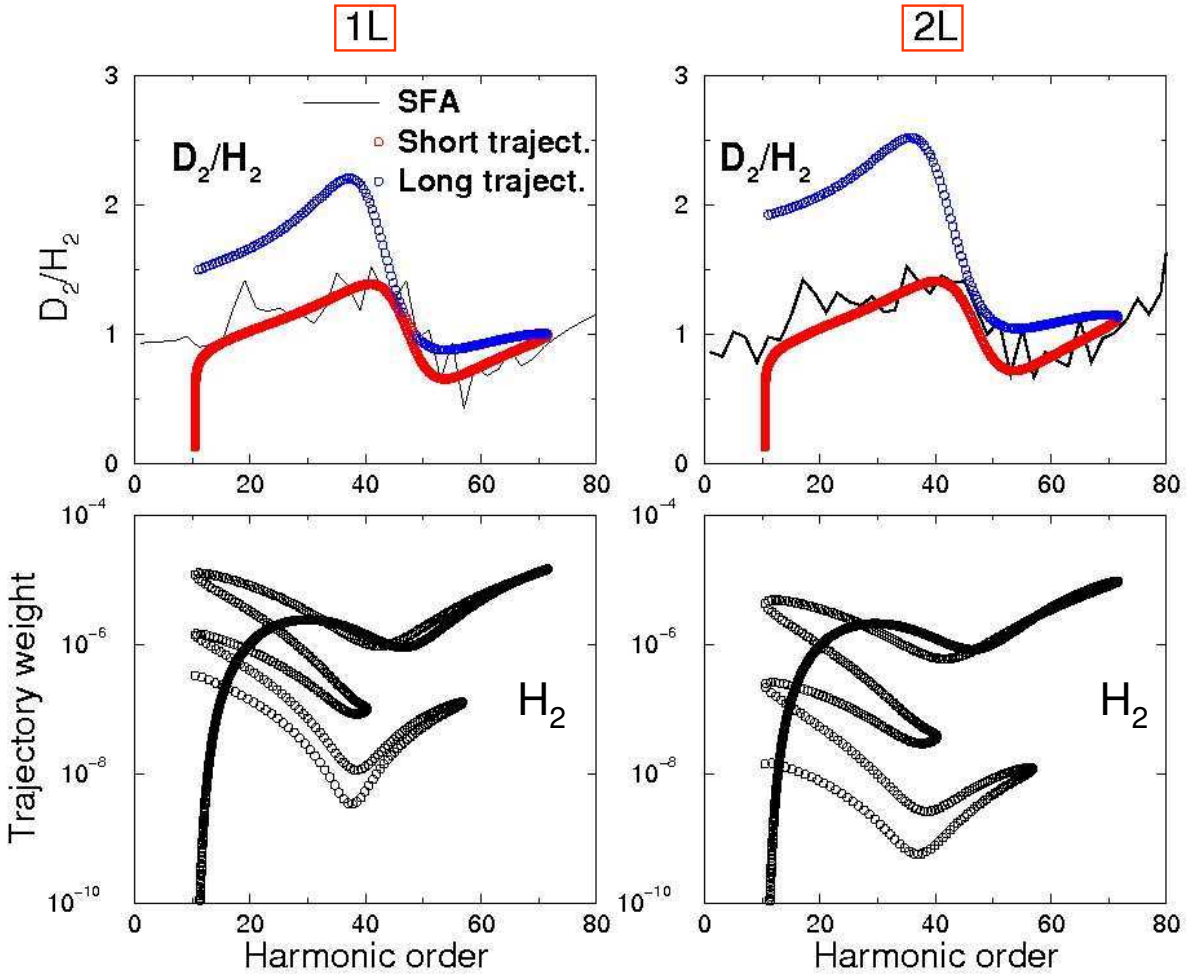
Simple-man's model: weight of an electronic trajectory

Given a certain classical electronic trajectory, that starts with the electron tunnelling out at time t' and recombination taking place at time t, the weight of the trajectory (*i.e.* the contribution to the total harmonic yield) is:

$$\propto \exp[-2/3(2I_p)^{3/2}/|E(t')|]\left|\int_0^\infty dR\cos(k_{ret}R\cos\theta/2)[\chi_0(R),0]\hat{U}_R(t,t')\begin{bmatrix}\chi_0(R)\\0\end{bmatrix}\right|^2$$

where k_{ret} is the returning velocity, and θ is the angle between the molecular axis and the laser polarization axis.

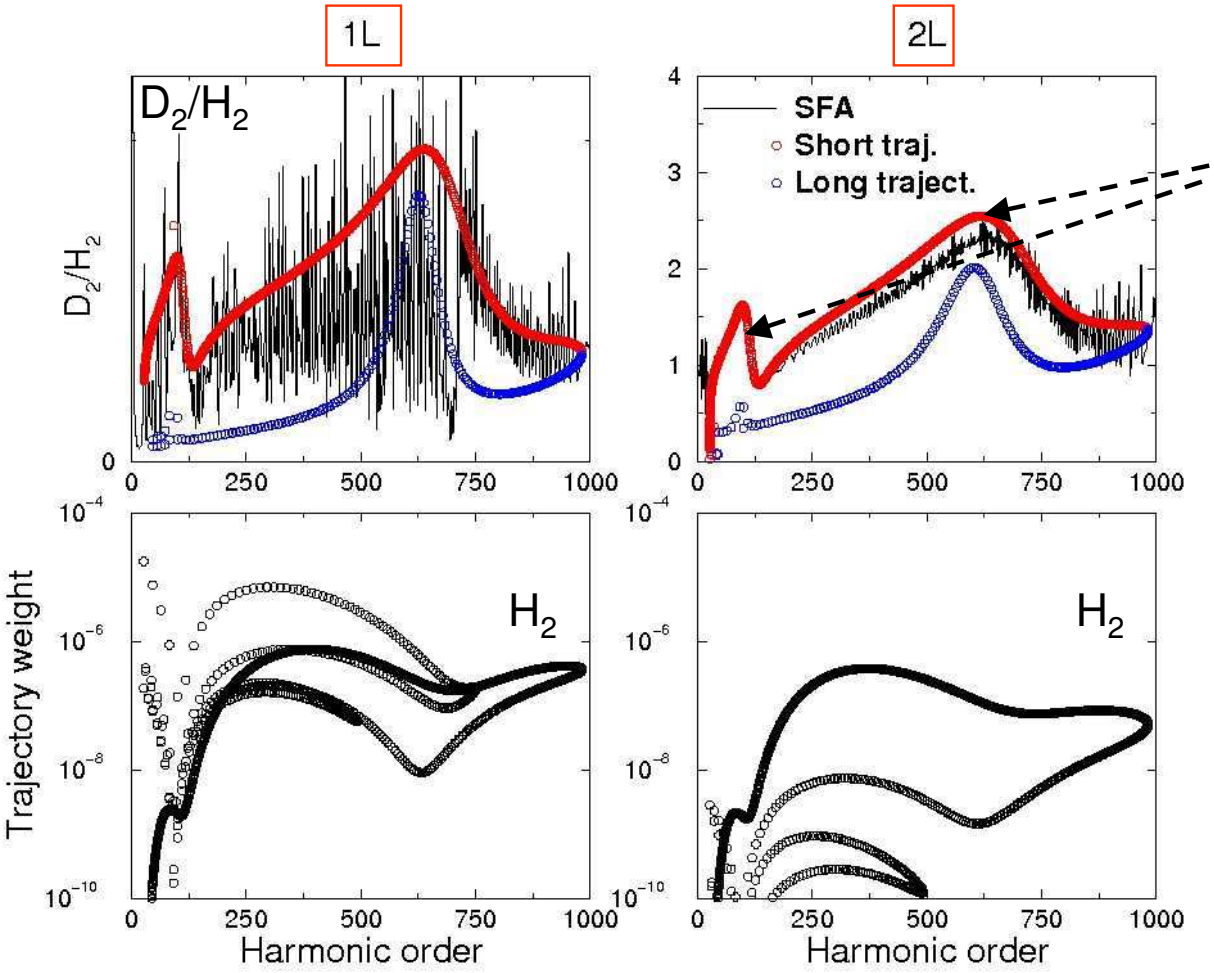
Results (800 nm)



The results are hardly affected by the field dressing.

* $\theta = 0$, laser intensity: I = 5 x 10^{14} W/cm^2 .

Results (2000 nm)



Signatures of the two-center interference !

The results are significantly affected by the field dressing.

The dressing strongly affects the long electronic trajectories.

Field dressing selects short trajectories!

* $\theta = 0$, laser intensity: I = 5 x 10^{14} W/cm^2 .

Conclusions

- The strong-field approximation can be extended to take into account the effects of the molecular vibration on the harmonic emission.

- The laser dressing of the BO-potential surfaces causes non-negligible changes in the harmonic emission.

- The effect of the field coupling in the molecular ion increases with the increase of the laser wavelength.

Thank you for your attention !