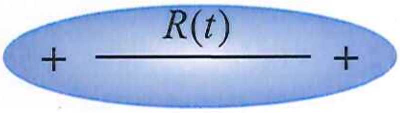
R - dependent harmonic analysis



Vibrational wave packet

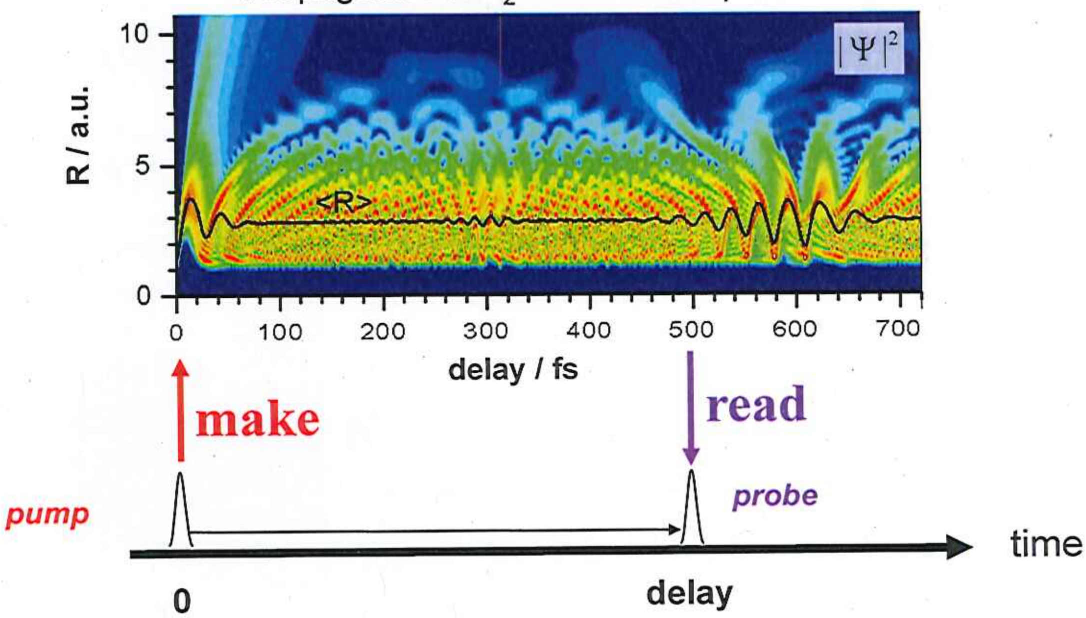
$$\Psi(R,t) = \sum_{\nu} a_\nu \, \chi_\nu(R) \, e^{-i\omega_\nu t}$$

Pump – probe measurement → **time -series**

Fourier analysis → **quantum-beat spectrum**

R - dependent harmonic analysis

Propagation of D_2^+ vibr. wave packet



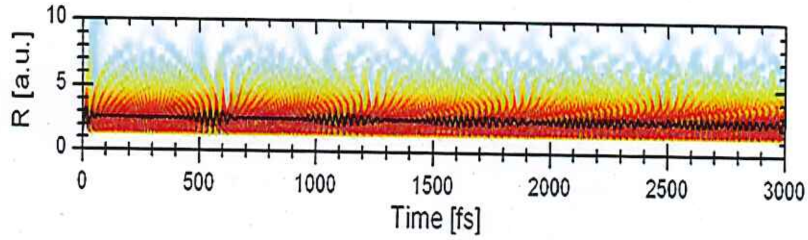
Basic idea: Fourier transform time-dependent probability density - separately at each ***R***

R - dependent harmonic analysis

Nuclear wave packet:

$$\Psi(R,t)=\sum_{\nu} a_{\nu}\ \chi_{\nu}(R)\ e^{-i\omega_{\nu}t}$$

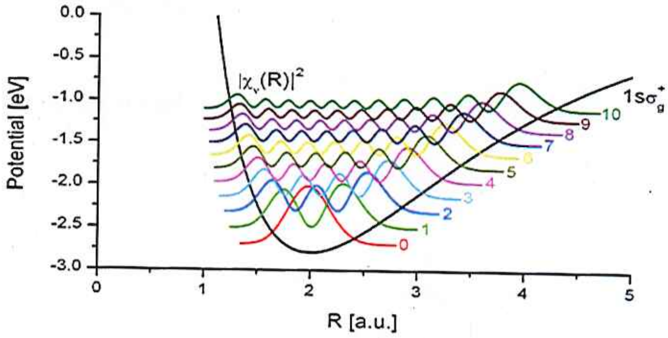
coefficient D_2^+ vibr. state



Probability density:

$$|\Psi(R,t)|^2=\sum_{\nu}|a_{\nu}|^2\ |\chi_{\nu}(R)|^2$$

$$+\sum_{\mu\neq\nu} a_{\mu}^{*}a_{\nu}\ \chi_{\mu}^{*}(R)\chi_{\nu}(R)\ e^{-i(\omega_{\nu}-\omega_{\mu})t}$$



Quantum beats: $\omega_{\nu\mu}=\omega_{\nu}-\omega_{\mu}=2\pi\ f_{\nu\mu}$

R - dependent harmonic analysis

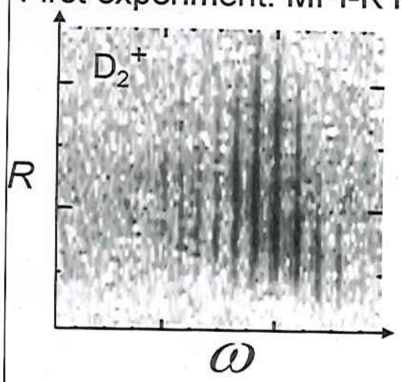
Probability density: $|\Psi(R,t)|^2=\sum|a_{\nu}|^2|\chi_{\nu}(R)|^2+\underbrace{\sum_{\mu\neq\nu} a_{\mu}^{*}a_{\nu}\ \chi_{\mu}^{*}(R)\chi_{\nu}(R)\ e^{-i\omega_{\nu\mu}t}}_{\equiv c(R,t)}$

Fourier transform over **finite** sampling time *T*:

$$\tilde{c}(R,\omega)\sim\sum_{\mu\neq\nu} a_{\mu}^{*}a_{\nu}\ \chi_{\mu}^{*}(R)\chi_{\nu}(R)\ \delta_T(\omega_{\mu,\nu}-\omega)$$

Power spectrum: $P(R,\omega)=|\tilde{c}(R,\omega)|^2$

First experiment: MPI-K HD



PRL 99, 153002 (2007)

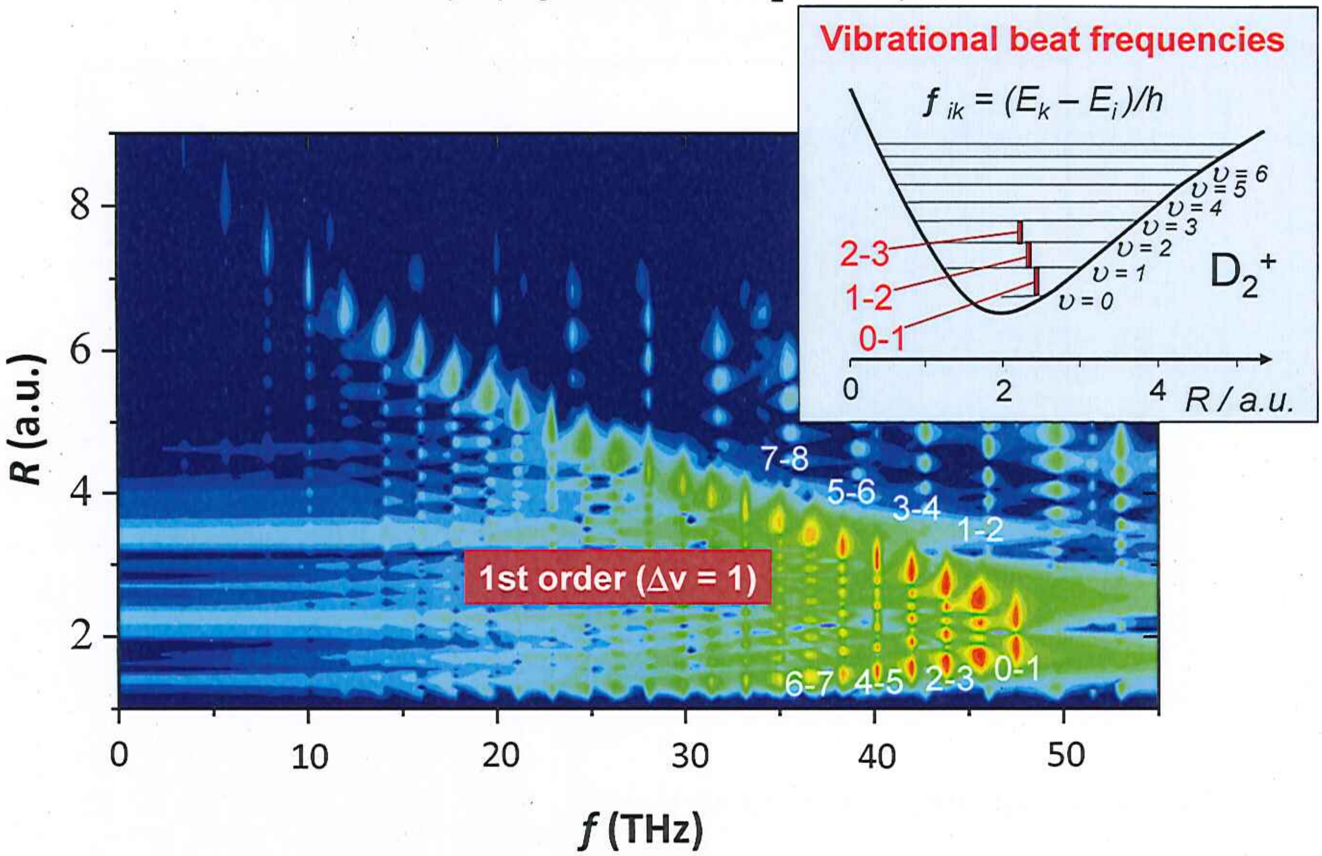
*Feuerstein et al., PRL **99**, 153002 ('07)*

*Thumm et al., PRA **77**, 065401 ('08)*

*Magrakvelidze et at., PRA **79**, 033410 ('09)*

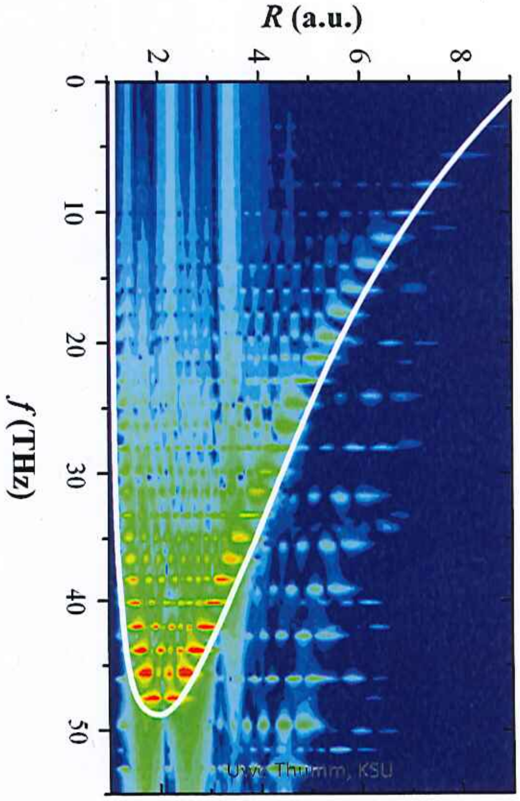
R - dependent harmonic analysis

Simulation: propagation of free D_2^+ wave packet



R - dependent harmonic analysis

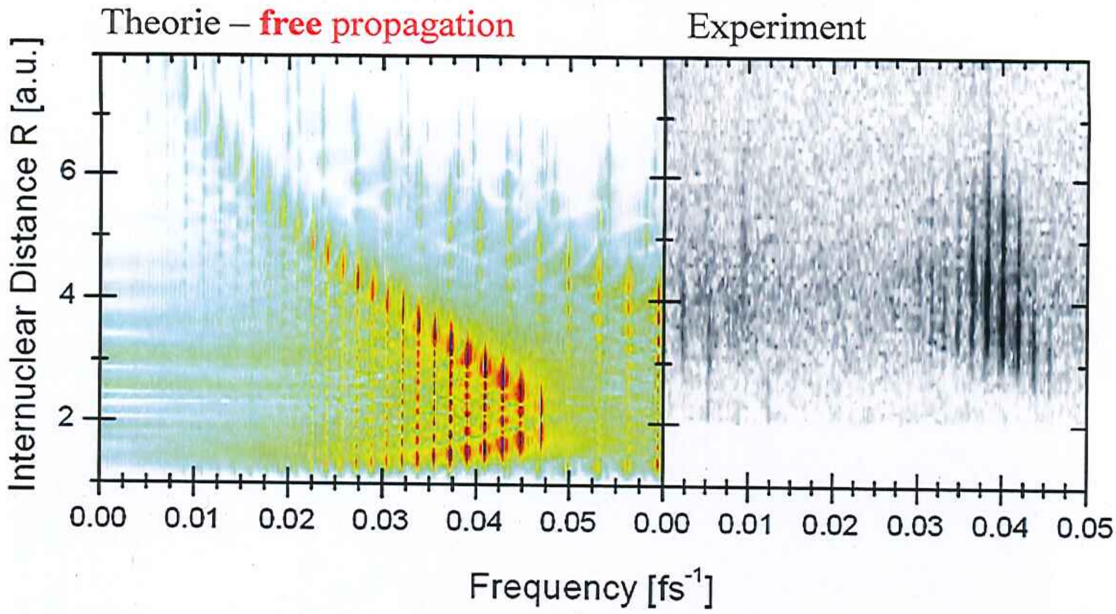
→ Reconstruction of:
1. molecular potential curves
2. nodes of vibrational states



100

R - dependent harmonic analysis

Comparison with experiment

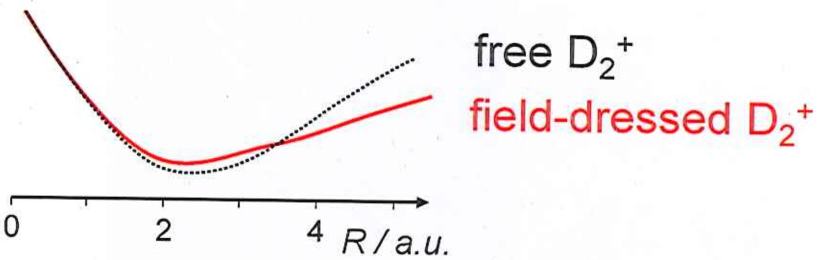


Phys. Rev. Lett. **99**, 153002 (2007)

R - dependent harmonic analysis

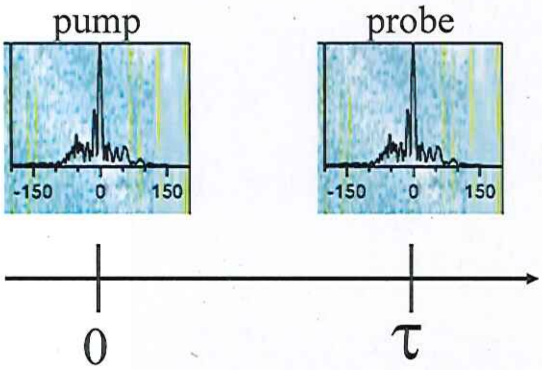
Propagation of D_2^+ vibrational wave packets in a laser field

Molecular potential curves:

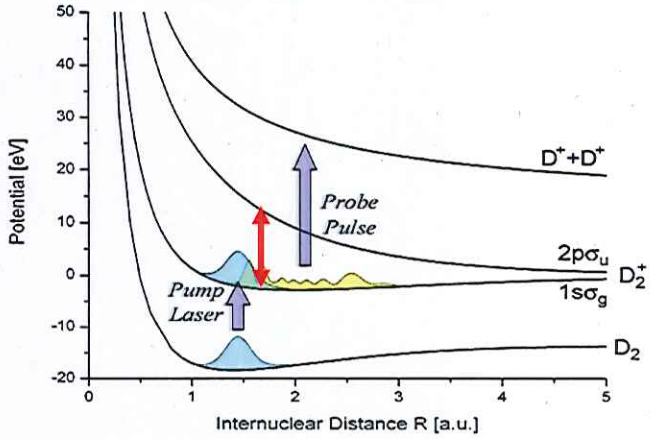


R - dependent harmonic analysis

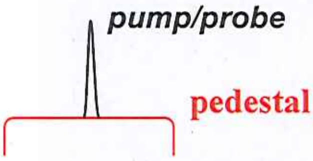
Realistic laser pulses:



coupling to ungerade state



Improved simulation:



Add: "pedestal" to pump and probe pulses

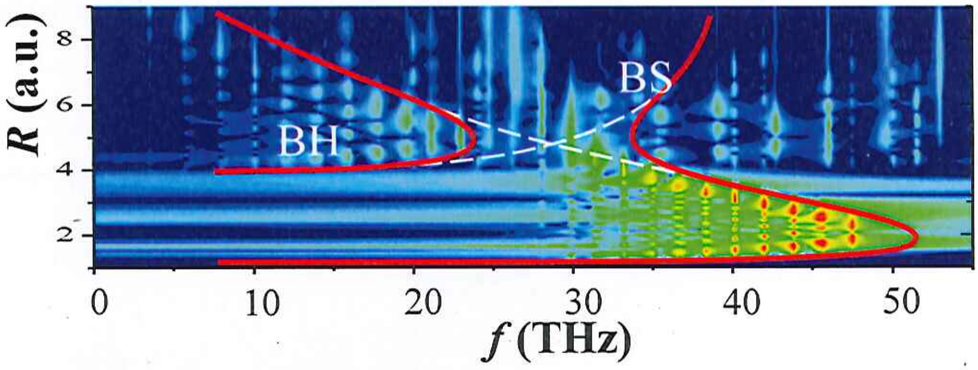
Shape: Gaussian

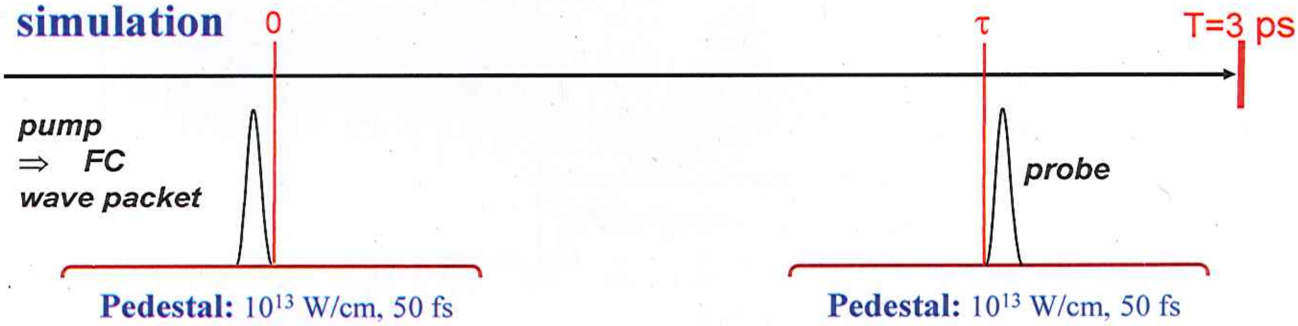
Intensity: 10^{13} W/cm

Length: 50 fs

R - dependent harmonic analysis

Propagation of D_2^+ wave packet **in a laser field** (800 nm)

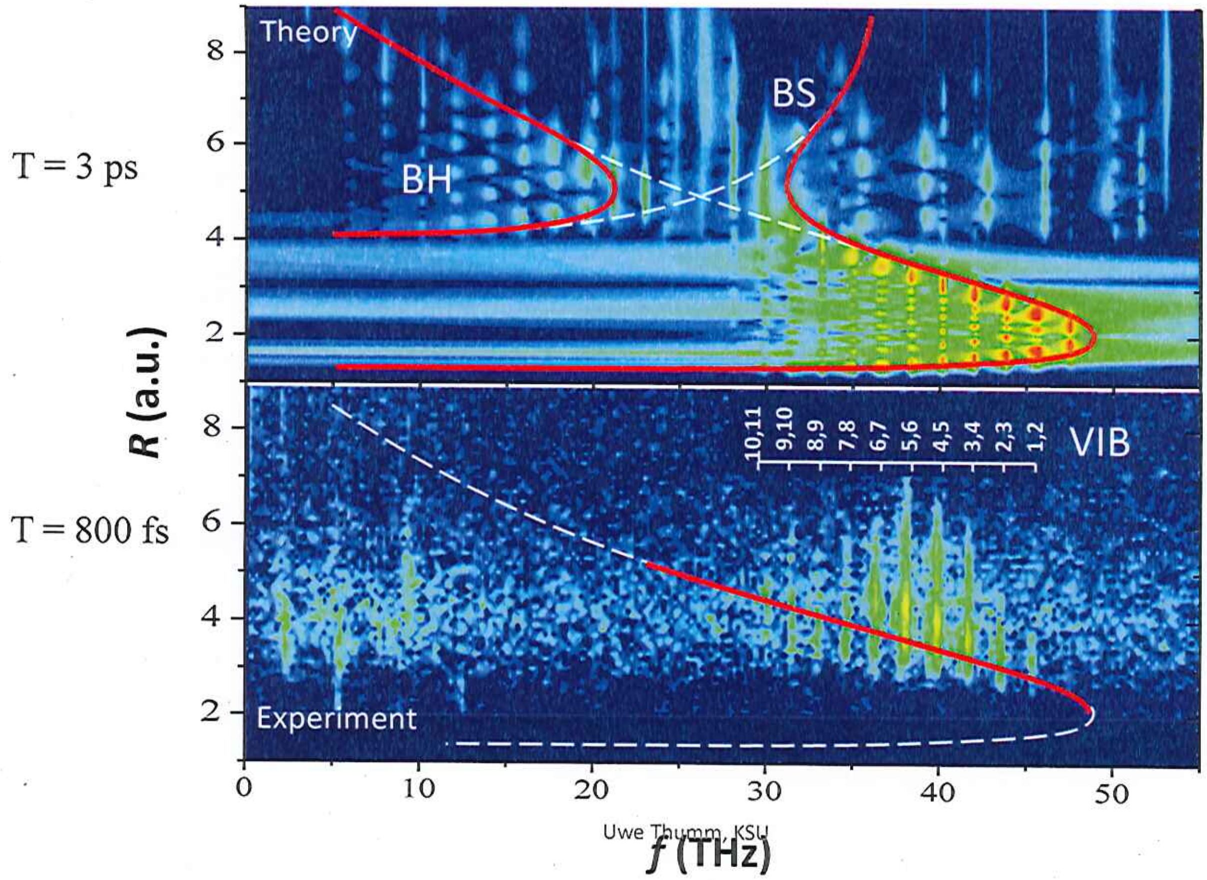




Feuerstein et al., PRL 99, 153002 ('07); Thumm et al., PRA 77, 065401 ('08)

R - dependent harmonic analysis

Comparison with experiment



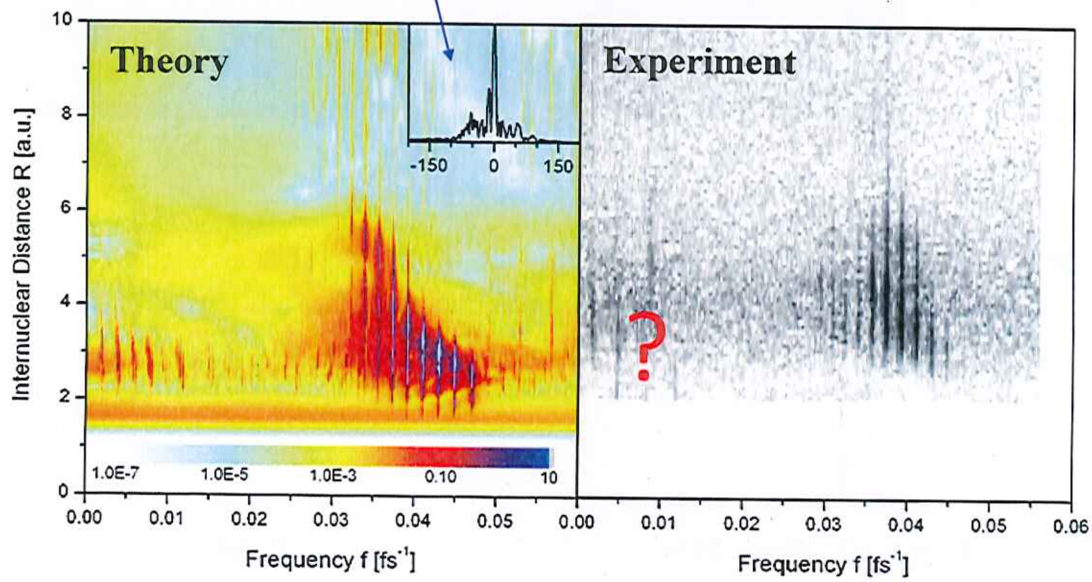
R - dependent harmonic analysis

Comparison with experiment

Further improved simulation:

exp. (SPIDER - analyzed) **pulse shapes:**
pump: 6 fs, 3×10^{14} W/cm^2
probe: 6 fs, 6×10^{14} W/cm^2

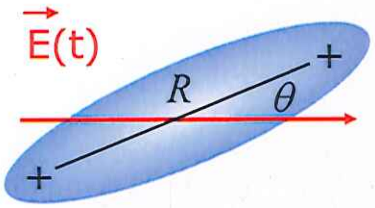
T = 800 fs

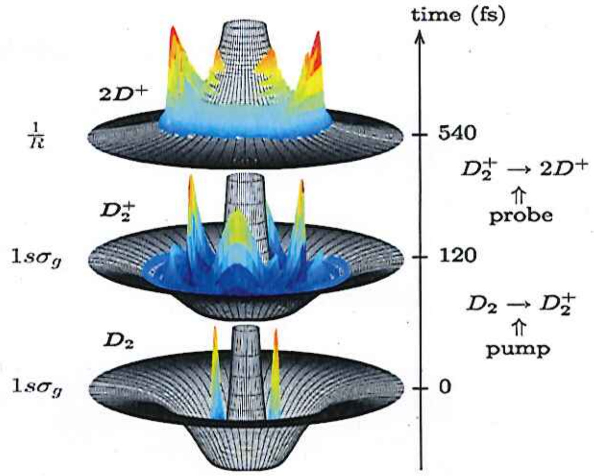


Ro-vibrational dynamics

… add rotation:

D_2^+ ({|v, lm>})





Ab-initio solution of the time-dep. Schrödinger equation

Convergence on three lowest BO surfaces ($\sigma_{g/u}$, π_u)

$$\Psi(R,\theta,\vec{r},t) \propto \sum_{i=\sigma_{g,u},\pi_u} \Omega_i(R,\theta,t)\ \varphi_i^{BO}(R,\theta;\vec{r})$$

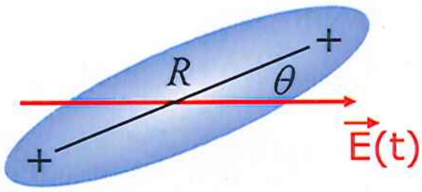
Technique: numerical propagation on R and θ grid

Ro-vibrational harmonic analysis

Nuclear wave packet:

$$\Omega_{\sigma_g}(R,\theta,t) = \sum_{\nu l} a_{\nu l}\ \chi_\nu(R)\ \Theta_{lm}(\theta)\ e^{-i\omega_{\nu l} t}$$

coefficient · vibr. state · rot. state



Fourier transform $|\Omega(R,\theta,t)|^2 - \sum_{\nu,l} |a_{\nu,l}|^2 \ldots$ over **finite** sampling time *T*:

$$\tilde{\rho}(R,\theta,\omega) \sim \sum_{\mu l \neq \mu' l'} \ldots\ \delta_T(\omega_{\mu l,\mu' l'} - \omega) + \sum_{\mu l \neq \mu' l} \ldots\ \delta_T(\omega_{\mu l,\mu' l} - \omega) + \sum_{\mu l \neq \mu l'} \ldots\ \delta_T(\omega_{\mu l,\mu l'} - \omega)$$

Quantum beats: $\omega_{\mu l,\mu' l'} = \omega_{\mu l} - \omega_{\mu' l'}$

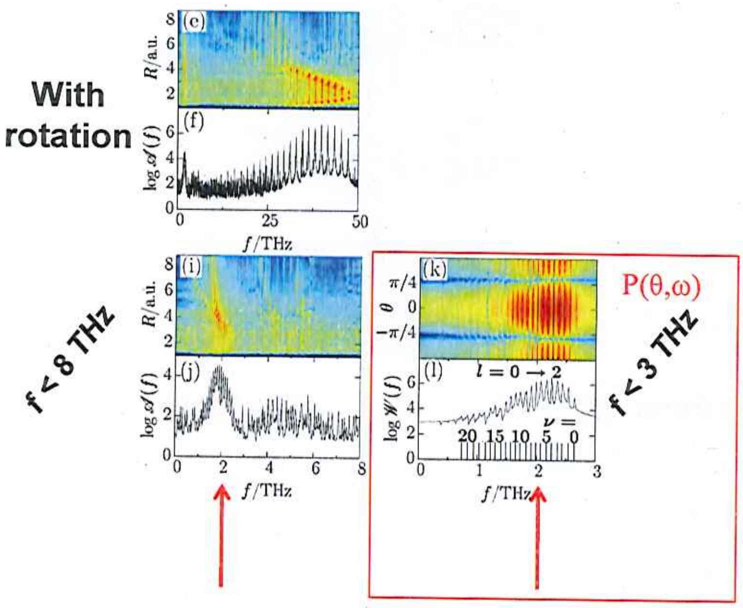
Power spectra:

$$P(R,\omega) = \left| \int d\theta \sin\theta\, \tilde{\rho}(R,\theta,\omega) \right|^2 \sim \left| \sum_{\mu \neq \mu', l} \ldots \delta_T(\omega_{\mu l,\mu' l} - \omega) \right|^2$$

$$P(\theta,\omega) = \left| \int dR\, R^2\, \tilde{\rho}(R,\theta,\omega) \right|^2 \sim \left| \sum_{\mu, l \neq l'} \ldots \delta_T(\omega_{\mu l,\mu l'} - \omega) \right|^2$$

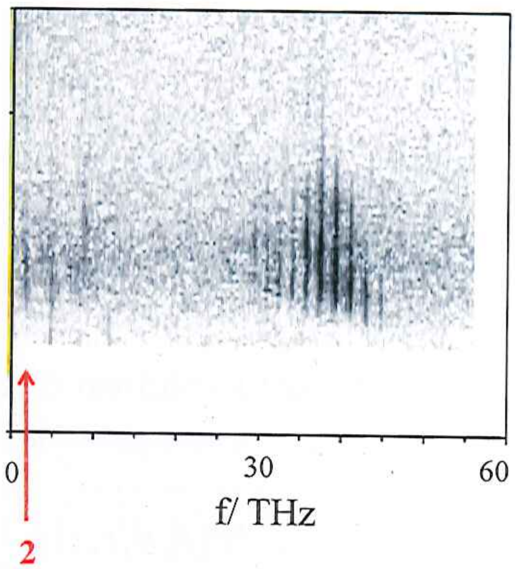
R & θ - dependent harmonic analysis: ro-vibrational coupling (104)

50fs, 10^{13}W/cm^2 probe pulse pedestal



Experiment:

Feuerstein et al., PRL 99, 153002 ('07)



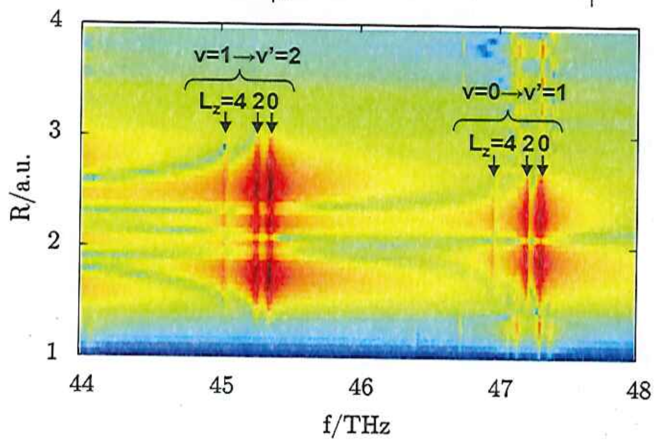
Measured 2 THz line likely due to ro-vib. coupling in D_2^+

Uwe Thumm, KSU

R&θ - dependent harmonic analysis: ro-vibrational coupling

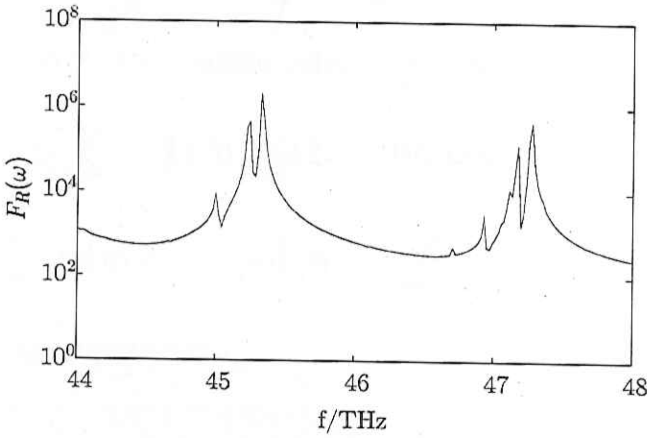
Angle-integrated power spectrum

$$P(R,\omega)=\left|\int d\theta \sin\theta\, \tilde{\rho}(R,\theta,\omega)\right|^2$$



Spectral line intensity

$$F_R(\omega)=\int dR\, R^2\, P(R,\omega)$$

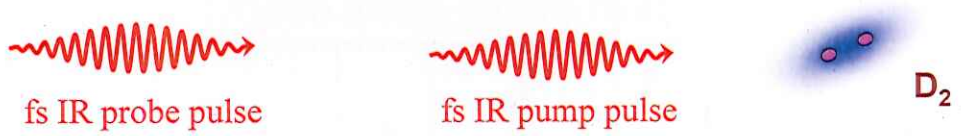


Due to ***ro-vibrational couplings***:

- Lines for same Δv and different L_z don't coincide
- Vibrational transitions at larger L_z appear at lower frequencies

Initial distribution:	Franck-Condon (vib.), 250K Boltzmann (rot.)
Propagation:	Field-free, T=3 ps

Summary: ro-vibrational harmonic analysis



Multi-dimensional quantum-beat spectroscopy can

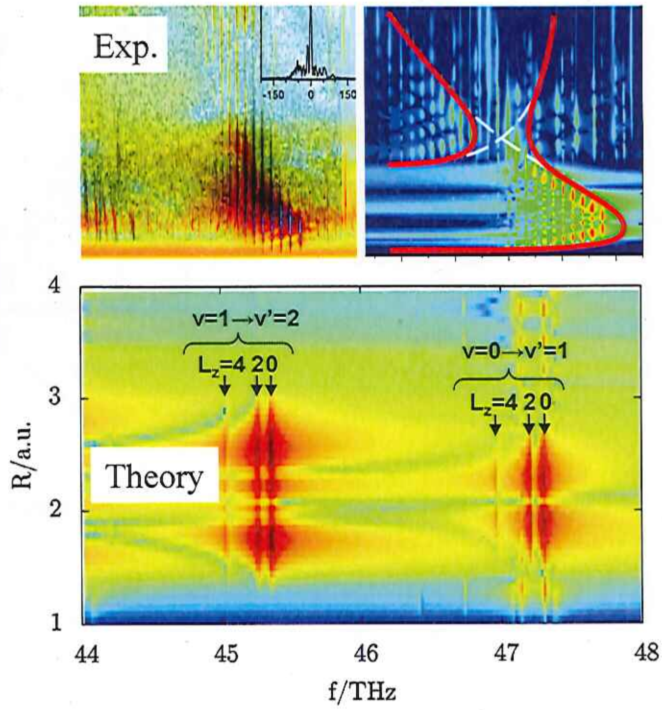
- image the ro-vibrational nuclear motion in small molecules
- map molecular potentials and nuclear wave functions
- determine molecular & ro-vib. coupling constants

based on a time-series of nuclear KER spectra.

Feuerstein et al., PRL 99, 153002 ('07)

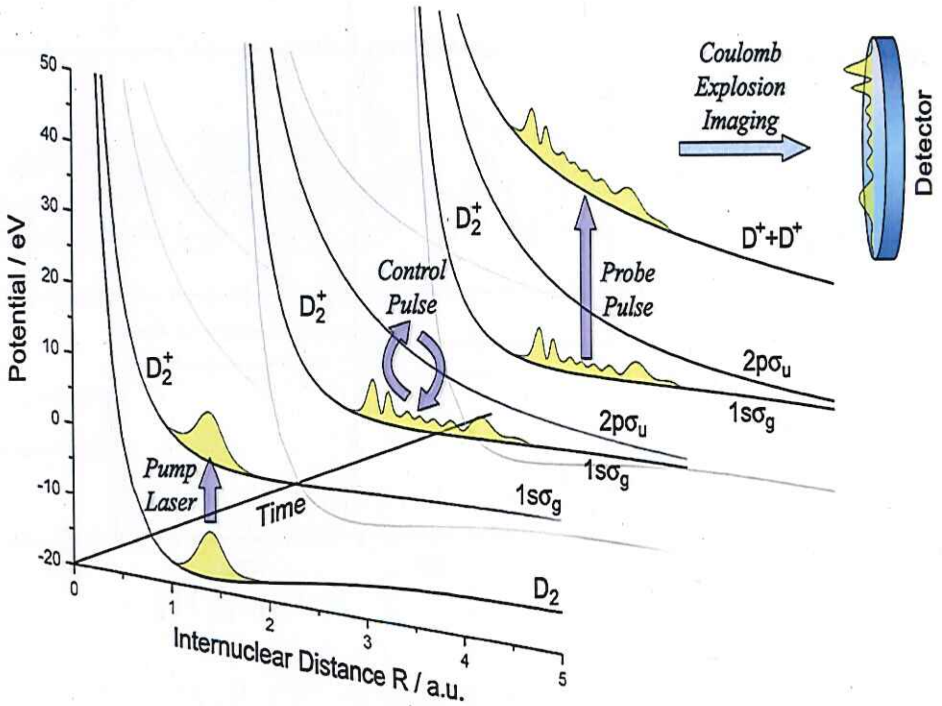
Thumm et al., PRA 77, 065401 ('08)

Magrakvelidze et at., PRA 79, 033410 ('09)



Uwe Thumm, KSU

Manipulating nuclear motion with "*control*" pulses



Niederhausen, Thumm, PRA **77**, 013407 (2008)

Niikura, Villeneuve, Corkum, PRA **73**, 021402 (R) (2006)

Uwe Thumm, KSU

Addition of ONE "*control*" pulse (0.1 PW / cm², 6 fs FWHM)

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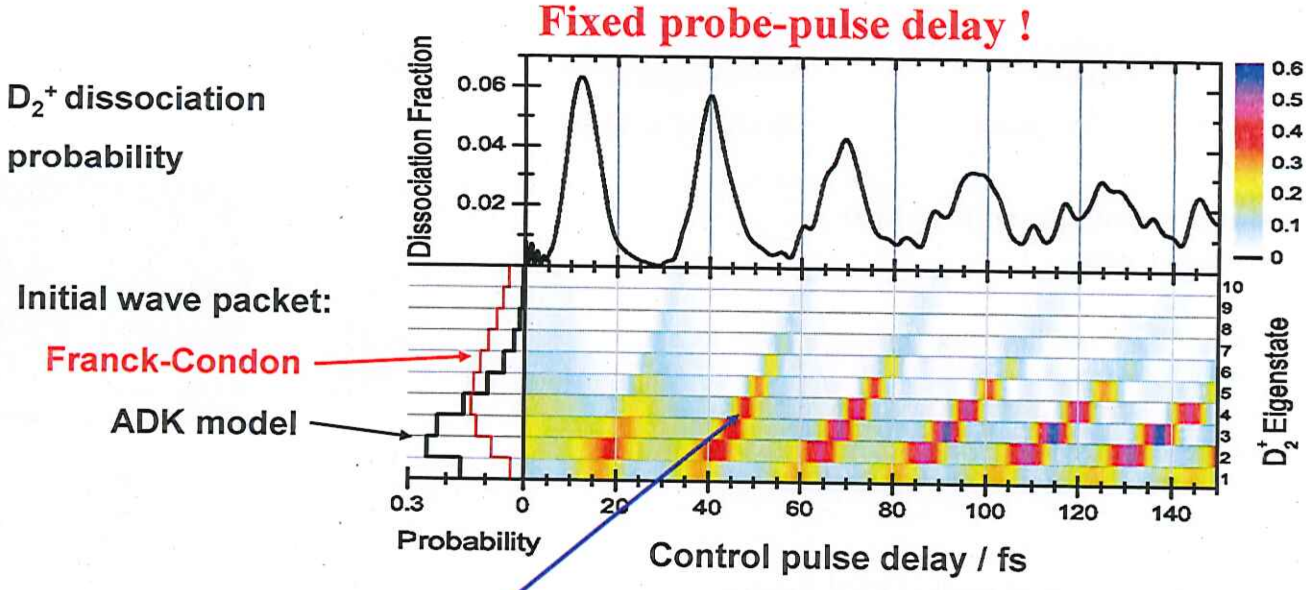
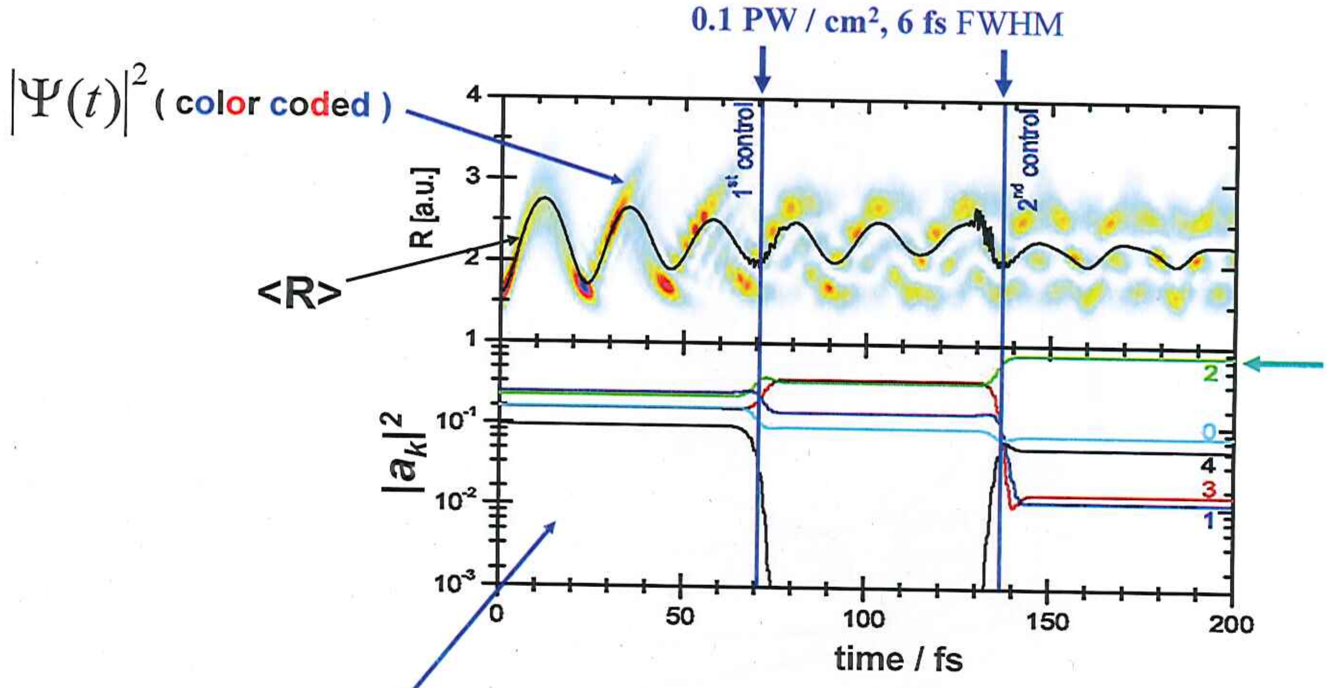


Distribution { $|a_k|^2$ } of stationary vibr. states in $\Psi(R,t) = \sum_k a_k \, e^{-i\omega_k t} \, \chi_k(R)$

"Stopping" a wavepacket with TWO "*control*" pulses



Distribution { $|a_k|^2$ } of stationary vibr. states in $\Psi(R,t) = \sum_k a_k \, e^{-i\omega_k t} \, \chi_k(R)$

$|a_2|^2 = .78$: *79 % in* χ_2 , ***only 3 % dissociation***

Suggested experiment:

1. "*Stop*" moving nuclear wave packet using sequence of control pulses

⟶ stationary state χ_k of molecular ion

2. Coulomb explosion imaging

⟶ nodal structure of $\chi_k(R)$ measures quality of control scheme !

Uwe Thumm, KSU

Moving on to heavy diatomic molecules...

Heavier molecules are more complicated.....

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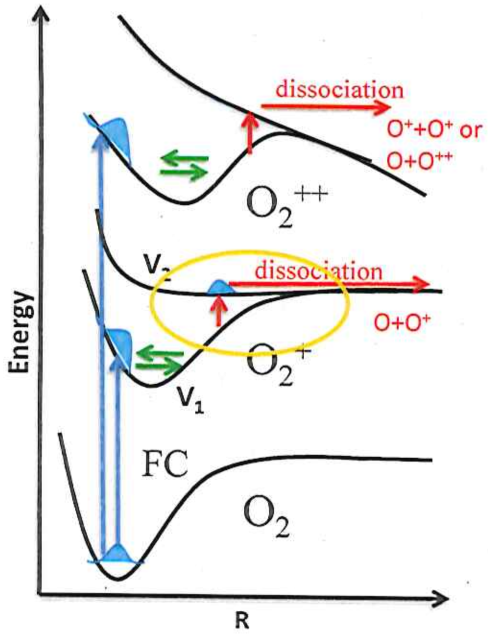
Example: O_2



S. De *et al.*, PRA 84, 043410 (2011)

Scheme for identifying dissociation paths:

1. Rapid ionization of O_2

Franck–Condon transition => wave packets Ψ_i (R, t=0) on **several** potential curves $V_i(R)$ of O_2^+ or O_2^{++}.

2. Field-Free propagation

Propagate wave packets $\Psi_i(R,t) = \sum_\upsilon a_{i,\upsilon}\varphi_{i,\upsilon}(R)e^{-i\omega_{i,\upsilon}t}$ on **individual** (trial) potential curves V_i. **Select relevant curves!**

3. Coupled propagation in the probe pulse

Dipole-couple the nuclear motion on pre-selected curves.

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

$D_{ij}(R)=d_{ij}E$: dipole coupling

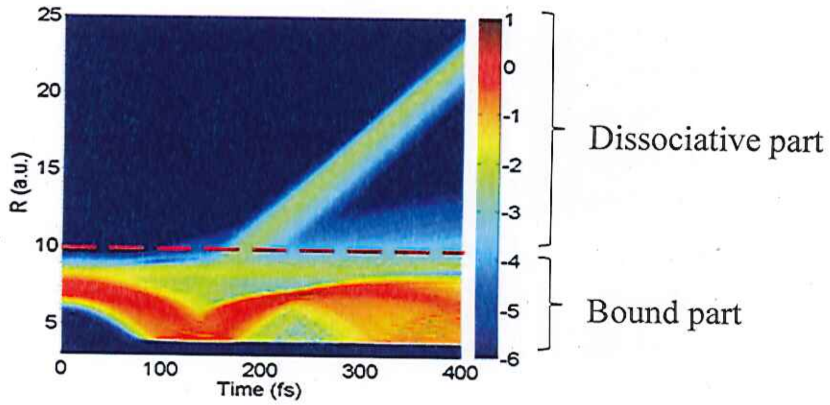
KER spectrum: Fourier transformation of the dissociated wave packet :

$$\tilde{\Psi}^{diss}(P,T) = \int_{R_1}^{R_{max}} dR\Psi^{diss}(R,T)\exp(-iPR)$$

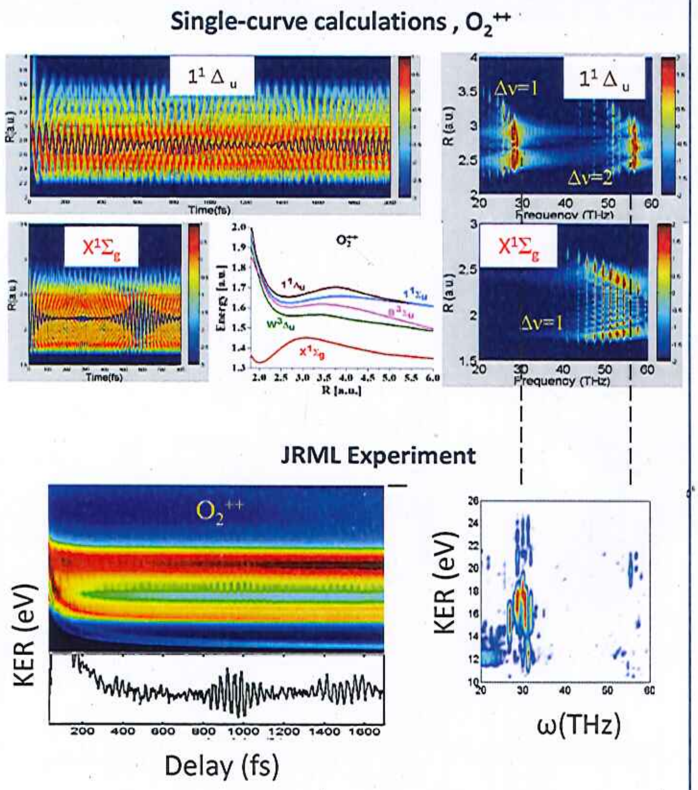
$$C^{diss}(E,\tau) \propto |\tilde{\Psi}^{diss}(P,\tau)|^2$$

$E = P^2/2M$: energy per Ar^+ fragment with mass M

R_1: cut-off parameter



Scheme for determining transient adiabatic states



Selection criteria

- Vibrational periods
- (Fractional) revival times
- Quantum-beat frequencies
- Energy releases

De *et al.*, PRA **84**, 043410 (2011)
Bocharova *et al.*, PRA **83**, 013417 (2011)
Magrakvelidze, Aikens, Thumm, PRA **86**, 023402 (2012)

Mapping the **light-induced ro-vibrational dynamics in small molecules** with intense short IR pulses

Hung Hoang
(postdoc)

Paul Abanador
(postdoc)

Thomas Pauly
(undergrad. student)

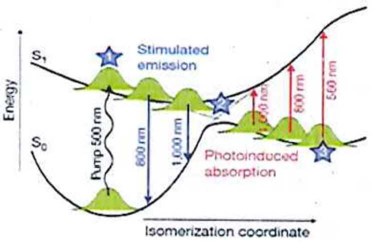
Bond softening
Bond hardening
Dissociation **stabilization**
(Light-induced) **conical intersections**

Examples: H_2^+ **and** O_2^+

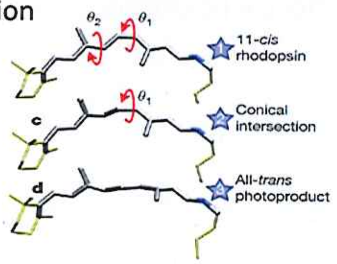
Natural vs. Light-Induced Conical Intersections

(110)

Rhodopsin
wave-packet dynamics through **CI**

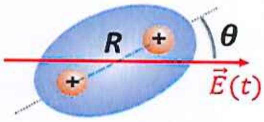


primary photochemical process in vision

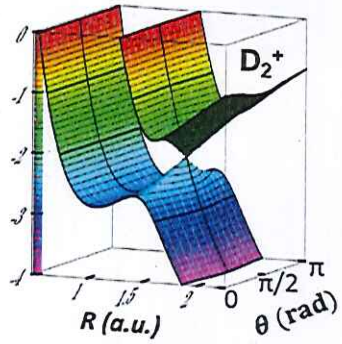


Polli *et al.*, Nature 467, 440 (2010)

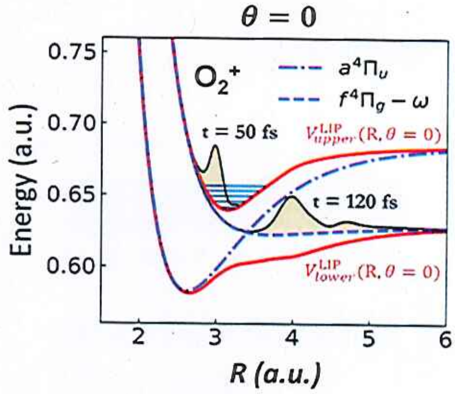
Diatomic molecules
no natural CI



LICI – controllable:
intensity → strength
ħω → position



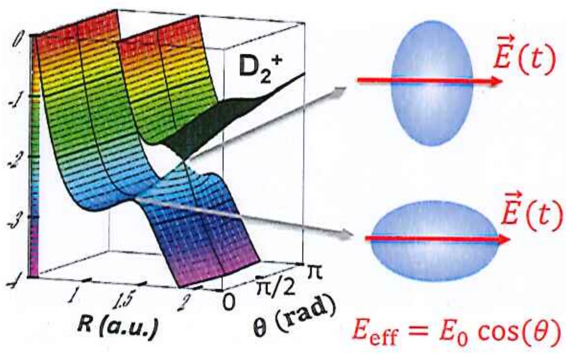
Halász *et al.*,
J. Phys. Chem. Lett 6, 348 (2015)



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

LICI effects in dissociation. Examples: H_2^+, D_2^+

Light-induced potentials



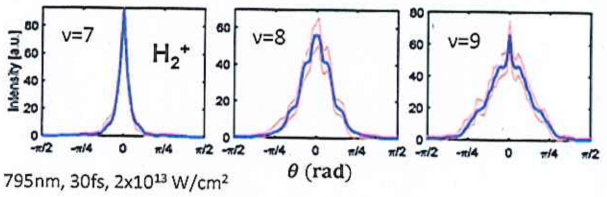
$E_{\text{eff}} = E_0 \cos(\theta)$

Effect of rotational excitation ?

Observable interference of
- **Adiabatic motion** near $\theta = 0$ and
- **Non-adiabatic transfer** near $\theta = \pi/2$?

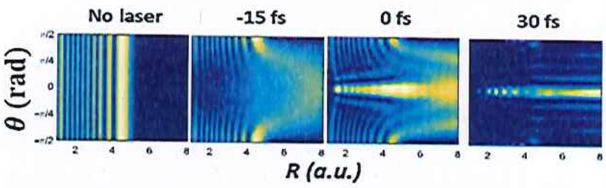
Observable effects of light-induced conical intersections

Modulations in measured fragment angular distributions



795nm, 30fs, 2x10¹³ W/cm²

Nuclear probability density (Simulation)



Natan, ..., Bucksbaum, PRL **116**, 143004 (2016)

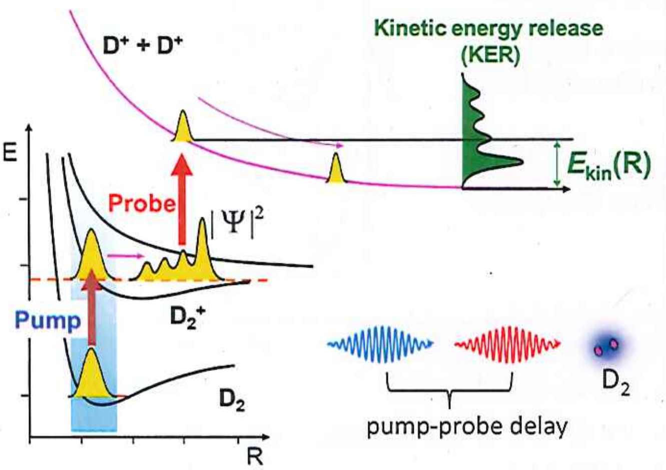
Characterization of light-induced potentials in the strong-field dissociation of O_2^+,
Abanador, Thumm, PRA **102**, 053114 (2020)

Strong-field modulated diffraction in the correlated electron & nuclear motion in H_2^+,
He, Becker, Thumm, PRL **101**, 213002 (2008)

Strong-field dynamics in small molecules

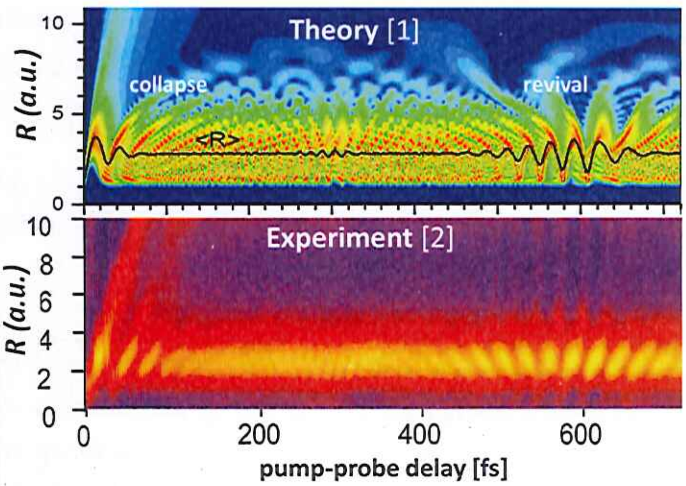
111

Recall: Pump-probe imaging



Magrakvelidze *et al.*, J. Phys. B **47**, 124003 (2014) and refs.

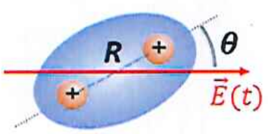
Time-resolved nuclear motion in D_2^+

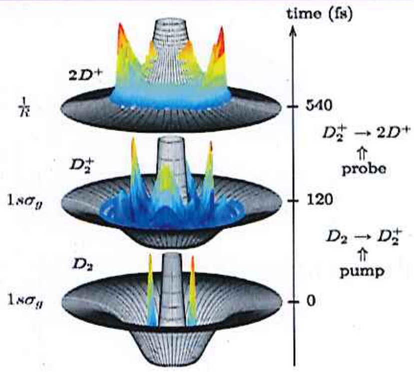


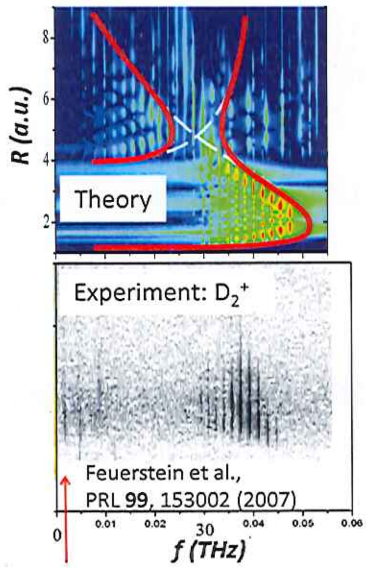
[1] Feuerstein, Thumm, PRA **67**, 063408 (2003)
[2] Ergler, Rudenko, *et al.*, PRL **97**, 193001 (2006)

Ro-vibrational dynamics:

Recall: D_2^+

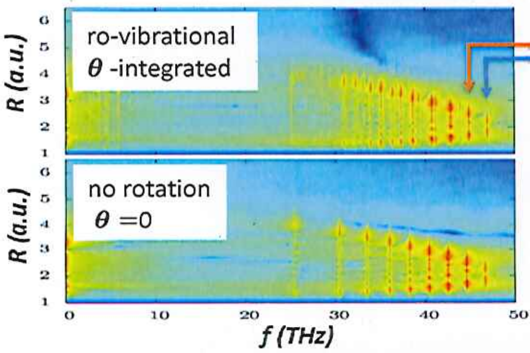


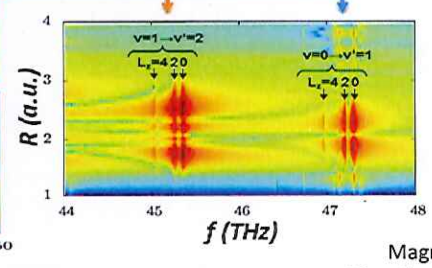




2 THz: ro-vib. coupling

Power spectra





Magrakvelidze *et al.*, J. Phys. B **47**, 124003 (2014)
O2+: Abanador *et al.*, Phys. Rev. A 101, 043410 (2020)