Multielectron effects on strong-field multiphoton ionization of polyatomic molecules

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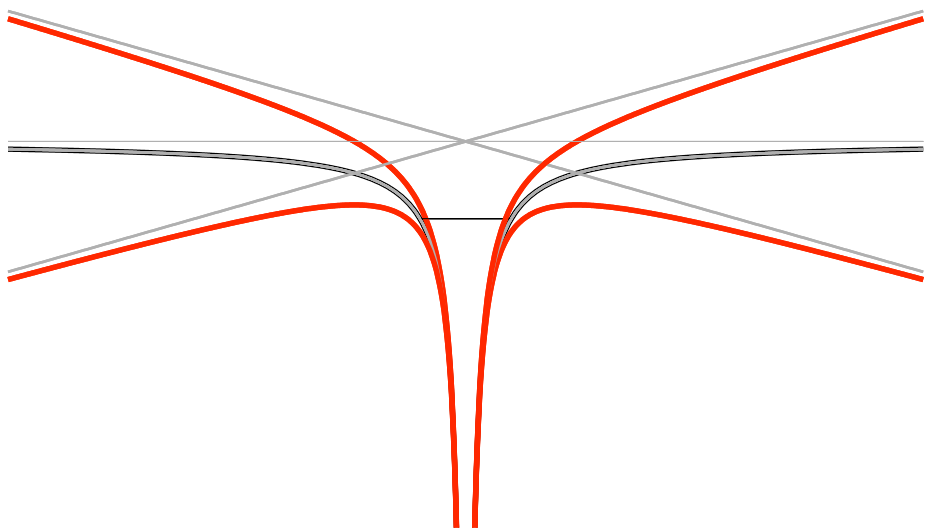
Abstract

We present time-dependent density-functional theory (TDDFT) studies of multiphoton ionization (MPI) of several polyatomic molecules in intense short-pulse laser fields with proper treatment of multielectron effects. For an accurate all-electron solution for polyatomic molecules, we develop a new time-dependent Voronoi-cell finite difference (TDVFD) method with highly adaptive multicenter molecular grids. We apply the method to investigate the orientation dependence of MPI of N_2, CO_2, and H_2O, revealing the importance of multielectron effects from multiple orbital dynamics.

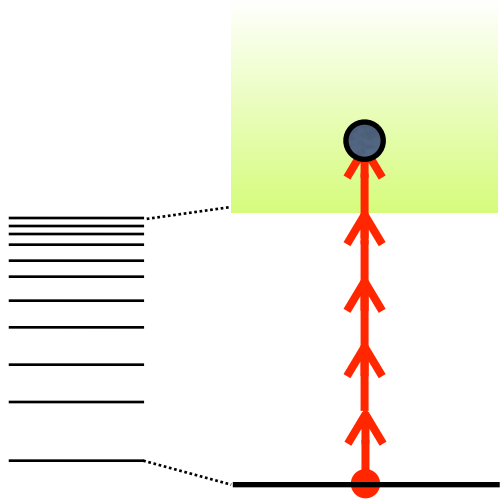
Keywords

We present time-dependent density-functional theory (**TDDFT**) studies of multiphoton ionization (**MPI**) of several **polyatomic molecules** in intense short-pulse laser fields with proper treatment of multielectron effects. For an accurate all-electron solution for polyatomic molecules, we develop a new time-dependent Voronoi-cell finite difference (**TDVFD**) method with highly adaptive multicenter molecular grids. We apply the method to investigate the **orientation dependence** of MPI of N_2, CO_2, and H_2O, revealing the importance of **multielectron effects** from multiple orbital dynamics.

Strong-field multiphoton phenomena



A strong external laser field tilts and oscillates the Coulomb potential.

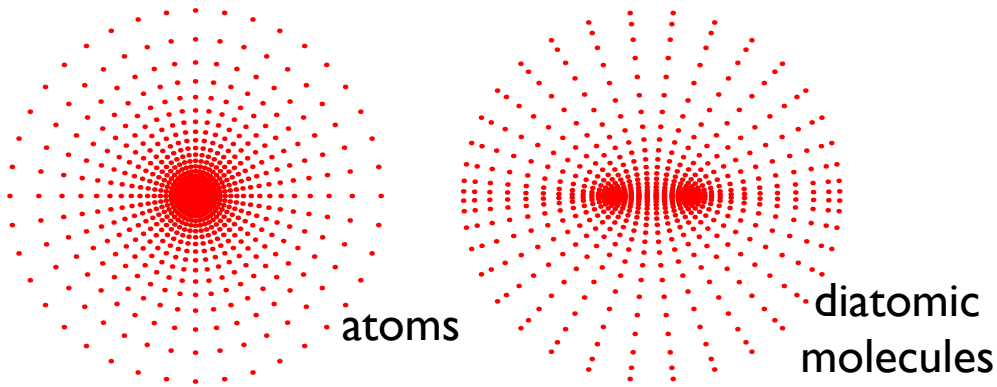


multiphoton excitation / ionization

Multiphoton excitation (MPE), ionization (MPI), and dissociation (MPD), above-threshold ionization (ATI) and dissociation (ATD), multiple high-order harmonic generation (HHG), Coulomb explosion (CE), etc

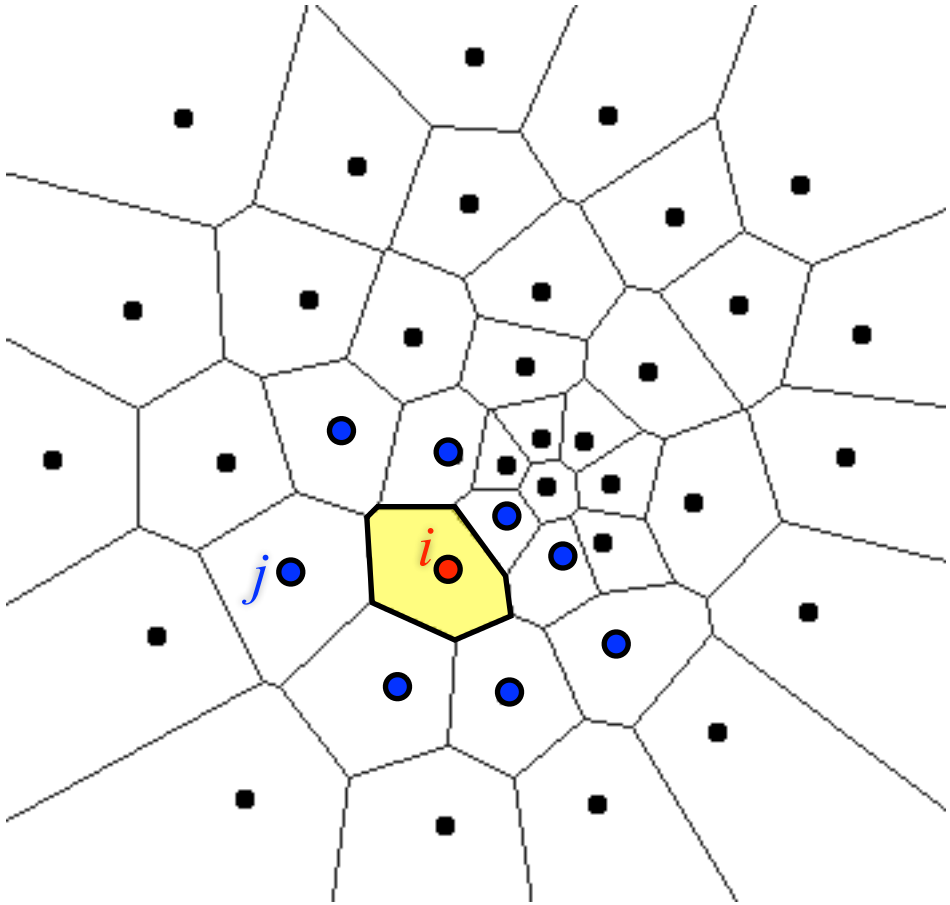
Numerical simulation for strong-field processes

- Challenges in *ab initio* calculations for strong-field processes
  - electronic structure for bound / continuum states
  - short- and long-range interactions of the Coulomb potential
  - multielectron effect
  - large spatial dimension & efficient time propagator required
- Many theoretical treatments are limited to simple one-electron models without detailed electronic structures.
- Generalized pseudospectral (GPS) and TDGPS on *nonuniform* grids developed by Prof. Chu's group



- A new method for polyatomic molecules in demand

Voronoi diagram



- On randomly distributed grids
- Discretize the whole space into Voronoi cells encapsulating each grid
- PDE solvers utilizing geometrical advantages of the Voronoi diagram

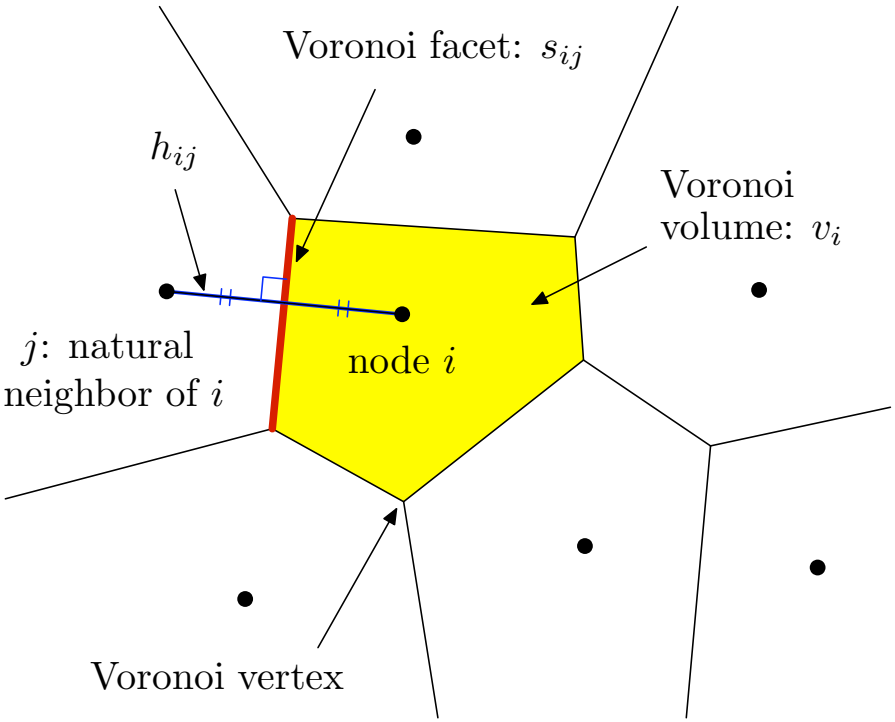
NEM: Braun & Sambridge, *Nature* **376**, 655 (1995)

VFD: Sukumar & Bolander, *CMES* **4**, 691 (2003) / Sukumar, *Int. J. Numer. Meth. Engng* **57**, 1 (2003)

Voronoi diagram: $T_i = \{\mathbf{x} \in \mathbb{R}^n : d(\mathbf{x}, \mathbf{x}_i) < d(\mathbf{x}, \mathbf{x}_j) \text{ for } \forall j \neq i\}$

All points in T_i are closer to $\mathbf{x}_i$ than any other grids.

Voronoi-cell finite difference



Laplacian definition from Gauss's theorem

$$\nabla^2\varphi = \lim_{\int_V dV \to 0} \frac{\int_S \nabla\varphi \cdot \mathbf{n}\, d\sigma}{\int_V dV}$$

Discrete Laplacian after Voronoi discretization

$$\left(\nabla^2\varphi\right)_i = \frac{1}{v_i} \sum_{j}^{\text{natural neighbors}} \frac{\varphi_j - \varphi_i}{h_{ij}} s_{ij}$$

i) volume and surface integrals are computed by Voronoi volumes and Voronoi facet areas

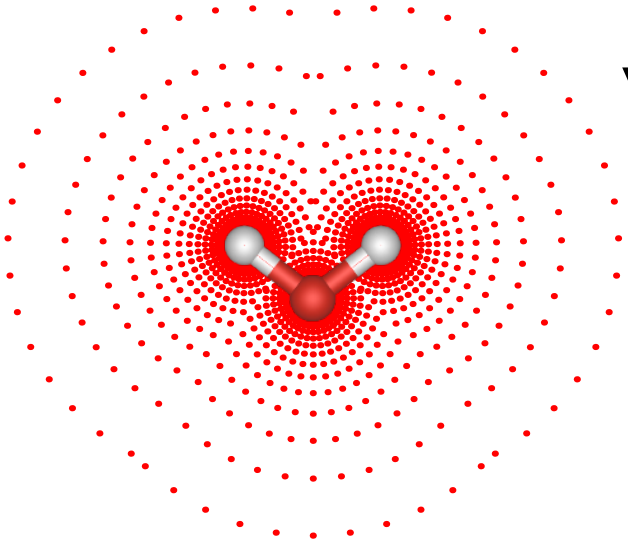
ii) a simple difference scheme is used for directional derivatives

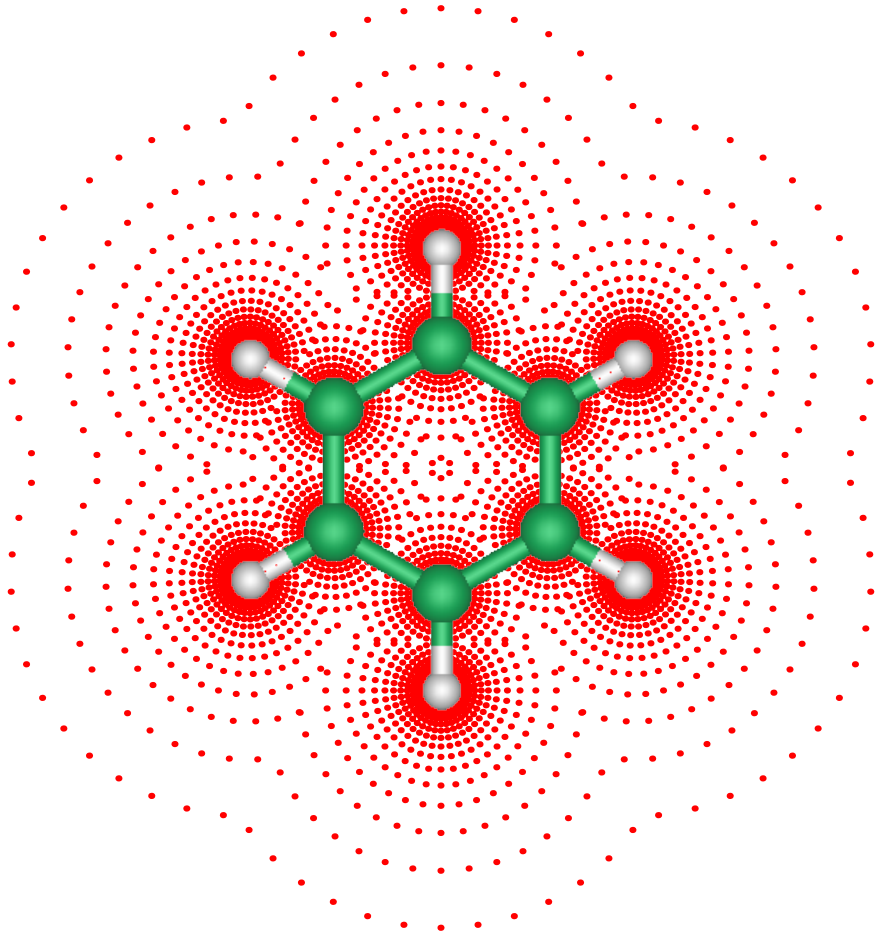
VFD has been extended for accurate electronic structure and dynamics calculations for the first time.

Son (submitted) / Son & Chu, *Chem. Phys.* (in press)

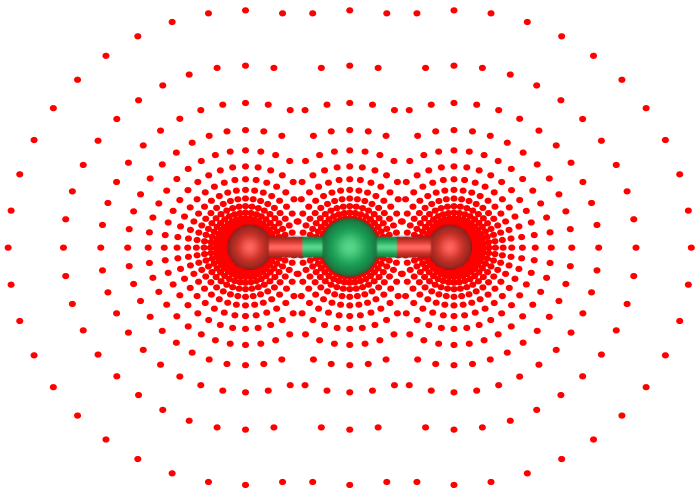
Molecular grids

water: H_2O





carbon dioxide: CO_2



benzene: C_6H_6

VFD works on multicenter molecular grids.

TDDFT

- Time-dependent Kohn-Sham equation for *N*-electron system in laser fields

$$i\frac{\partial}{\partial t}\psi_{i\sigma}(\mathbf{r},t) = \left[-\frac{1}{2}\boldsymbol{\nabla}^2 + u_{\mathrm{eff},\sigma}(\mathbf{r},t)\right]\psi_{i\sigma}(\mathbf{r},t),$$

$$(i = 1, 2, ..., N_\sigma).$$

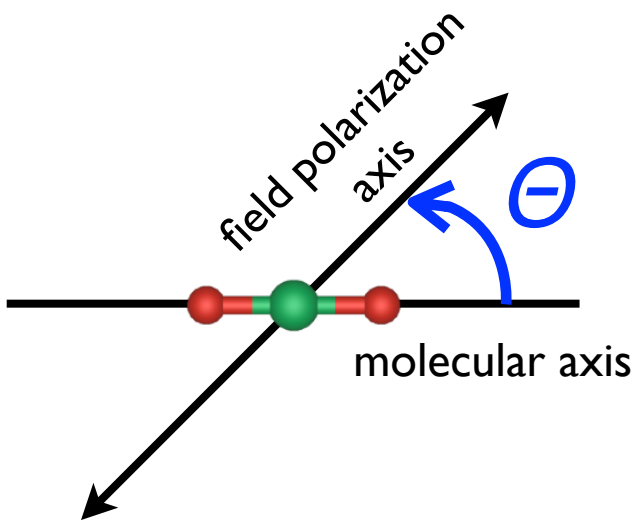
$$u_{\mathrm{eff},\sigma}(\mathbf{r},t) = u_{\mathrm{ne}}(\mathbf{r}) + u_{\mathrm{h}}(\mathbf{r},t) + u_{\mathrm{xc},\sigma}(\mathbf{r},t) + \mathbf{F}(t)\cdot\mathbf{r}$$

- TDDFT considers responses in multiple orbital dynamics, which are ignored in most of model calculations based on the single-active electron approximation.

- Self-interaction-correction and proper long-range potential are necessary to investigate strong-field multiphoton processes.

Chu, *J. Chem. Phys.* **123**, 062207 (2005)

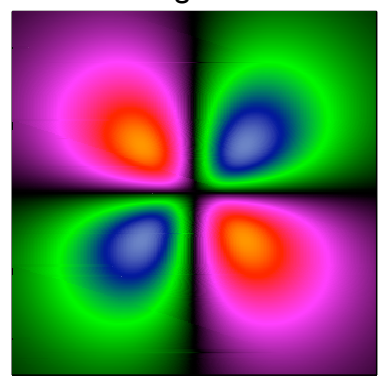
Orientation dependence



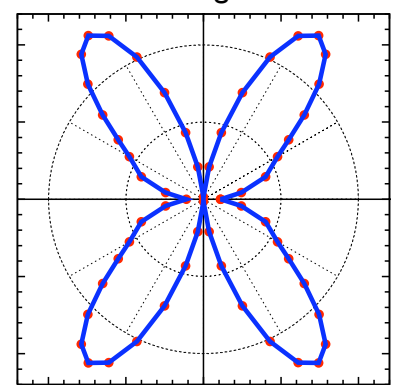
- Laser-induced molecular alignment with an intermediate-intensity laser field
- Probe aligned molecules with a linearly polarized strong laser field
- Measure ionization yields as a function of the orientation angle

- Orientation-dependent MPI plot is reflected by the molecular orbital symmetry.
- Most of theoretical models consider only HOMO in many-electron systems.

H_2^+ π_g orbital



H_2^+ π_g MPI



Kamta & Bandrauk, *Phys. Rev. A* **74**, 033415 (2007)

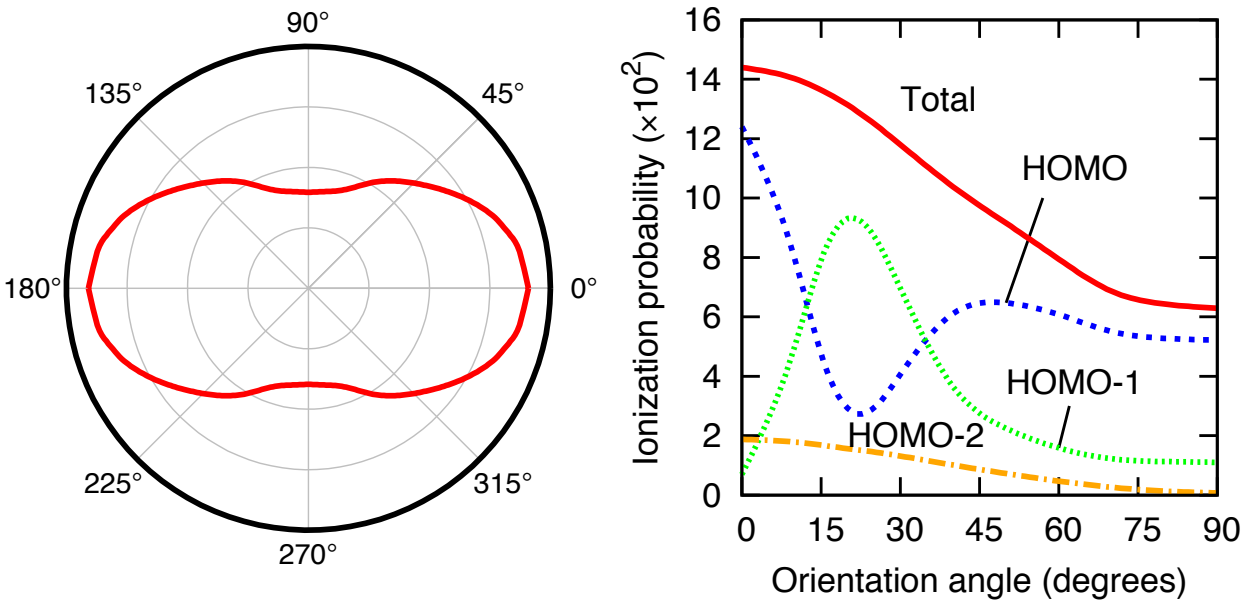
Keywords (again)

Our results of **TDDFT** solved by TDVFD show **multielectron effects** on the orientation dependence of MPI of polyatomic molecules.

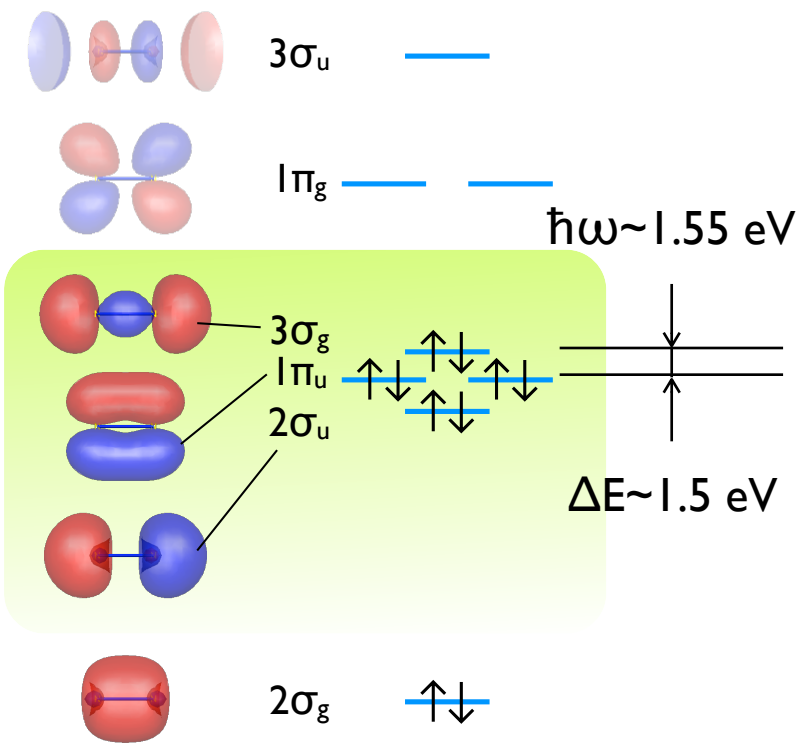
MPI of N_2

Orientation dependence of N_2 MPI

800 nm, 2×10^{14} W/cm^2



N_2 MO diagram



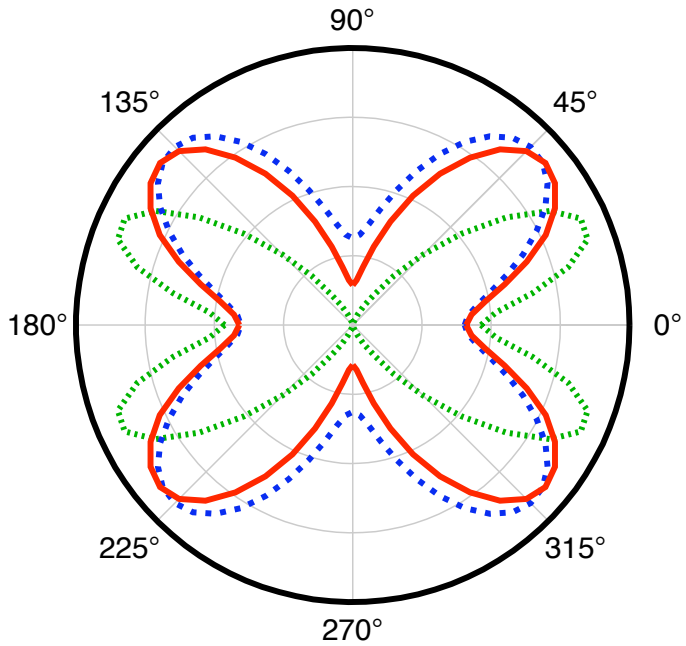
A possible one-photon resonance between HOMO and HOMO–1 yields a strong mixing of their contributions to the total ionization probability.

Son & Chu, *Chem. Phys.* (in press, DOI: 10.1016/j.chemphys.2009.09.006)

MPI of CO_2

Orientation dependence of total ionization probability

800 nm, 5×10^{13} W/cm^2

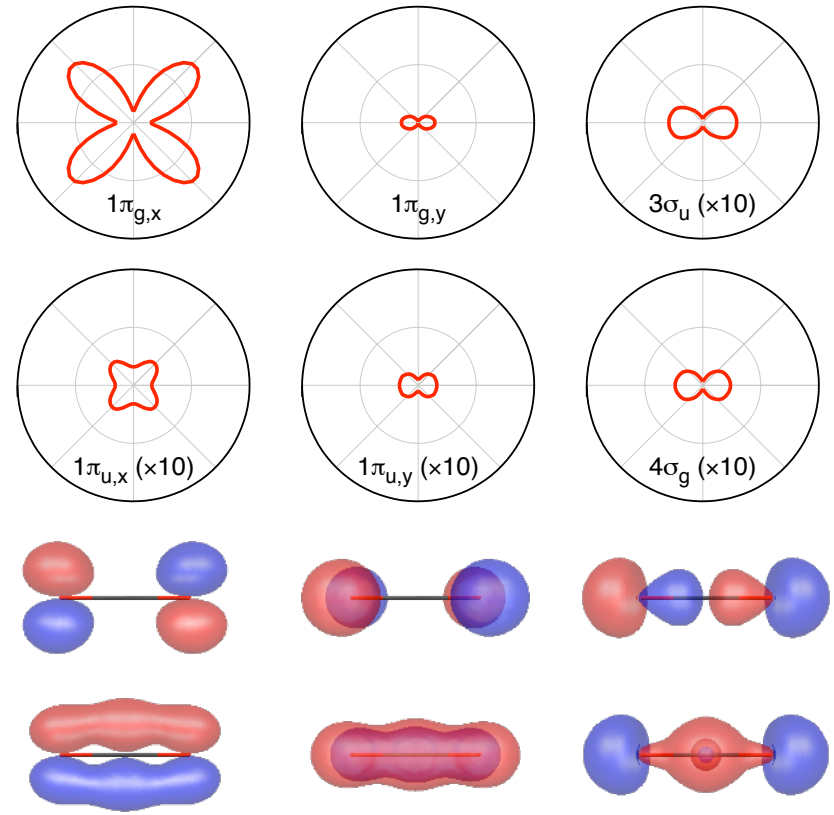


TDDFT: Son & Chu, *Phys. Rev. A* **80**, 011403(R) (2009)

EXP: Thomann *et al.*, *J. Phys. Chem. A* **112**, 9382 (2008)

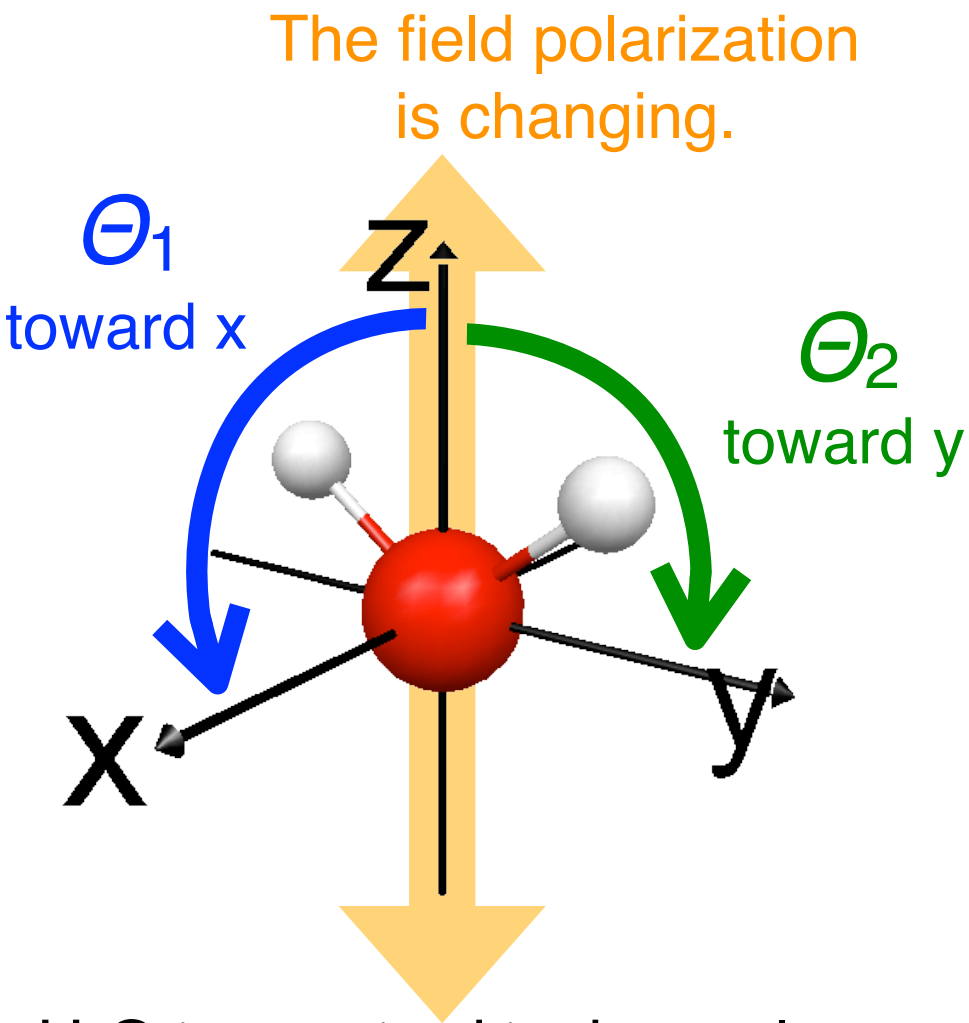
MO–ADK: Le *et al.*, *J. Mod. Opt.* **54**, 967 (2007)

Orientation dependence of individual ionization probability from multiple orbitals

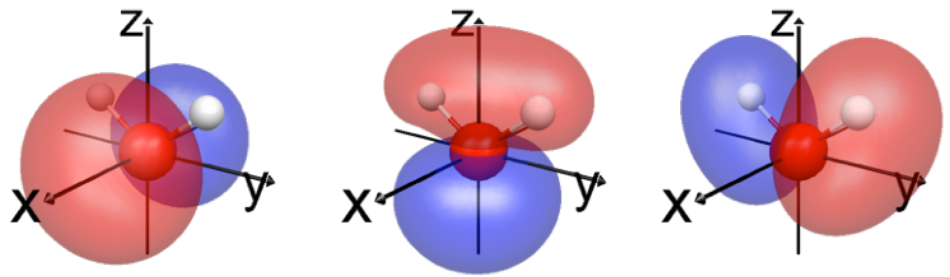


The TDDFT results agree well with recent experiments of the orientation dependence of CO_2 MPI.

Selectively probing of multiple orbitals in H_2O



H_2O is contained in the *yz*-plane.



HOMO ($1b_1$) −12.6 eV

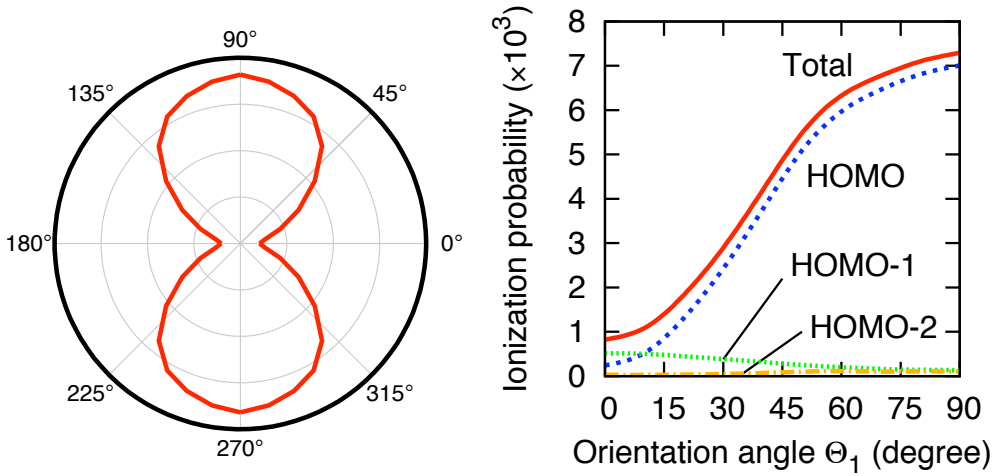
HOMO–1 ($3a_1$) −14.8 eV

HOMO–2 ($1b_2$) −18.7 eV

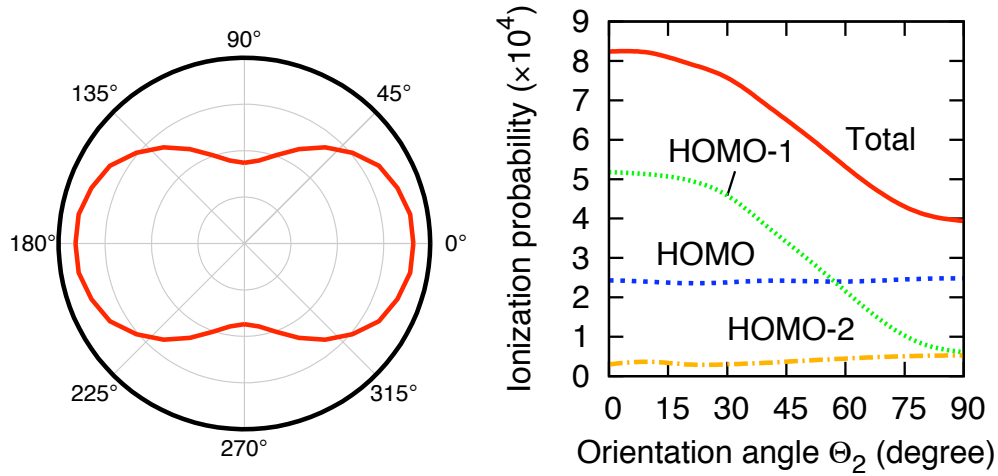
- Increasing Θ_1 toward x
  - Maximize MPI of HOMO
  - Minimize MPI of HOMO–1
  - No effect on MPI of HOMO–2
- Increasing Θ_2 toward y
  - No effect on MPI of HOMO
  - Minimize MPI of HOMO–1
  - Maximize MPI of HOMO–2

MPI of H_2O

H_2O at 800 nm, 5×10^{13} W/cm^2
orientation-dependent plot w.r.t. Θ_1



H_2O at 800 nm, 5×10^{13} W/cm^2
orientation-dependent plot w.r.t. Θ_2



- HOMO is dominant to the orientation-dependent MPI pattern when Θ_1 changes.

- The change of Θ_2 in the *yz*-plane does not affect HOMO ionization because HOMO has a nodal plane of the *yz*-plane.
- HOMO–1 shows dominant contribution to the overall pattern when Θ_2 changes.

Son & Chu, *Chem. Phys.* (in press, DOI: 10.1016/j.chemphys.2009.09.006)

Conclusion

- TDDFT is a promising tool to investigate strong-field electronic dynamics of many-electron systems in intense ultrashort laser fields.
- TDVFD provides accurate TDDFT solutions for polyatomic molecules on highly adaptive multicenter molecular grids.
- Detailed electronic structure and responses in multiple orbital dynamics are important in strong-field electronic dynamics.
- Orientation-dependent studies of MPI of N_2, H_2O, and CO_2 demonstrate the importance of multielectron effects such as multiple orbital contributions.

Acknowledgment

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