Dissociative ionization of O_2

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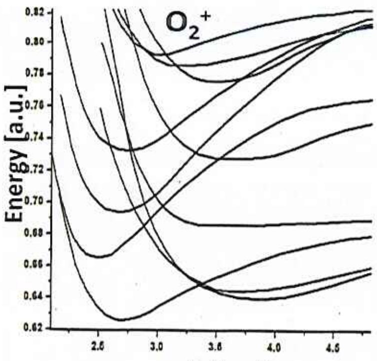
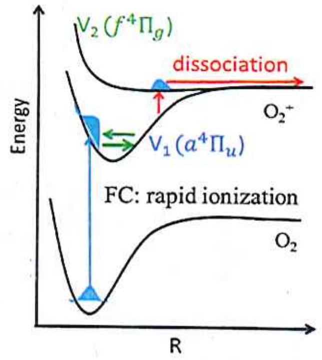
Heavier molecules are more complicated...



Marian *et al.*, Mol. Phys., **46** 779 (1982)

Two dominant O_2^+ BO states (low KER): $a^4\Pi_u$ and $f^4\Pi_g$

- Highest dipole coupling strength (as calculated using GAMESS)[2,6]
- O_2^+ vibr. oscillation / q-beat / revival periods in measured KER spectra[2,3,4,5]
- Adding O_2^+ ($b^4\Sigma_g$) state insignificantly affects KER spectra (< 0.6 eV)[5]

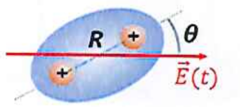


[1]De, Ben-Itzhak *et al.*, PRA **79**, 043410 (2011)	E+T	JRML
[2]Magrakvelidze *et al.*, PRA **86**, 023402 (2012)	T	JRML/KSU-Che.
[3]Magrakvelidze *et al.*, JPB **47**, 124003 (2014) & refs.	T+E	JRML
[4]Coerlin *et al.*, PRA **91**, 043415 (2015)	E+T	MPI-K
[5]Xue, Lin, Le *et al.*, PRA **97**, 043409 (2018)	T	JRML
Malakar, Rudenko *et al.*, PRA **98**, 013418 (2018)	E	JRML
[6]Abanador, Pauly, Thumm, PRA **101**, 043410 (2020)	T	JRML
Abanador, Thumm, PRA **102**, 053114 (2020)	T	

Numerical method: nuclear wavepacket propagation

Coupled-state TDSE

$$i\frac{d}{dt}\begin{pmatrix}\Psi_1\\ \Psi_2\\ \vdots\end{pmatrix} = \begin{pmatrix}T_R+V_1 & D_{12} & \cdots\\ D_{21} & T_R+V_2 & \cdots\\ \vdots & \vdots & \ddots\end{pmatrix}\begin{pmatrix}\Psi_1\\ \Psi_2\\ \vdots\end{pmatrix}$$



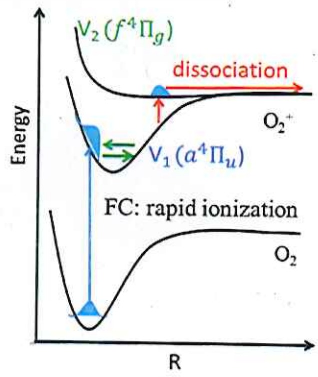
$D_{ij} = d_{ij}(R)\, E(t) \cos(\theta)$

"1D calculations": Fixed molecular orientation θ

$$\hat{H} = -\frac{1}{2M_r}\frac{\partial^2}{\partial R^2} + \begin{pmatrix} V_1 & d_{12}E(t)\cos(\theta)\\ \underbrace{d_{12}E(t)\cos(\theta)}_{E_{eff}} & V_2\end{pmatrix}$$

"2D calculations": Ro-vibrational dynamics

$$\hat{H} = -\frac{1}{2M_r}\frac{\partial^2}{\partial R^2} + \frac{L_\theta^2}{2\mu R^2} + \begin{pmatrix} V_1 & d_{12}E(t)\cos(\theta)\\ d_{12}E(t)\cos(\theta) & V_2\end{pmatrix}$$



Comparison:
Quantify effects of rotational excitation, e.g., ***motion toward LICI***

Nuclear probability density: $\rho(R,\theta,t) = \sum_i |\Psi_i(R,\theta,t)|^2$

Abanador, Pauly, Thumm, PRA **101**, 043410 (2020)

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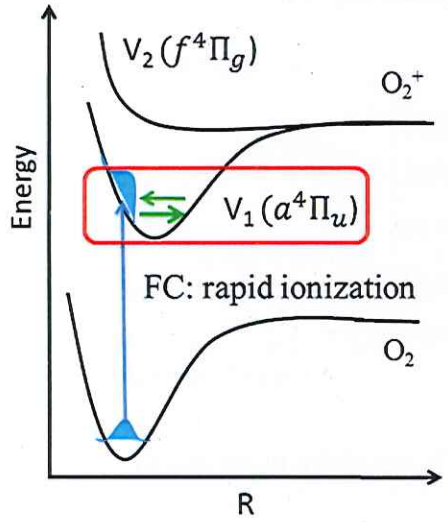
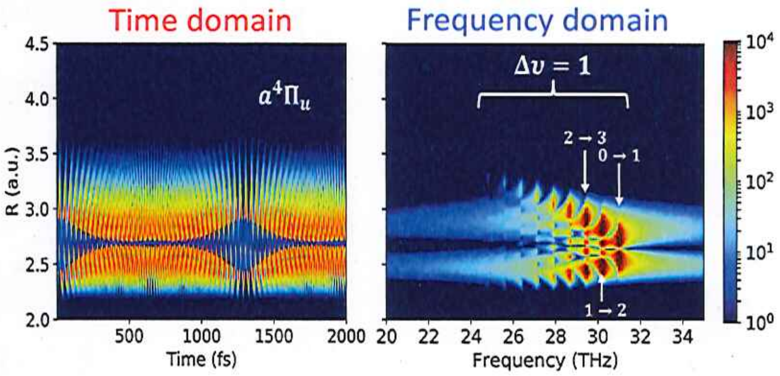
O_2^+ : Field-free propagation

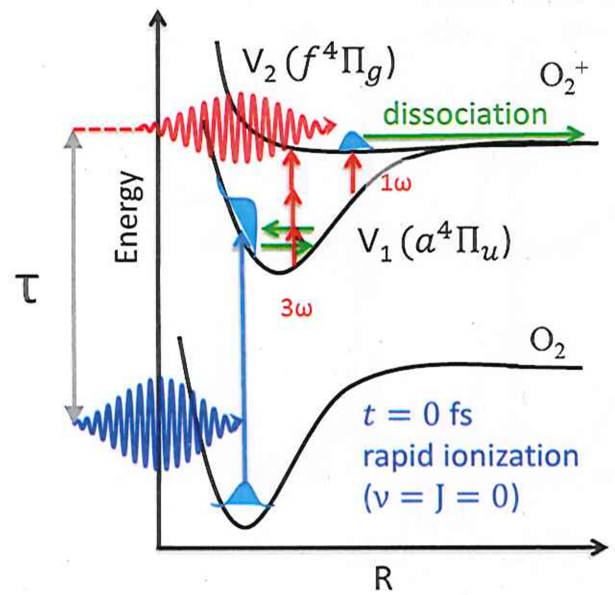




- Oscillation period
- Revival times

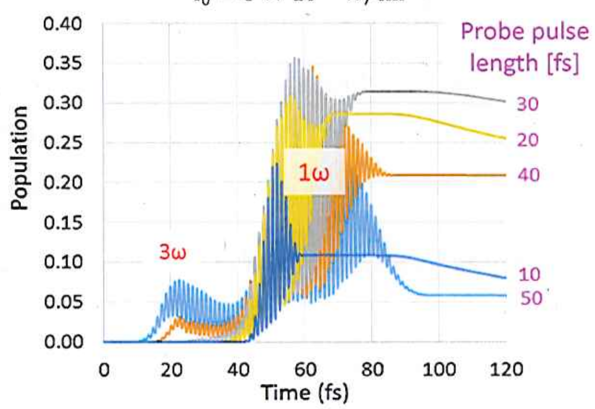
- Vibrational beat frequencies
- Nodal structure of stationary vibrational states
- O_2^+ ($a\ ^4\Pi_u$) potential curve

O_2^+ : Molecular bond stabilization (bond hardening)



Population transfer to the O_2^+ ($f\ ^4\Pi_g$) state

$I_0 = 6 \times 10^{14}$ W/cm^2



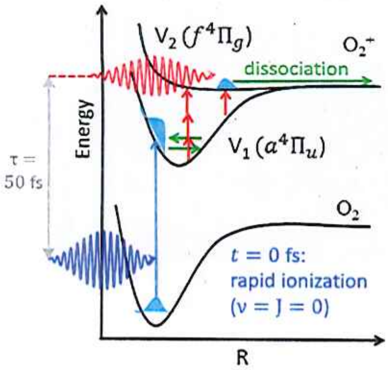
- O_2^+ ($a\ ^4\Pi_u \leftrightarrow f\ ^4\Pi_g$) Rabi flopping
- Dissociation suppression
  For long pulses, less final population in dissociating O_2^+ ($f\ ^4\Pi_g$) state.

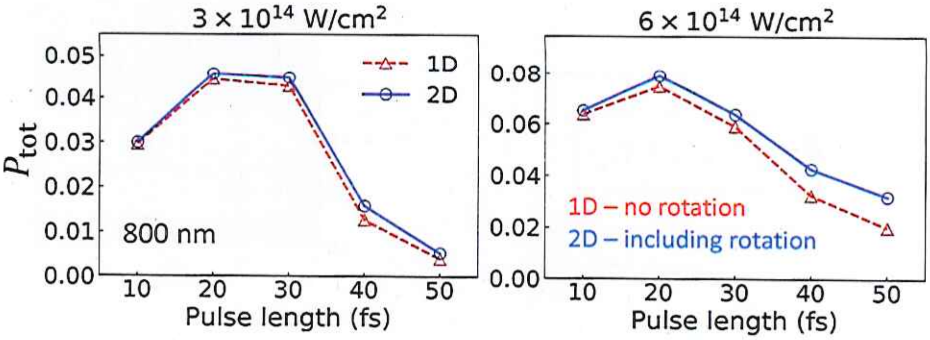
Abanador, Pauly, Thumm, Phys. Rev. A **101**, 043410 (2020)

O_2^+ : Molecular bond stabilization

(114)

Probe-pulse duration dependence of dissociation probability (integrated over θ)



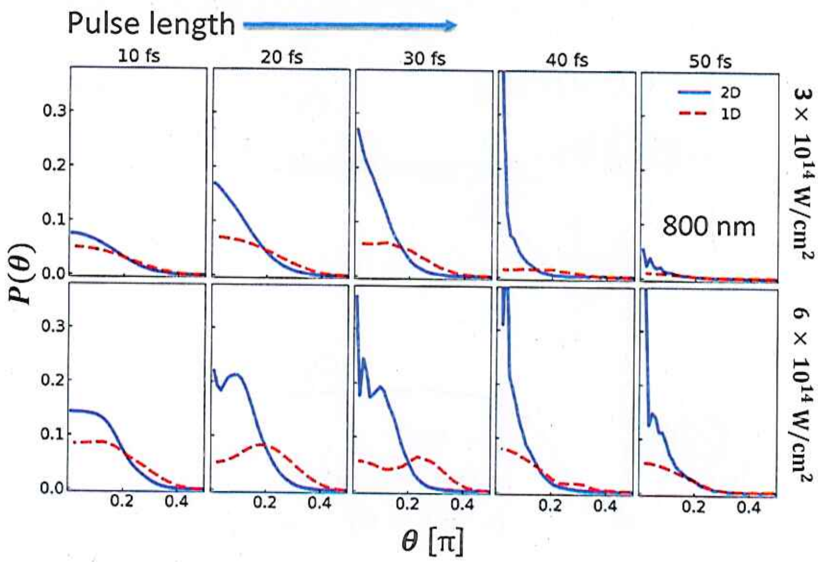


- Nonmonotonic dependence of P_{tot} on probe-pulse length
- Dissociation suppression persists when including molecular rotation

Abanador, Pauly, Thumm, Phys. Rev. A **101**, 043410 (2020)

O_2^+ : Angular distribution of photofragments

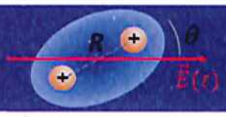
- In longer pulses
  - Rotational excitation
  - Molecular stabilization (reduced dissociation)
- Modulations in the angular distribution
  - Higher excited rotational states
  - Dynamics near LICI intersection [1]



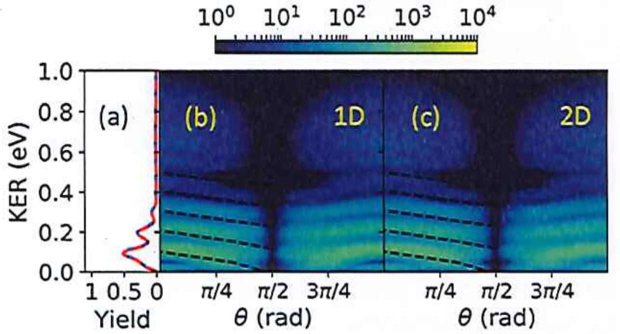
[1] **cf., H_2^+ :** Halasz, Vibok, Cederbaum, J. Phys. Chem Lett. **6**, 348 (2015)
Natan, Bucksbaum *et al.*, Phys. Rev. Lett. **116**, 143004 (2016)

Abanador, Pauly, Thumm, Phys. Rev. A **101**, 043410 (2020)

O_2^+ : KER spectra — Transient trapping in LIP



Probe pulse:
40 fs, 800 nm, 50 fs delay, 10^{13} W/cm²



(a) Angle-integrated
(b,c) Angle-resolved (1D,2D)
- - - Floquet model

- **Rotational excitation irrelevant:** Similar 1D and 2D KER spectra
- **Fringe structures** shift downward in energy for $\theta = 0 \rightarrow \pi/2$ & follow Floquet model

Angle-resolved spectra calculated by Fourier transformation at $R > 6$ a.u.

Abanador, Thumm, Phys. Rev. A **102**, 053114 (2020)

"Floquet model"
Adiabatic vibrational states in bond-hardening well

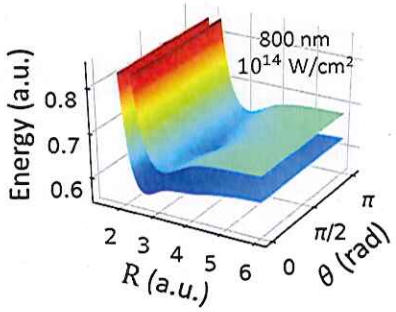
10^{13} W/cm²

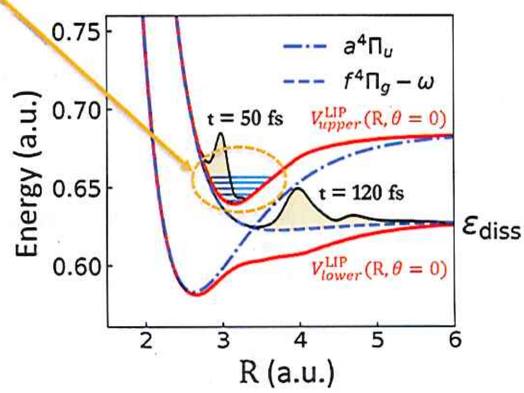
For fixed alignment angle $0 \leq \theta \leq \pi/2$:

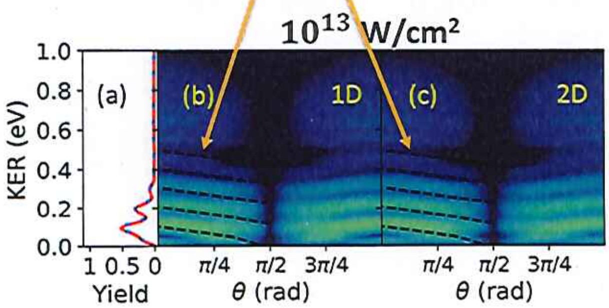
(i) Calculate upper light-induced potential $V_{upper}^{\mathrm{LIP}}(R,\theta)$ for $E_{\mathrm{eff}} = E_0 \cos(\theta)$

(ii) Calculate vibrational energies $\varepsilon_v^{\mathrm{LIP}}$ in $V_{upper}^{\mathrm{LIP}}(R,\theta)$

(iii) Draw $\varepsilon_v^{\mathrm{KER}}(E_0,\theta) = \varepsilon_v^{\mathrm{LIP}}(E_0,\theta) - \varepsilon_{\mathrm{diss}}$ in spectrum







Abanador, Thumm, Phys. Rev. A **102**, 053114 (2020)

O_2^+ : KER spectra — Intensity dependence of LIPs

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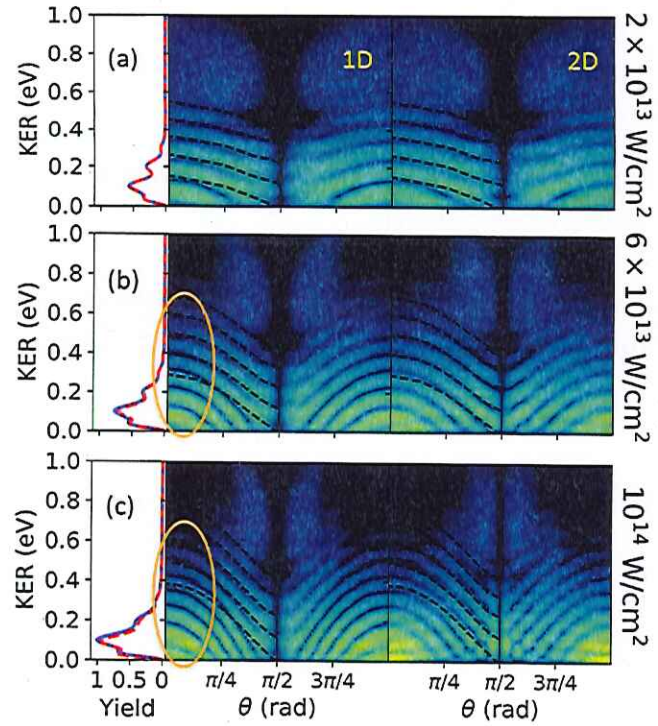
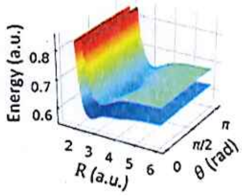


Evidence for bond-hardening in O_2^+ dissociation:

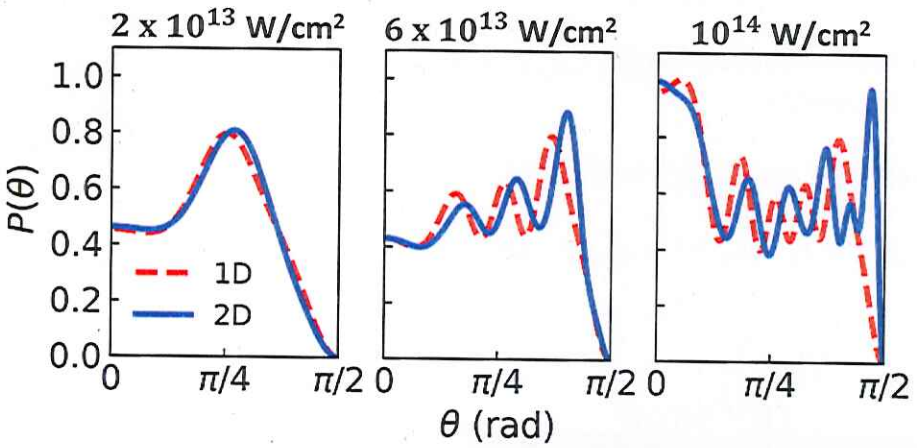
- ✓ Floquet LIP energies $\varepsilon_v^{\mathrm{KER}}(E_0, \theta)$ follow θ & KER dependent fringes
- ✓ Different 1D and 2D results: effects due to rotational excitations that increase with pulse intensity (bead-like structures)
- ✓ Fringes shift toward $\theta = \pi/2$ in the 2D results, due to the more prominent role of the LICI at higher peak intensities
- ➤ Difference between KER fringes & Floquet model due to temporal change of LIP



Abanador, Thumm, Phys. Rev. A **102**, 053114 (2020)

O_2^+ : Rotational dynamics near the LICI

Angular distribution of photofragments



- ➤ Relevance of rotational excitation
- ➤ Modulation frequency

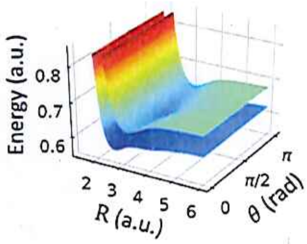
} increase with intensity

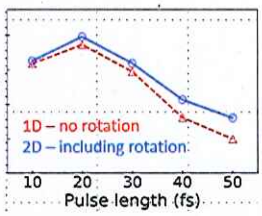
- ➤ Modulations shift toward π/2 (LICI)

Abanador, Thumm, Phys. Rev. A **102**, 053114 (2020)

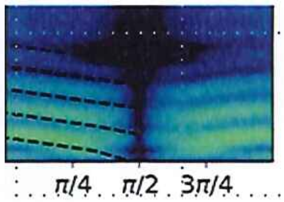
Summary: O_2^+

Examining the **bound & dissociative ro-vibrational dynamics of excited O_2^+** within a pump-probe scheme, we found:

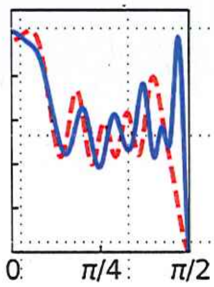




Dissociation stabilization, increasing with pulse length
- consistent with population trapping in light-induced state
- due to O_2^+ ($a\,^4\Pi_u \leftrightarrow f\,^4\Pi_g$) population transfer

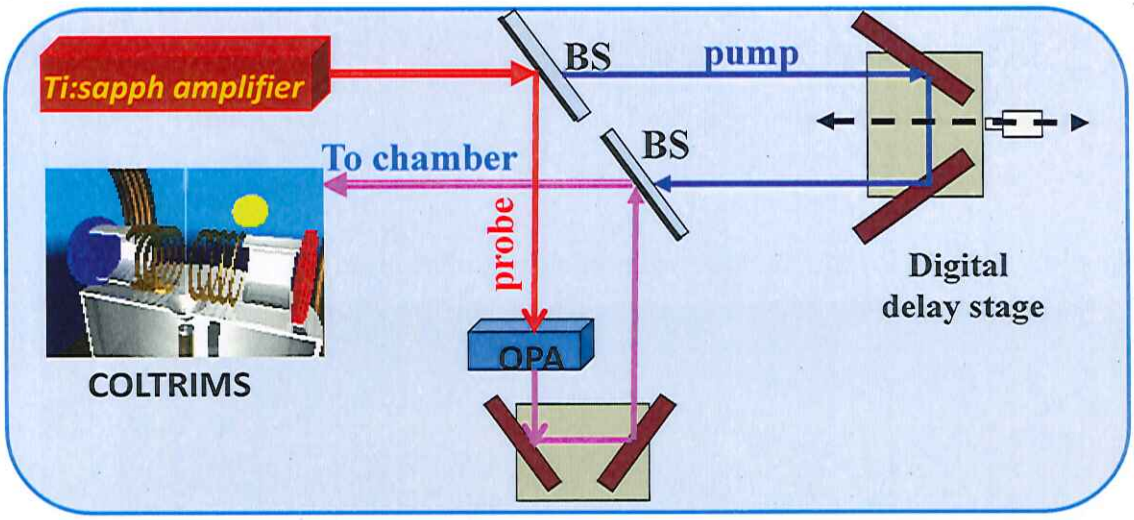


Fringe structures in angle-resolved KER spectra
- associated with the bond hardening and rotation
- ~ follow vibrational spectrum of bond-hardening well
- point to relevance of LICI at higher intensities



Modulations in photofragment angular distributions
- including hints at rotational motion near the LICI

Dissociation dynamics of Ar_2^+ in two-color intense laser fields

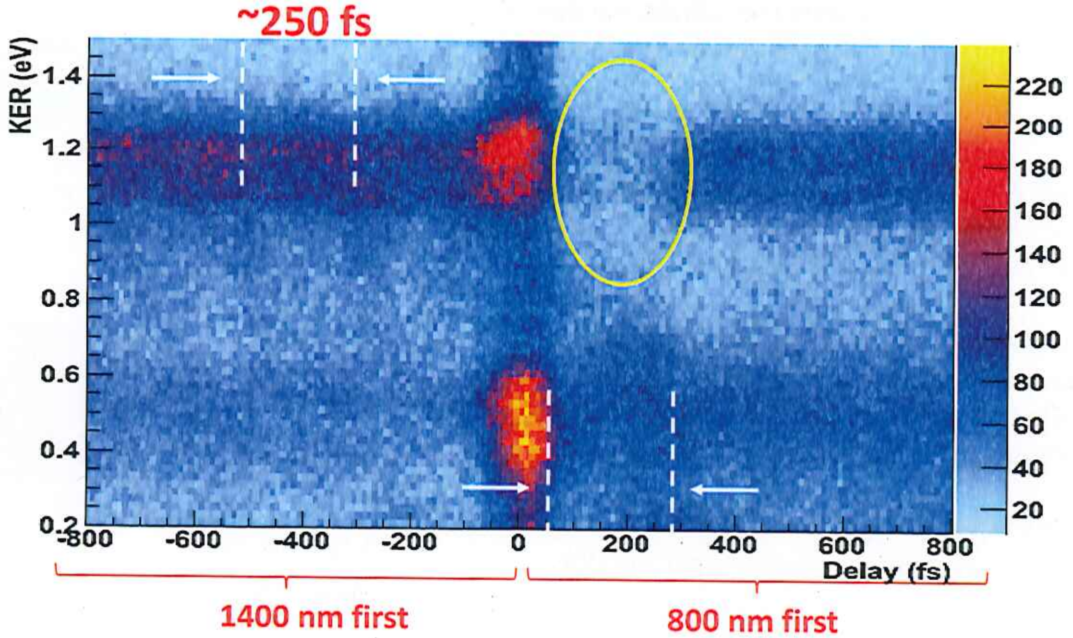


Pump (Probe) wavelength	**: 800nm (1400nm)**
Pump (Probe) Pulse duration	**: 60 fs**
Polarization	**: linear**
Peak intensity	**: 1 x10^{14} W/cm^2**

Wu, Magrakvelidze, Vredenborg, Schmidt, Jahnke, Czasch, Dörner, Thumm, PRL **110**, 033005(2013)

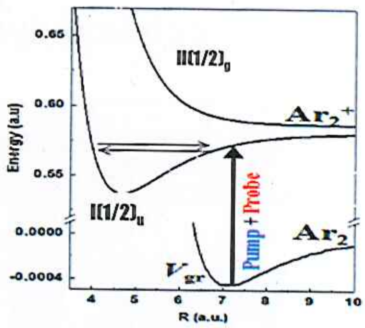
Dissociation dynamics of Ar_2^+ in two-color intense laser fields

Measured KER spectra

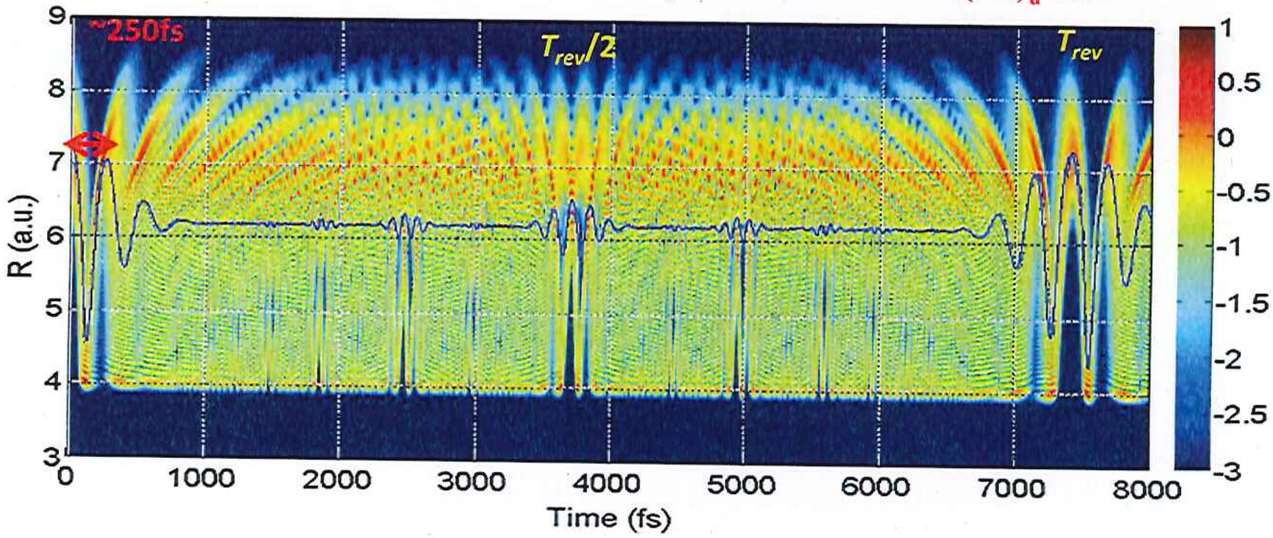


Wu, Magrakvelidze, Vredenborg, Schmidt, Jahnke, Czasch, Dörner, Thumm, PRL **110**, 033005(2013)

Single-cation curve calculations for Ar_2^+



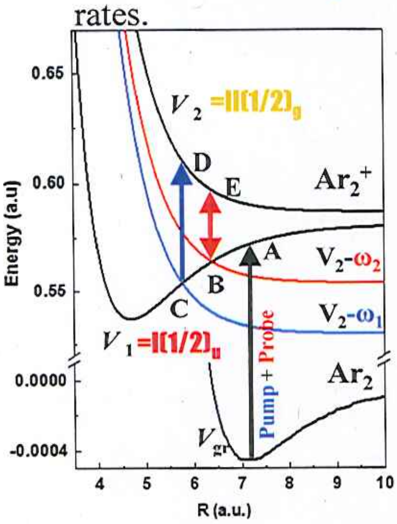
Density plots $\rho(R,t)$ for the nuclear wave-packet evolution on $I(1/2)_u$ state



Dissociation dynamics of Ar_2^+ in two-color intense laser fields

Dipole-coupled calculations

1. **Ionization of Ar_2** by the **pump** pulse modeled based on molecular ADK transition rates.



2. **Coupled propagation in the pump and probe pulse**

$$i\frac{d}{dt}\begin{pmatrix}\Psi_{gr}\\ \Psi_1\\ \Psi_2\end{pmatrix}=\begin{pmatrix}V_{gr}-i\Gamma_{ADK} & 0 & 0\\ 0 & T_R+V_1+i\Gamma_{ADK} & D_{12}\\ 0 & D_{21} & T_R+V_2\end{pmatrix}\begin{pmatrix}\Psi_{gr}\\ \Psi_1\\ \Psi_2\end{pmatrix}$$

$D_{ij}=E(t)d_{ij}$, $d_{ij}=\langle\Psi_i\,|\,R\,|\,\Psi_j\rangle$ $\quad\Gamma_{ADK}$: ADK ionization rates

$$E(t)=E_{01}\cos[\omega_1(t)]\exp[-2\ln 2\frac{(t)^2}{L_1^2}]$$

$$+E_{02}\cos[\omega_2(t-\tau)]\exp[-2\ln 2\frac{(t-\tau)^2}{L_2^2}]$$

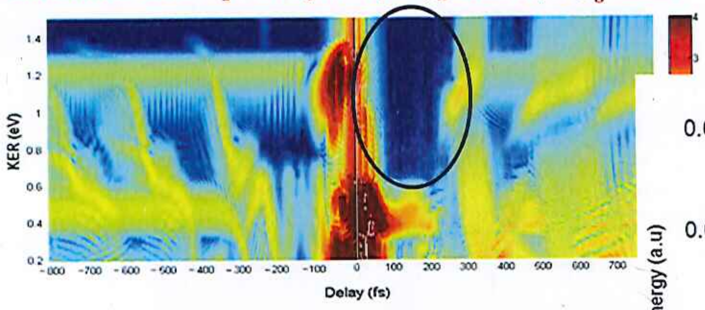
ω_1 (ω_2) : pump (probe) pulse frequency = 800 / 1400 nm
L_1 (L_2) : pulse length = 80 fs

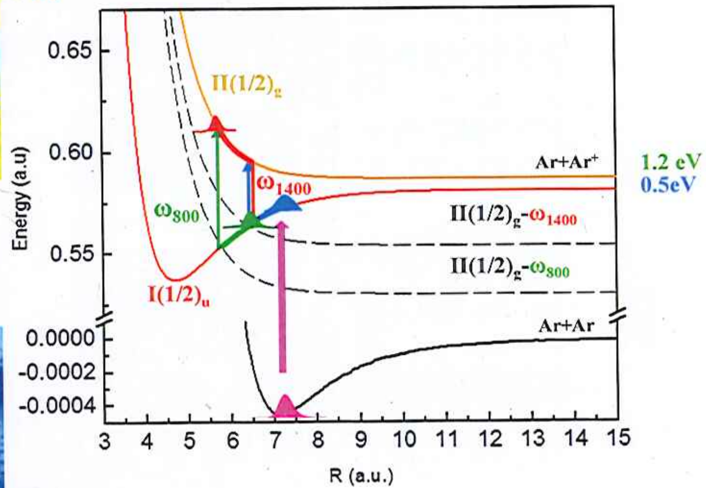
Dissociation dynamics of Ar_2^+ in two-color intense laser fields

Comparison with experiment

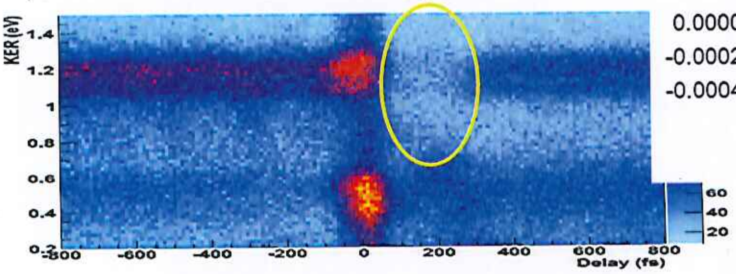
80 fs pulse lengths, 10^{14} W/cm^2 peak intensity

Calculated KER spectra for $I(1/2)_u$ and $II(1/2)_g$ states





Measured KER spectra



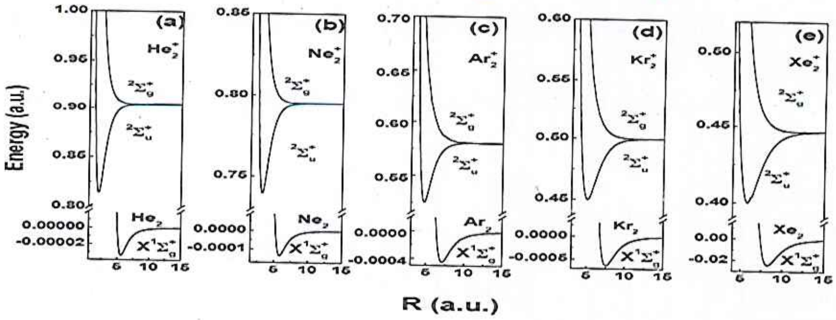
Wu, *et al.*, PRL **110**, 033005(2013)

Pump- 1400nm	Pump - 800nm
Probe - 800nm	Probe- 1400nm

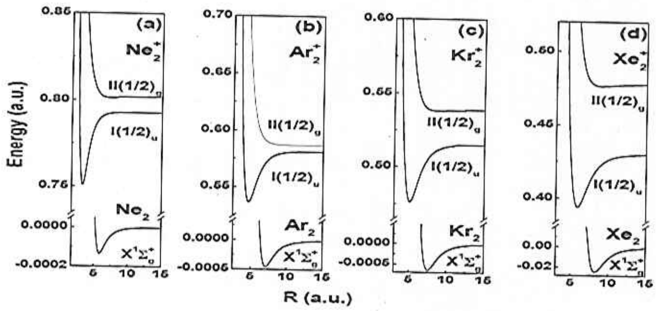
Dissociation dynamics of Noble Gas_2^+ in two-color intense laser fields

(120)

Adiabatic potential curves for He_2^+ .... Xe_2^+ without SO coupling



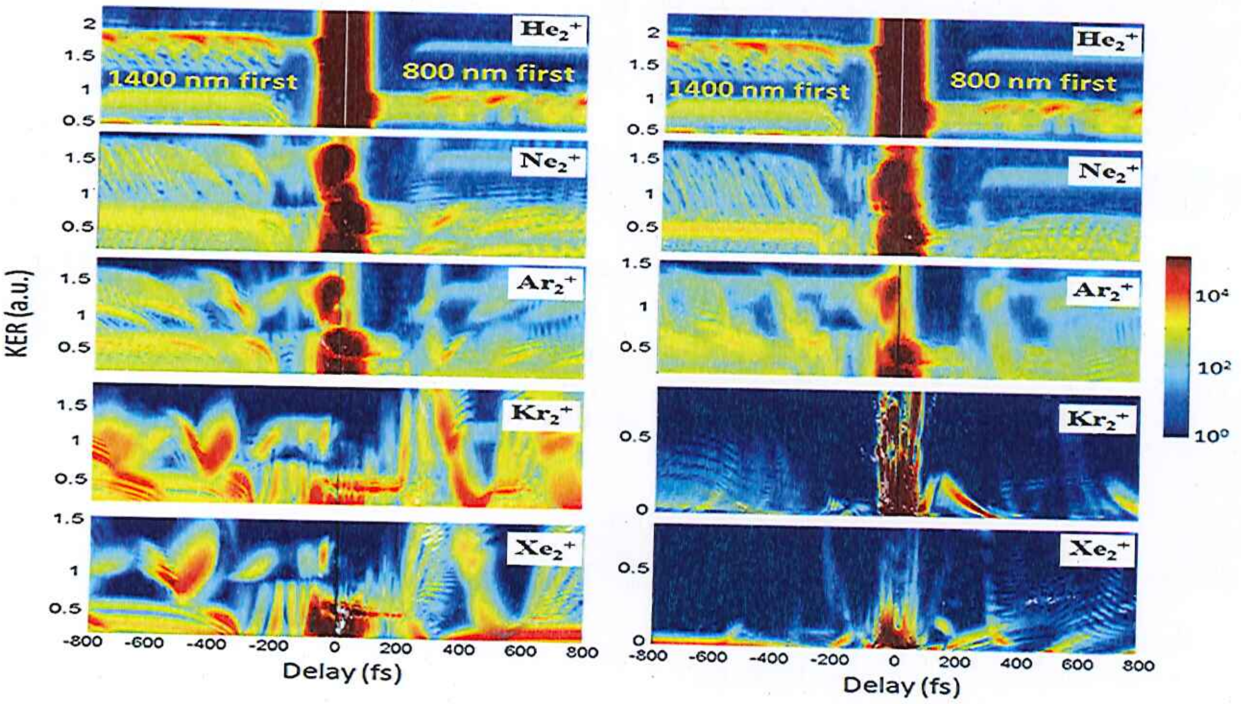
.... including SO coupling



Dissociation dynamics of Noble Gas_2^+ in two-color intense laser fields

Relativistic effects in nuclear kinetic energy spectra

$^2\Sigma_{u,g}^+$ (without SO coupling) $I(1/2)_u$, $II(1/2)_g$ (including SO coupling)



H_2 / D_2

Introduction

Numerical model

Single-pulse results

- dissociation / ionization

Pump-probe results

- time - space imaging
- dephasing & revivals
- pump-control-probe
- shaping wave packets

Quantum-beat analysis

- frequency – space imaging
- potential & wf reconstruction

N_2,O_2,CO, Ar_2,....

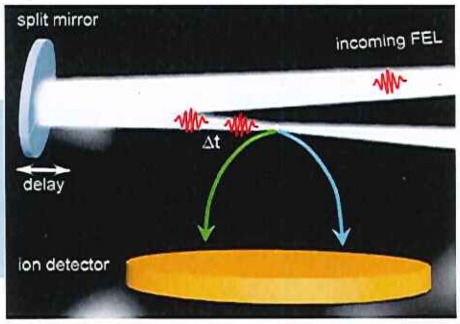
dissociation pathways

XUV pump – XUV probe

First XUV pump and XUV probe experiment on N_2 and O_2 at the **Free Electron Laser in Hamburg (FLASH)**

Photon energies: **38 ±0.5 eV**

- Pulse length: **~20-30 fs**
- Intensity: **~10^{13}-10^{14} W/cm^2**
- Coincident fragment detection



Identify chemical reaction pathways

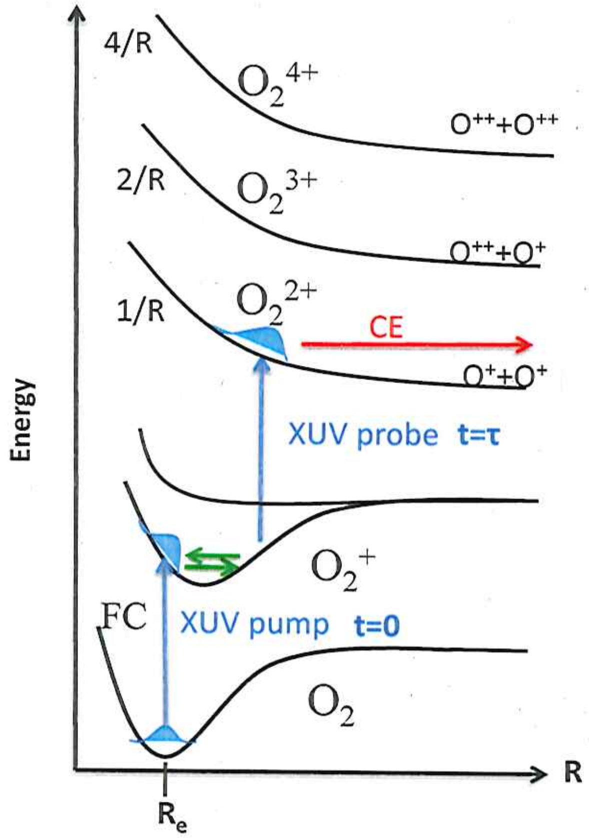
Kinetic energy release spectra ➡ identify intermediate & final electr. states of O_2^{q+} and N_2^{q+} , q=1,2,3,..

Trace nuclear wavepacket dynamics in molecular ions

Classical & quantum calculations for dissocative ionization of N_2 and O_2 compared with *measured* KER spectra

IR pump – IR probe:	Tunneling/MP ionization/excitation. Distortion of adiabatic potential curves.
XUV pump – XUV probe:	Ionization/excitation by known *small* number of photons.

"Classical" simulations



Initial conditions:

$R(t=0) = R_e \qquad v(t=0) = 0$

Newton's equation:

$$a(t) = -\frac{1}{\mu}\frac{dV(R(t))}{dR} \qquad \mu = \frac{m}{2}$$

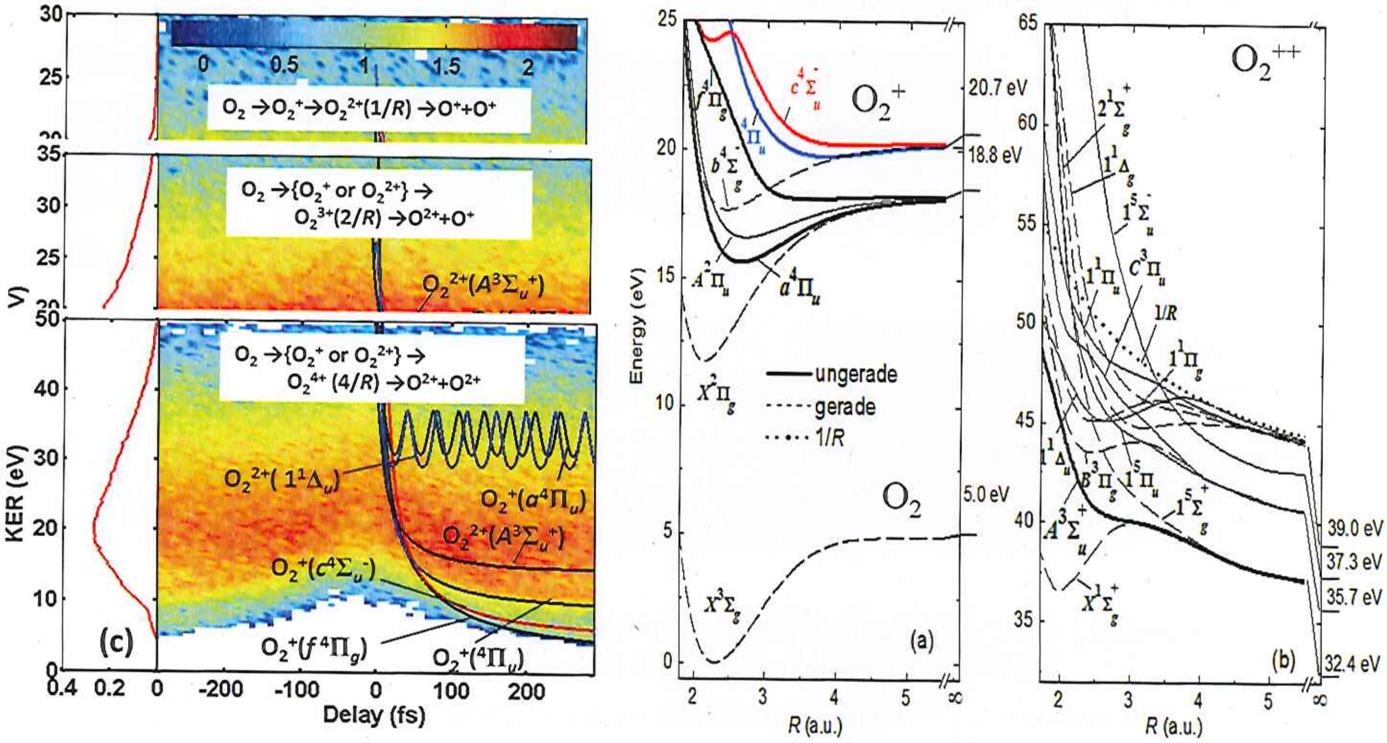
$\Rightarrow$ $R(t)$

Kinetik energy release:

$$CE(R(\tau)) \propto \frac{q_1 q_2}{R(\tau)}$$

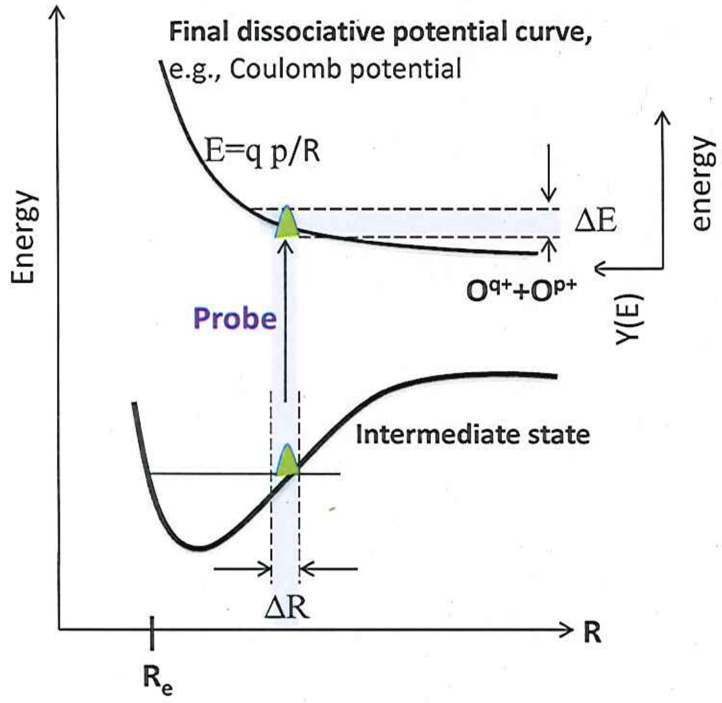
$$KER = KE(\tau) + CE(\infty)$$

Classical results for O_2



M. Magrakvelidze et al., PRA **86**, 013415 (2012)

Quantum mechanical KER simulations



Numerically propagate TDSE

Pump pulse:

Vertical ionization from ground state of the O_2 (FC approx.) .

➡ vibration nuclear wave packets $\Psi(R)$ on O_2^+, O_2^{++} ,… adiab. pot. curves

Probe (& pump) pulse:

$|\Psi(R)|^2 * \Delta R \sim Y(E) * \Delta E$

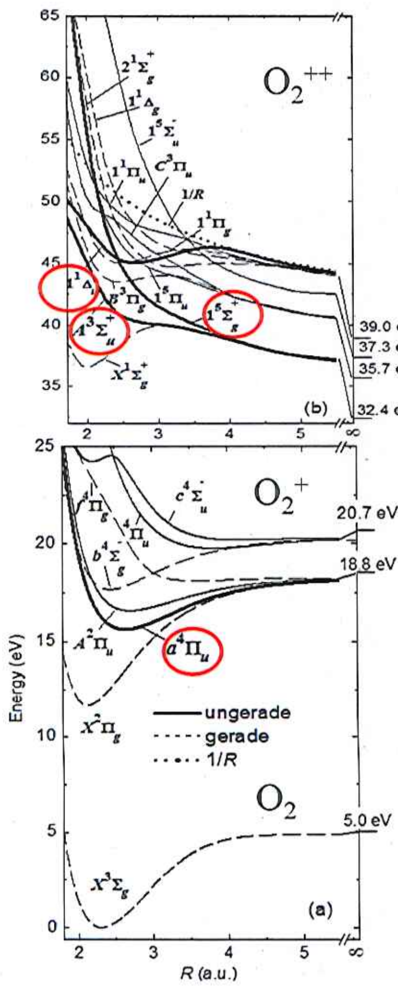
➡ KER at given pump-probe delay:

$Y(E) \sim |\Psi(R)|^2 (dE/dR)^{-1}$

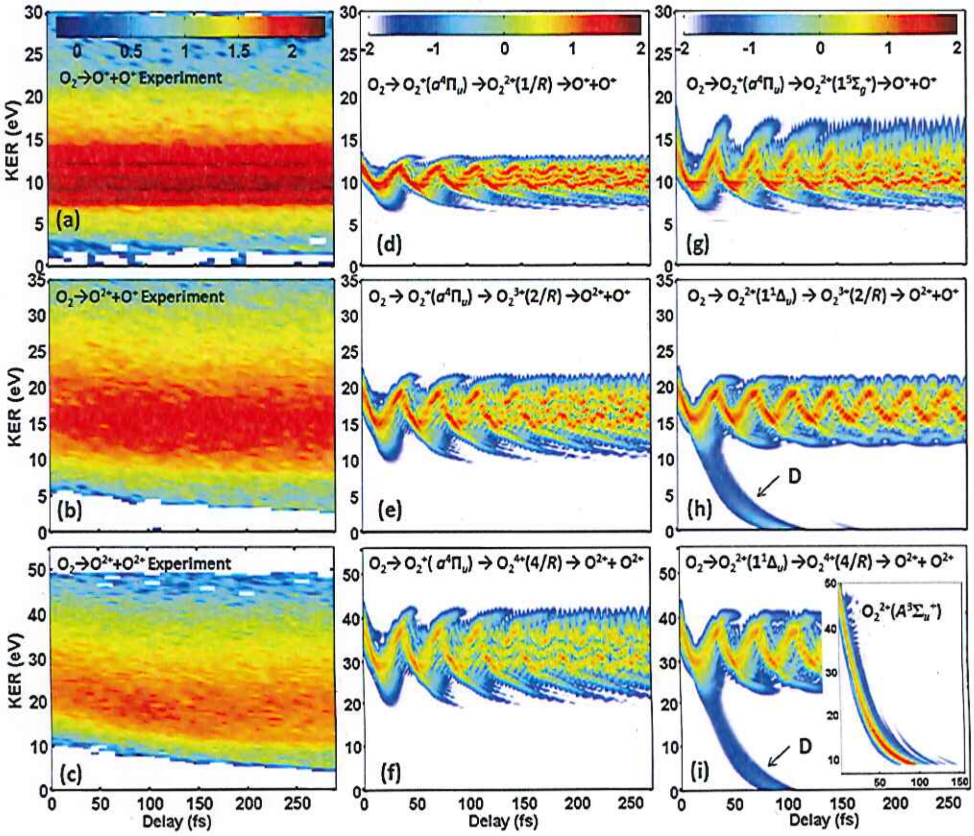
For Coulomb explosion, $E = q\,p/R$ **:**

$Y(E) \sim |\Psi(R)|^2 * R^2/(q\,p)$

(for break-up channel $O^{q+}+O^{p+}$)



Experiment   Quantum results for O_2



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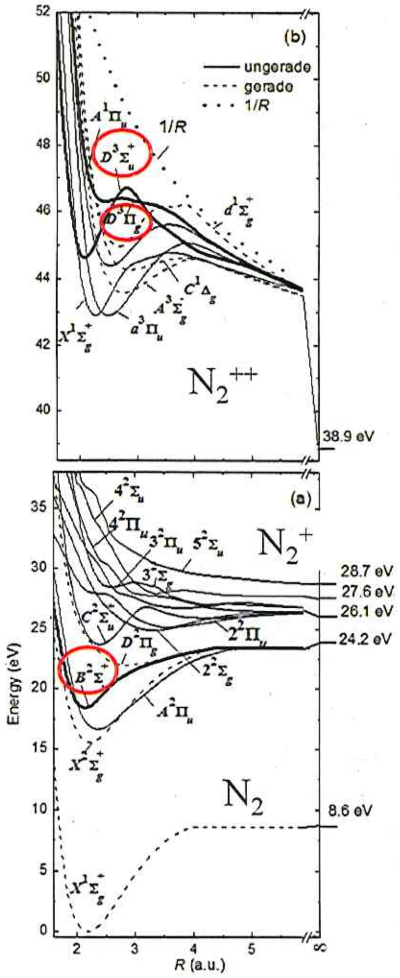
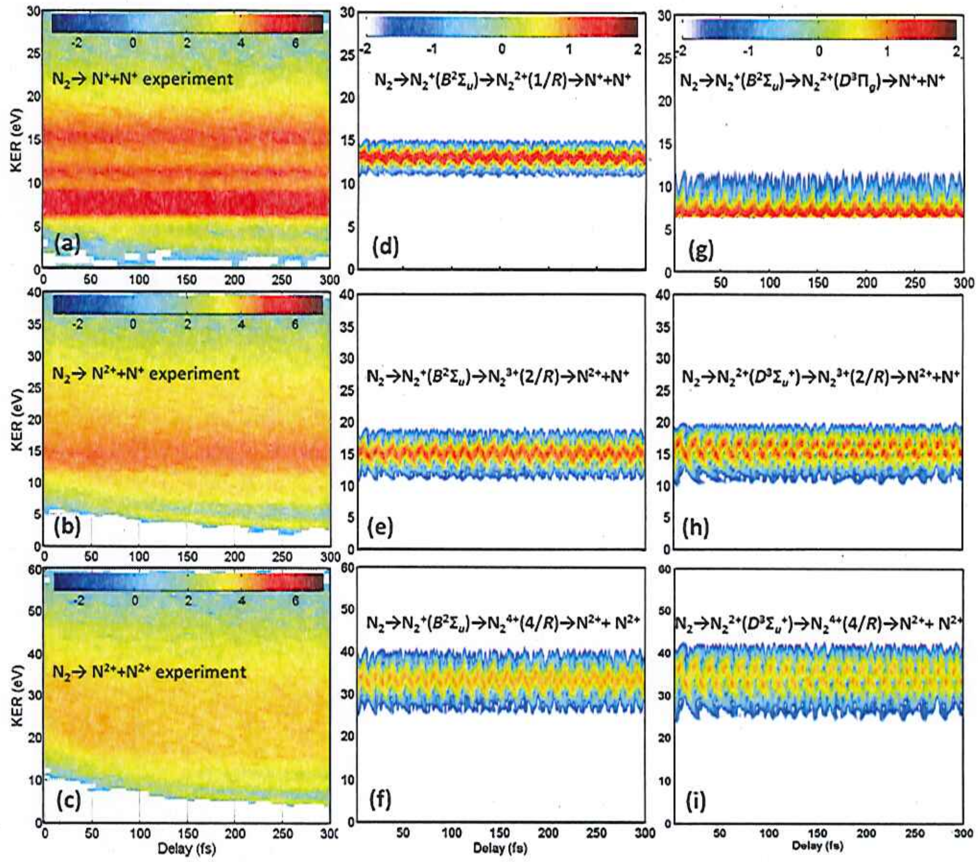
Experiment Quantum results for N_2





Summary (O_2, N_2)

- **"Classical" calculations:**
  reproduce the some features of the measured KER spectra.

- **Quantum-mechanical simulations:**

  $N_2 \rightarrow N^+ + N^+$: *different* KERs for 1/*R* Coulomb explosion and dissociation along N_2^{2+} ($D^3\Pi_g$)

  $O_2 \rightarrow O^+ + O^+$: *comparable* KERs for 1/*R* Coulomb explosion and dissociation along O_2^{2+} ($1^5\Sigma_g^+$)

  $N_2 \rightarrow N^{2+} + N^{2+}$: Coulomb explosion produces KER spectra that ~agree with the measured data. This is not the case for $O_2 \rightarrow O^{2+} + O^{2+}$

Attosecond timing of asymmetric chemical bond breaking

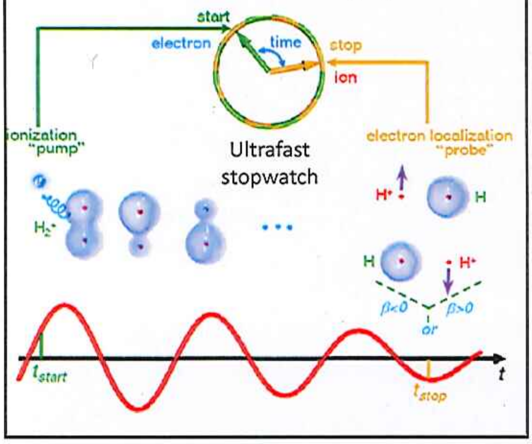
Observing **electrons** AND **fragments**

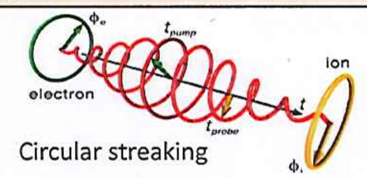
Pump → start signal

Probe → stop signal

Attosecond timing of asymmetric chemical bond breaking

Start & stop times obtained by coincident detection of emitted electron and ion from breaking H_2^+ bond.

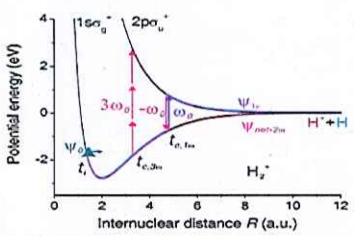




Single 35-fs circ. pol. IR pulse, 2×10^{14} W/cm²

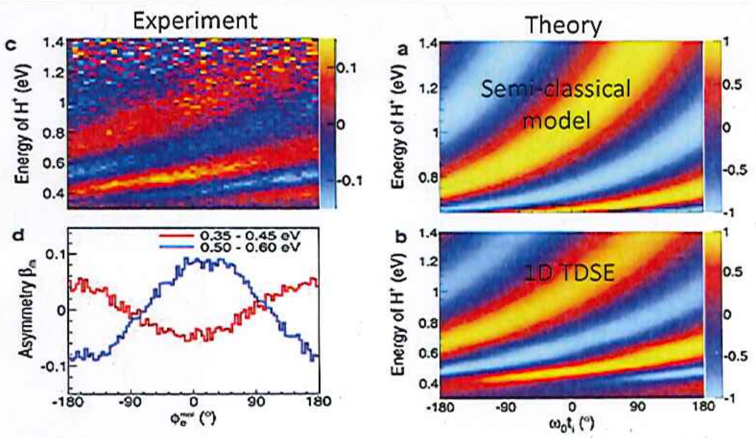
Pump time retrieved from angle of emitted electron Φ_e

Probe time retrieved from angle of coincidently detected ion Φ_i



Asymmetry parameter →

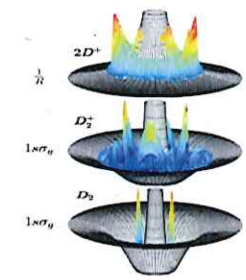
$$\beta_m(\phi_e^{mol}, E_k) = \frac{N(\phi_e^{mol}, E_k) - N(\phi_e^{mol}+180^\circ, E_k)}{N(\phi_e^{mol}, E_k) + N(\phi_e^{mol}+180^\circ, E_k)}$$



- Solve 2D TDSE
- Scale to > 2 particle coincidence
  e.g., $O_2 \rightarrow O^+ + O^{++} + e^-$

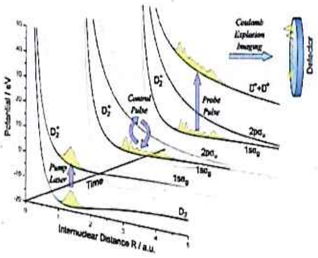
J. Wu et al., Nat. Commun. 4 (July 19, 2013)

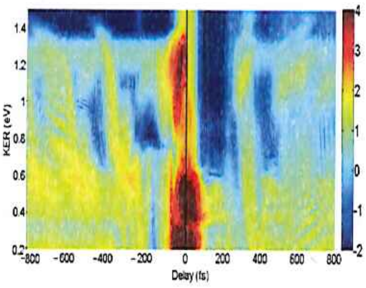
Conclusions



Timed ultra-short intense laser pulses can

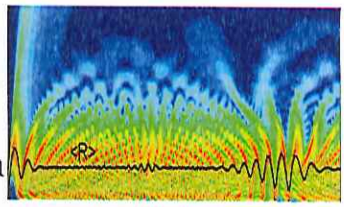
- provide a molecular clock with *1* in *10*^{14} accuracy
- control & image the nuclear motion in small molecules
- stop vibrational wave packets
- map (field-dressed) molecular potentials
- reconstruct (ro-) vibrational distributions & wavefunctions

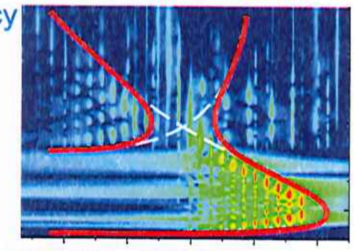


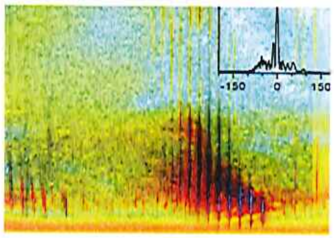


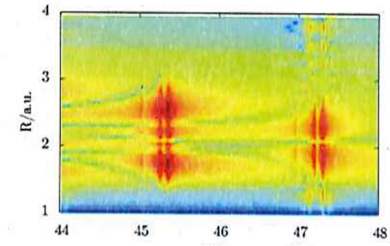
Future goals:

- resolve nuclear and *electronic* motion
- larger molecules
- follow chemical reactions in real time









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☻ - Manhattan: *"The Little Apple"*