Ultrafast Molecular Dynamics Probed by Coherent Electrons and X-Rays

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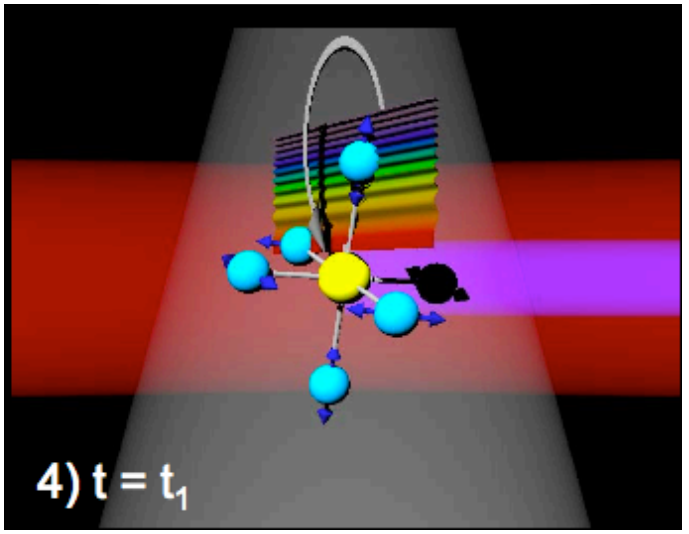
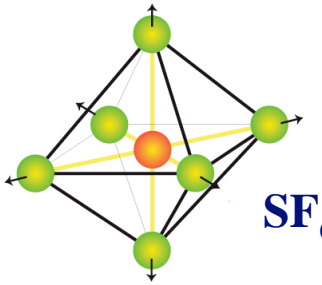
Ivan Christov, Chris Greene, Margaret Murnane and Henry Kapteyn

JILA
NIST-CU

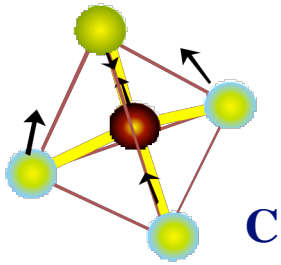
Outline

- **Probe internal dynamics in molecules using electrons coherently rescattered during the process of high harmonic generation - XISRS**
- **Preliminary theoretical models agree with experiment**
- **Probing attosecond dynamics in materials**





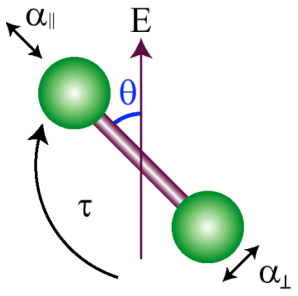
SF_6



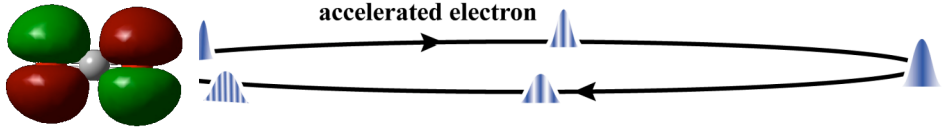
$CClF_3$

X-ray generation from molecules

- **Pump laser field can align molecules**

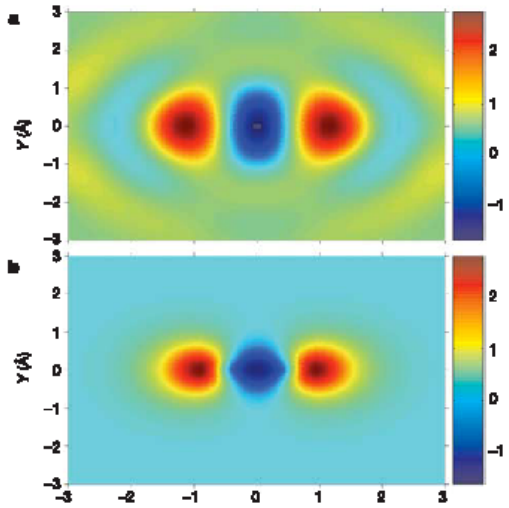


- **Probe pulse can generate harmonics from aligned molecules**



- **Since strength of emission depends on orientation, have a new probe of static molecular tomography**

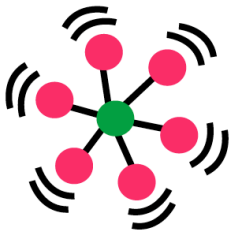
  (*Velotta, et al, PRL 8718 (18) (2001)*)

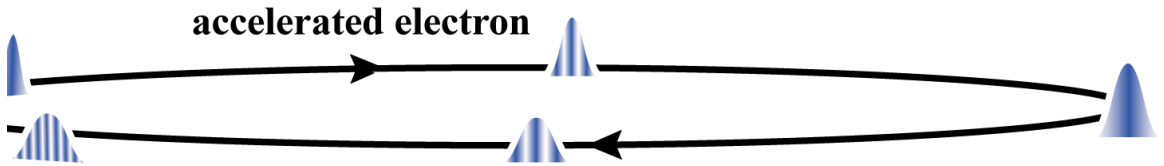


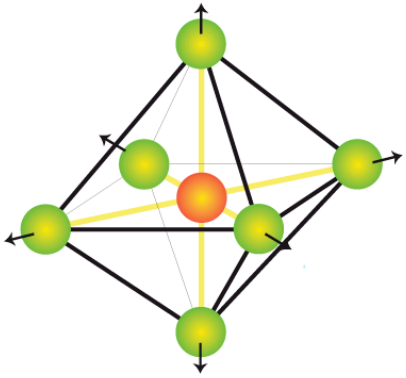
Itatani et al., Nature 432, 867 (2004)

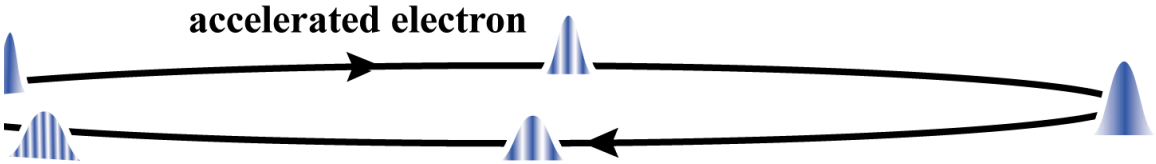
Can we observe intramolecular dynamics?

- **Is harmonic generation sensitive to small amplitude vibrational motions in a molecule? What modes can we observe?**



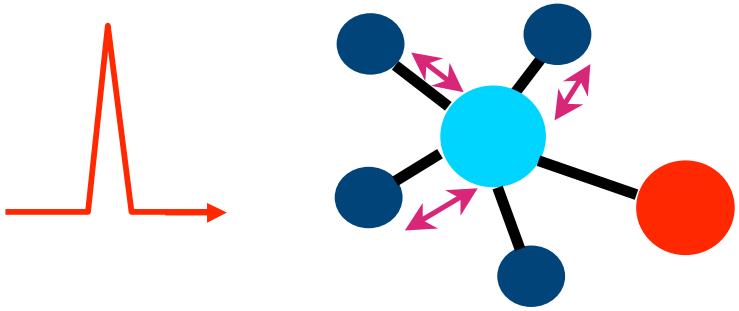




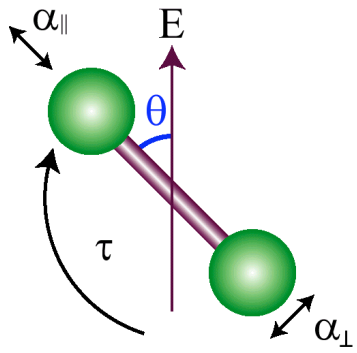


Exciting molecular dynamics using lasers

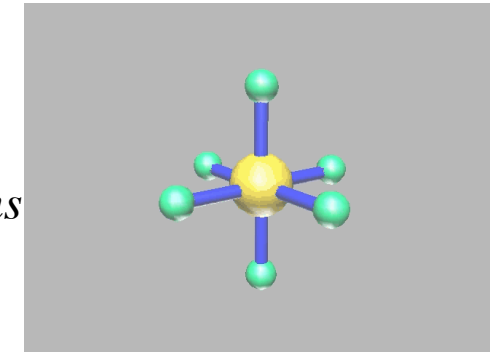
What happens when we hit a molecule with a short light pulse?



I. Molecule can align along the field



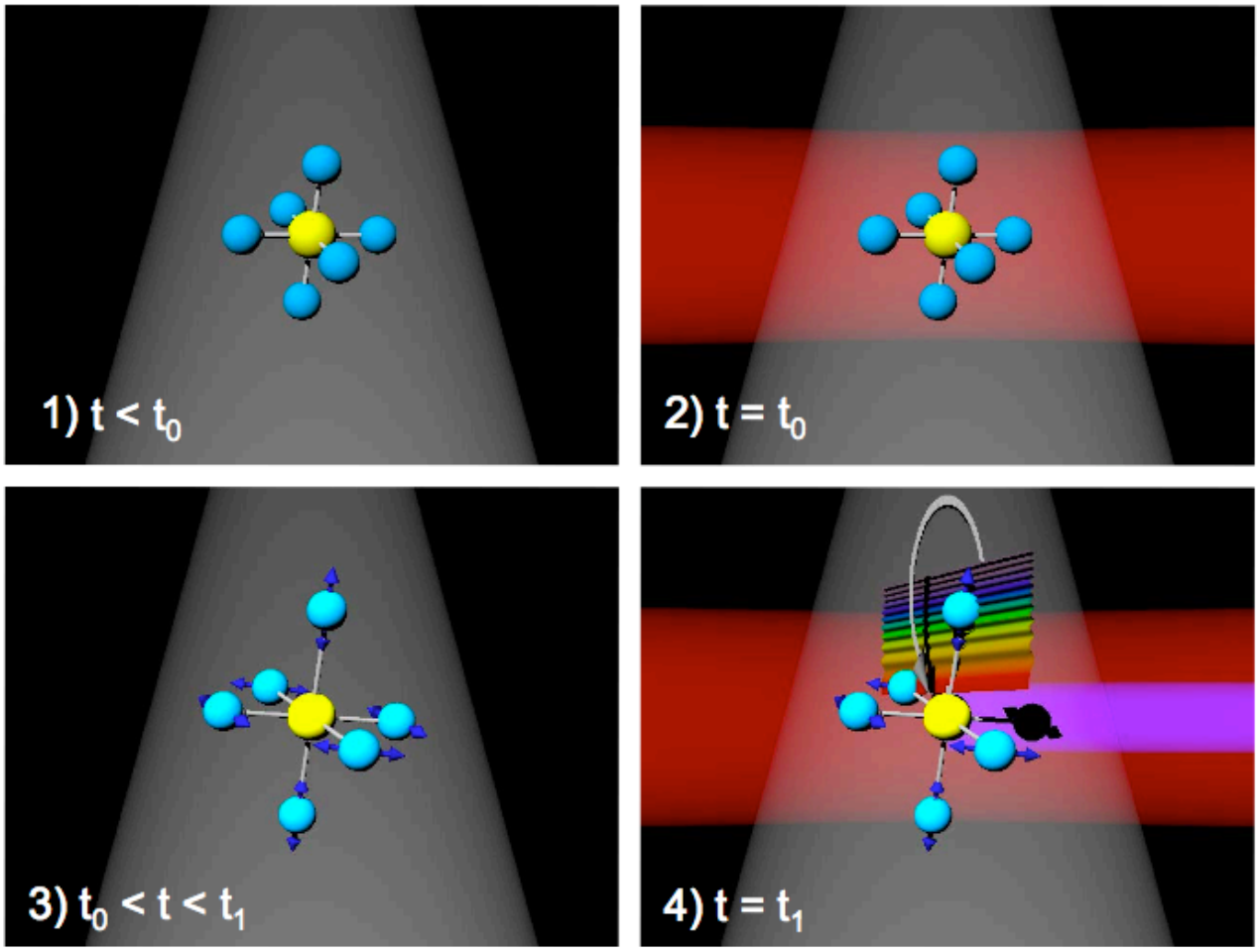
II. Excite Raman-active vibrations



K. Nelson, Science **247**, 1317 (1990
Weinacht, et. al, *Chem. Phys. Lett.* **344**, 333 (2001
Bartels, et al., *Phys. Rev. Lett.* **88**, 123 (2002

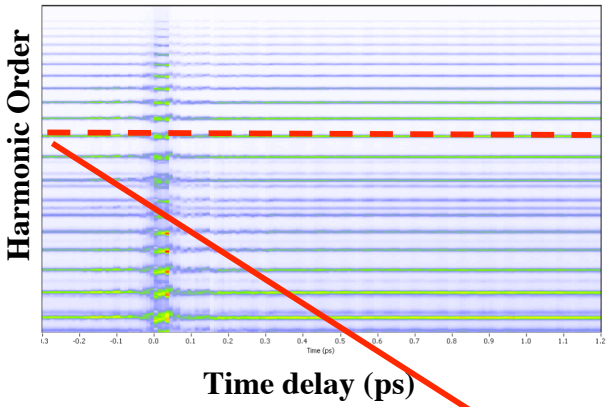
Experiment

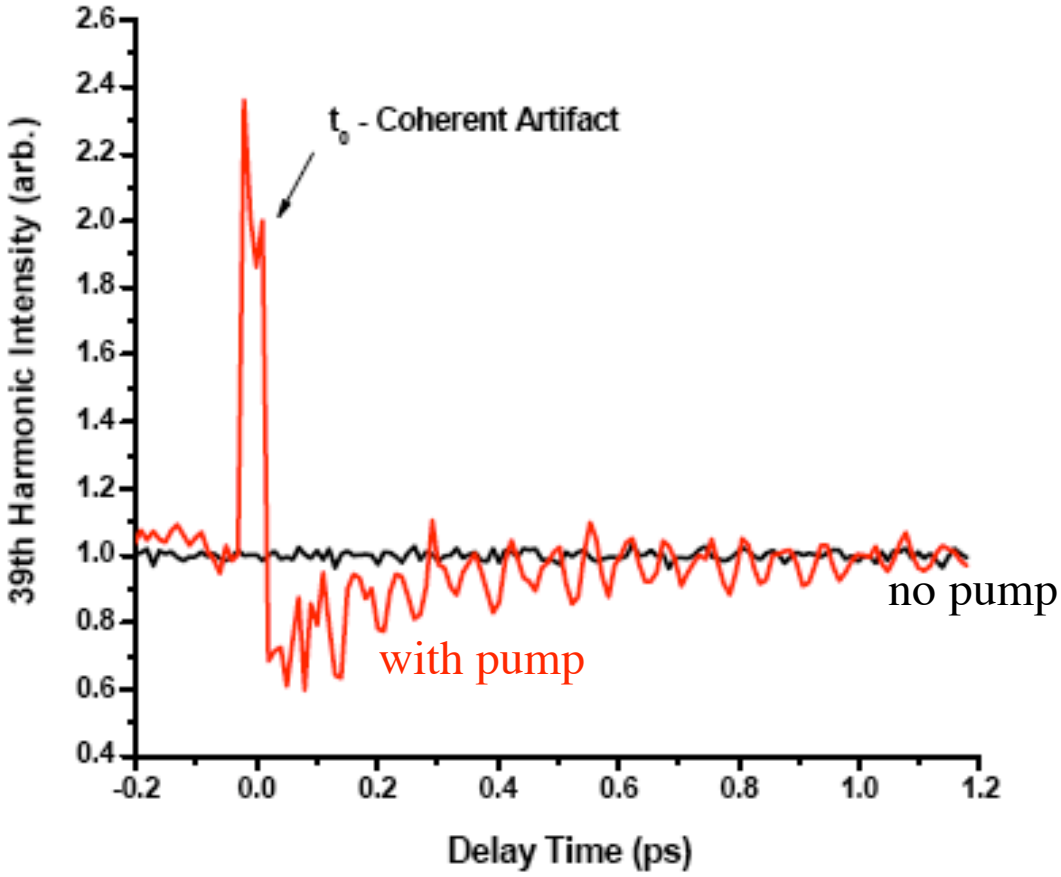
- **IR pump pulse excites vibrations using Impulsive Stimulated Raman excitation (ISRS) with $T_{pump} < T_{vib}$**
- **IR probe pulse excites harmonics from vibrational wavepacket with $T_{probe} < T_{vib}$**



PNAS
to be published
Aug 2006

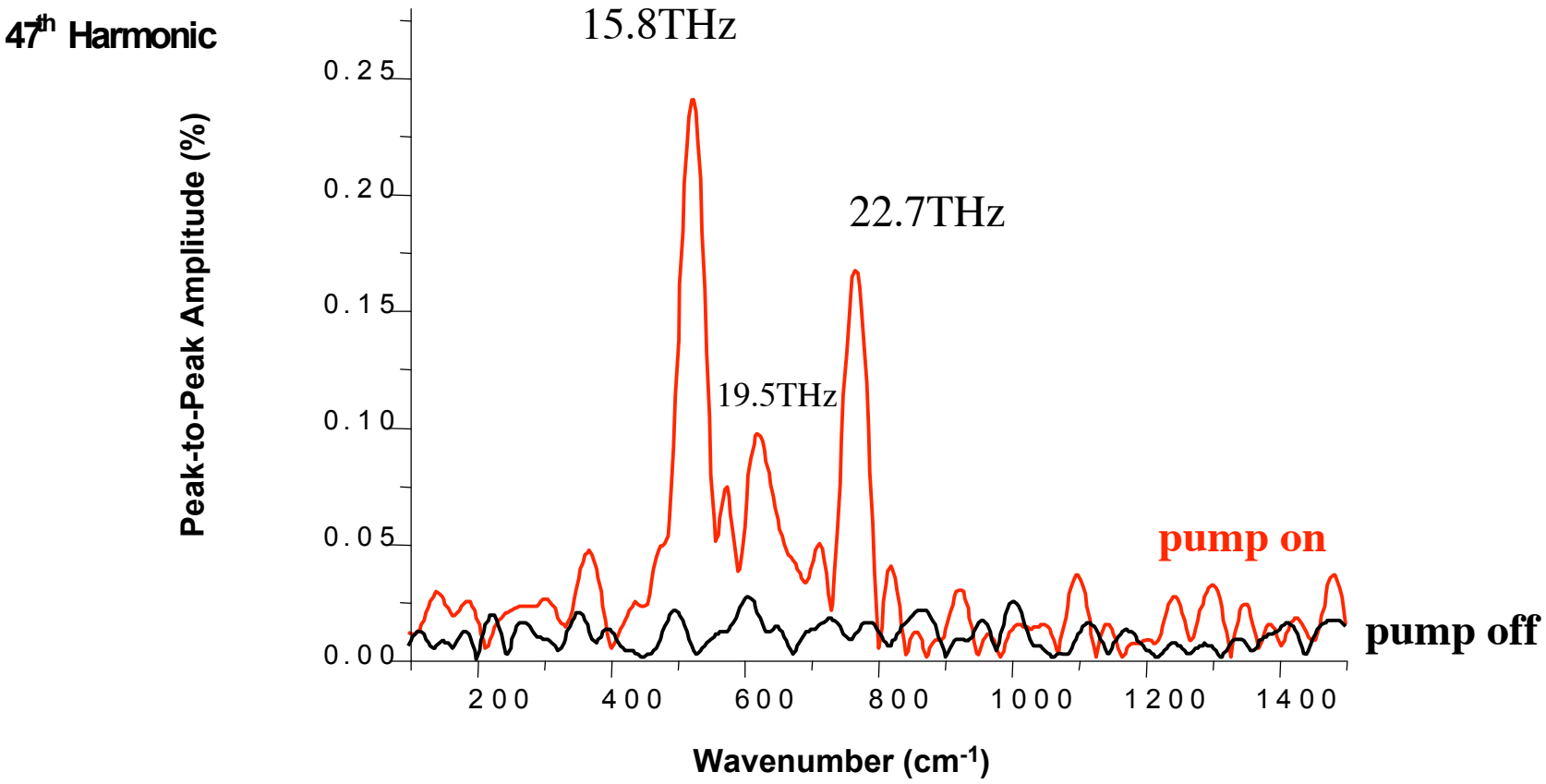
Observe modulation in the high harmonic emission





- **Observe oscillations in all harmonic orders vs. pump-probe delay**
- **Period of oscillations ≈ molecular vibrations**

Fourier analysis of oscillations -> vibrational spectrum

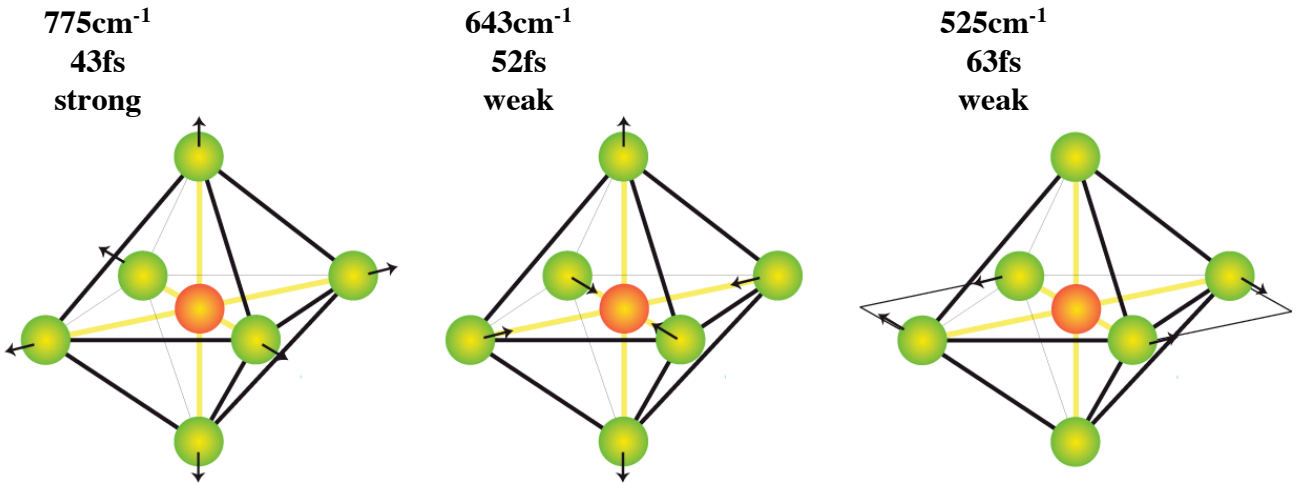


- **Observe three distinct peaks in the fourier transform**
- **High-order Impulsive Stimulated Raman Scattering?**

Vibrational modes in SF_6

$E(cm^{-1})$	Type	Assignment	Freq (THz)	T (fs)	Comment
351	Forbidden	$\nu_6(f_{2u})$ f.	10.53	94.96	Very weak
525	Raman	$\nu_5(f_{2g})$	15.75	63.49	Weak
615	Infrared	$\nu_4(f_{1u})$	18.45	54.20	Very strong
642.3	Raman	$\nu_2(e_g)$	19.27	51.90	Weak
774.5	Raman	$\nu_1(a_{1g})$	23.23	43.04	Very strong
948.1	Infrared	$\nu_3(f_{1u})$	28.44	35.16	Very strong

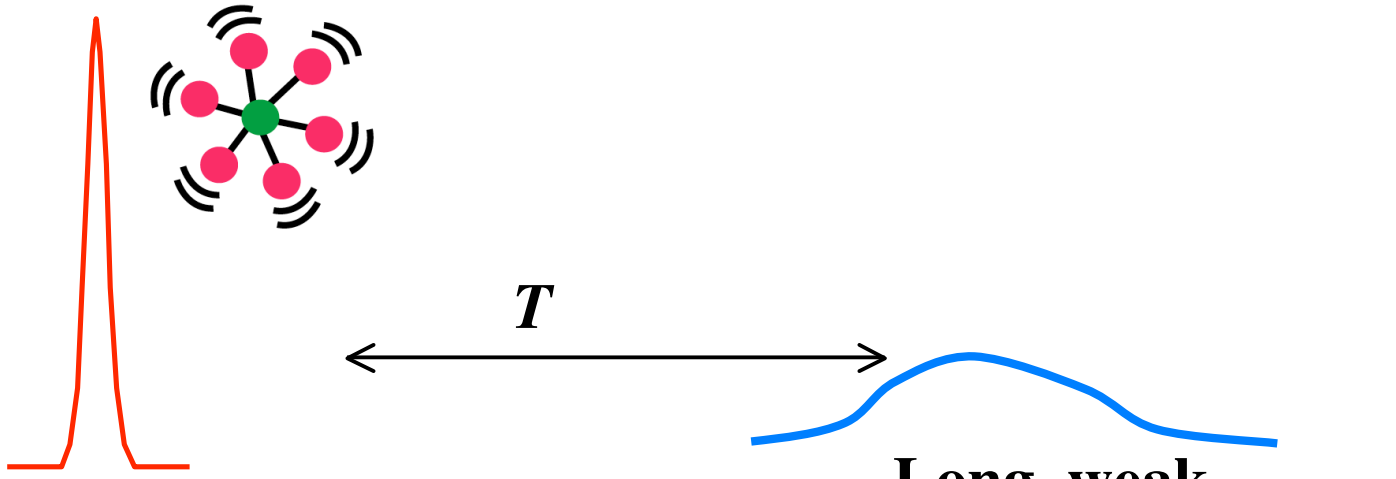
from "Infrared and Raman Spectra of Polyatomic Molecules", Herzberg



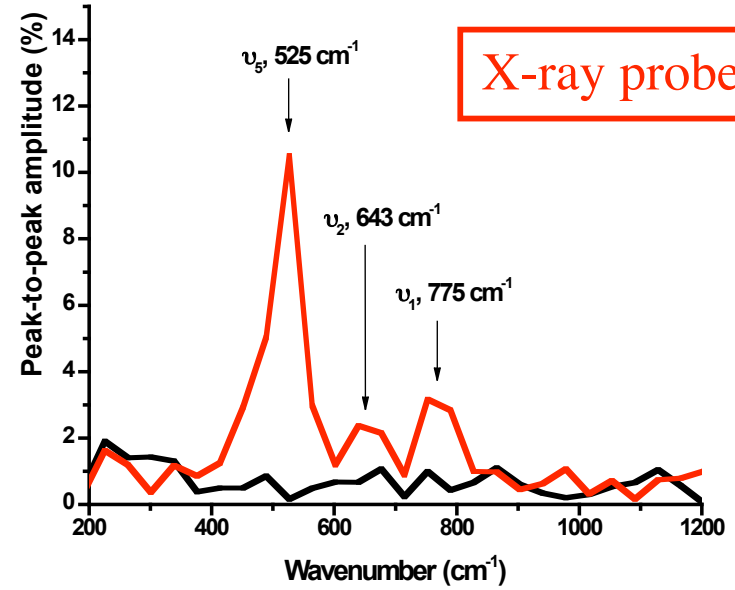
- **SURPRISE -- observe ALL the Raman-active modes**

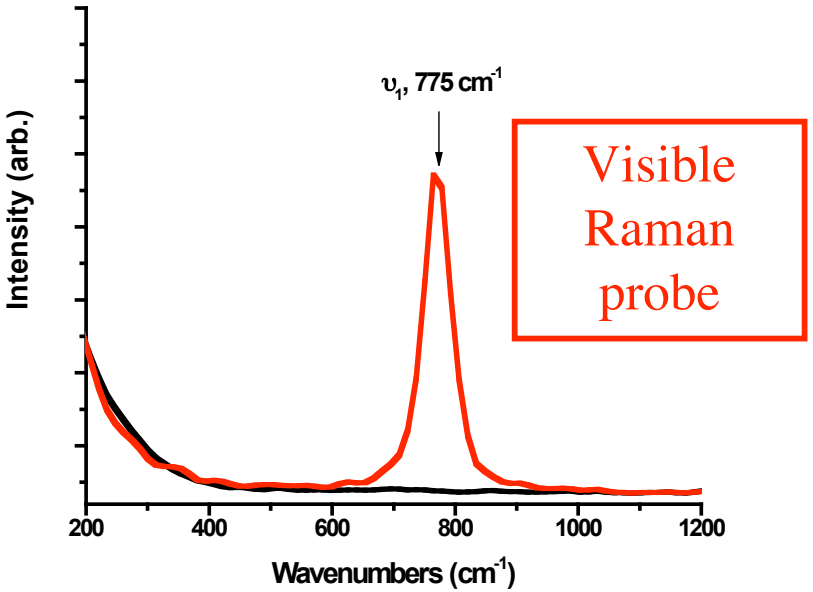
Probe vibrations using visible Raman scattering

- **Use spherically-symmetric, Raman active molecule: SF_6**
- **$T_{pump} < T_{vib}$ -- Impulsive Raman excitation (ISRS)**
- **$T_{probe} < T_{vib}$ -- measure Raman scattered narrow band visible**



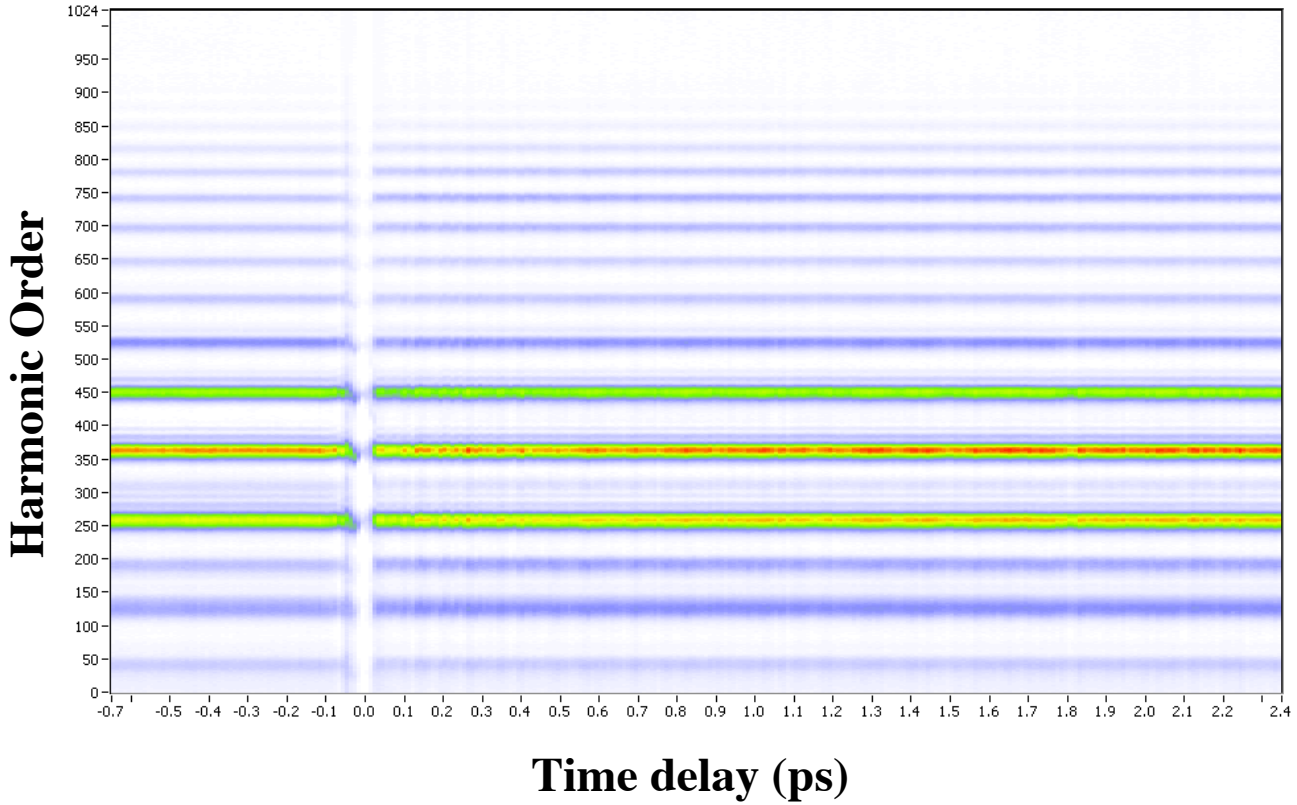
Direct comparison with visible-probed ISRS

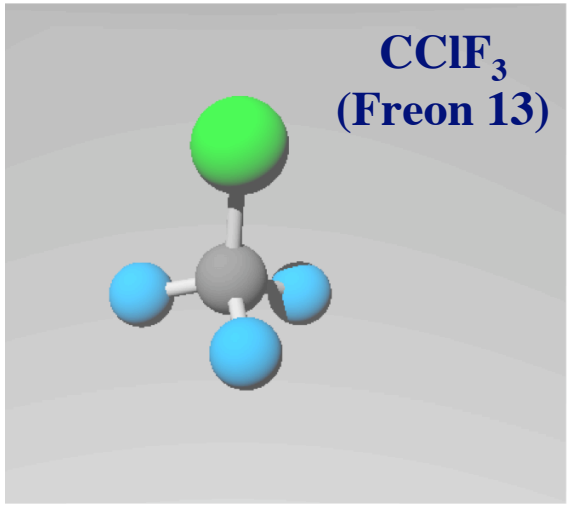




- **Conventional ISRS ONLY sees symmetric breathing mode**
  - **100x stronger than other modes** (*Chem. Phys. Lett.* **344**, 333 (2001); *Phys. Rev. Lett.* **88**, 123 (2002))
- **Ultrafast Raman is x10^3 less sensitive than x-ray signal because we needed to backfill entire chamber to see the visible signal!**
- **Harmonic emission MORE sensitive to MORE modes!**

Observe dynamics in non-spherically symmetric molecule - $CClF_3$





file:///Users/margaretmurnane/Desktop/Temporary%20Work%20June%2006/Data/Nick%20data/freon%20animations/CF3Cl_mode3.gif

- **$CClF_3$ is a non-spherically symmetric molecule with six normal modes**
- **Observe larger modulation of the HHG signal due to vibrations than SF_6**

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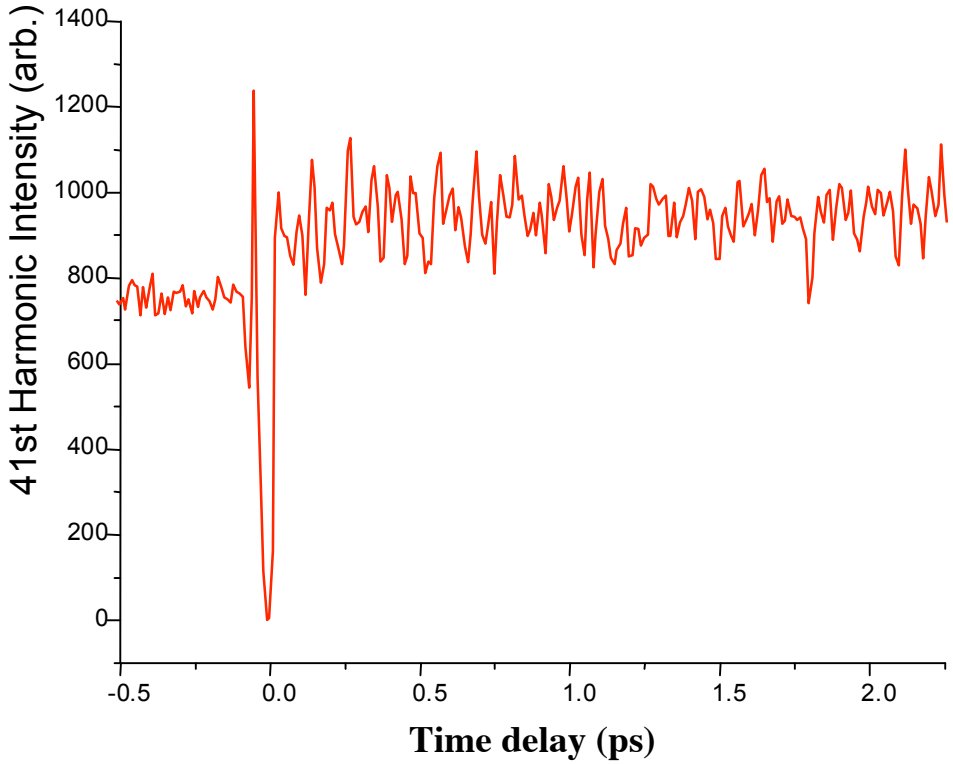

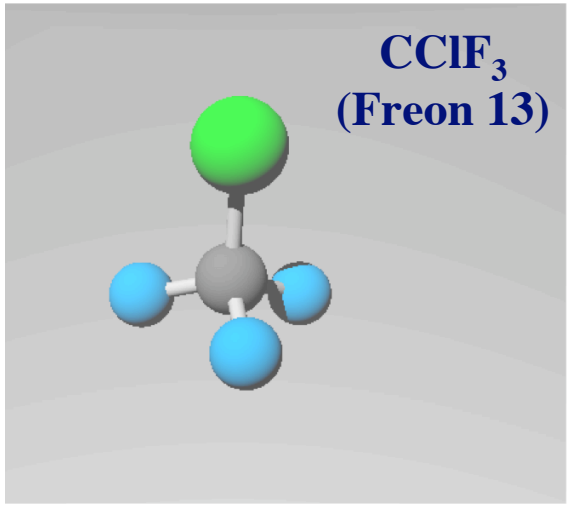

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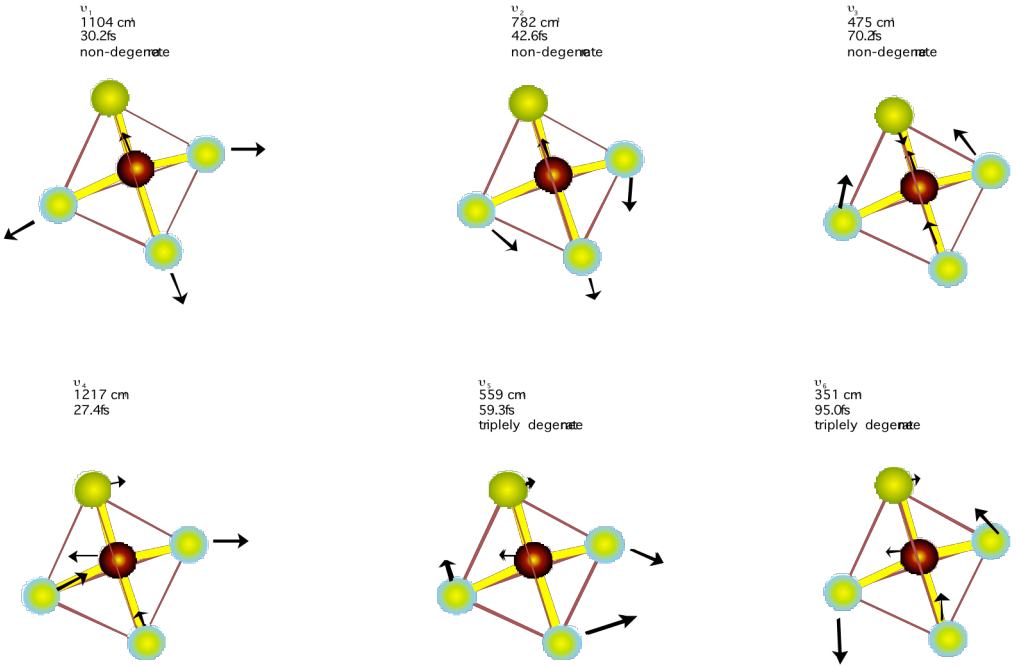
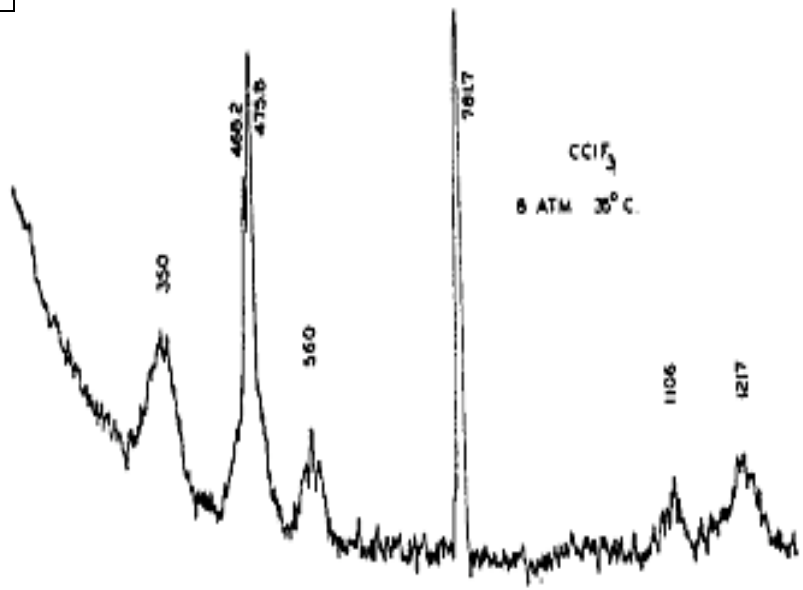
Vibrational modes in $CClF_3$

Wavenumber (cm^{-1})		Period (fs)
350	e fundamental	95
468	a_1 fundamental Cl^{37}	71
476	a_1 fundamental Cl^{35}	70
560	e fundamental	60
781	a_1 fundamental	43
1106	a_1 fundamental	30
1217	e fundamental	27





Spontaneous Raman spectrum of $CClF_3$
Claassen, J. Chem. Phys. 22, 50

- **C Cl F_3 has six normal modes with a range of periods (27 - 95 fs)**
- **Would not expect to see high-frequency modes since period ≈ pulsewidth**

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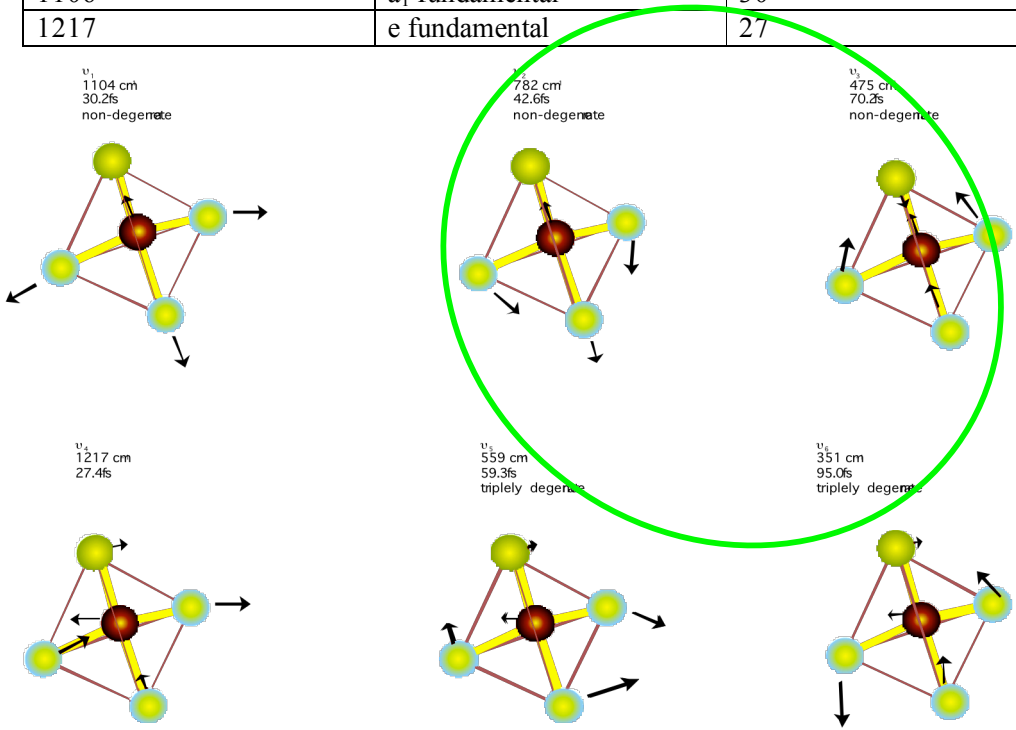

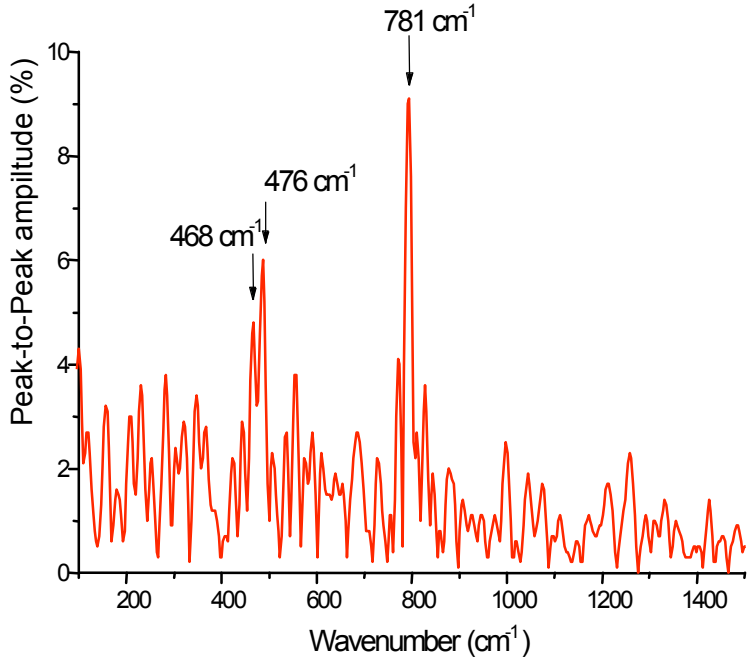

- **Observe two strongest Raman-active modes**
- **Likely due to signal-to-noise and pump pulse limitations**

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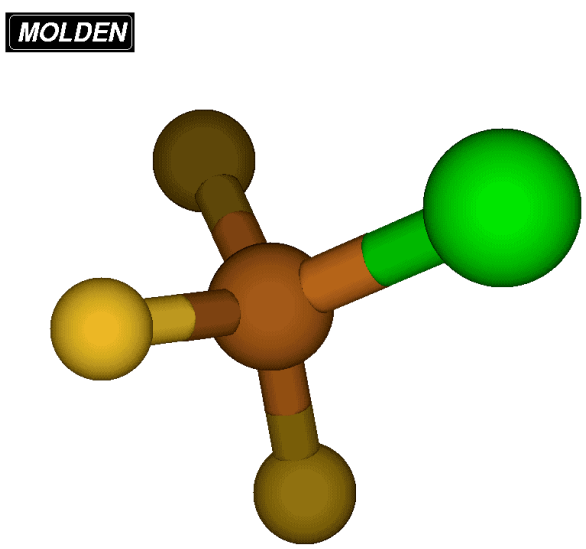
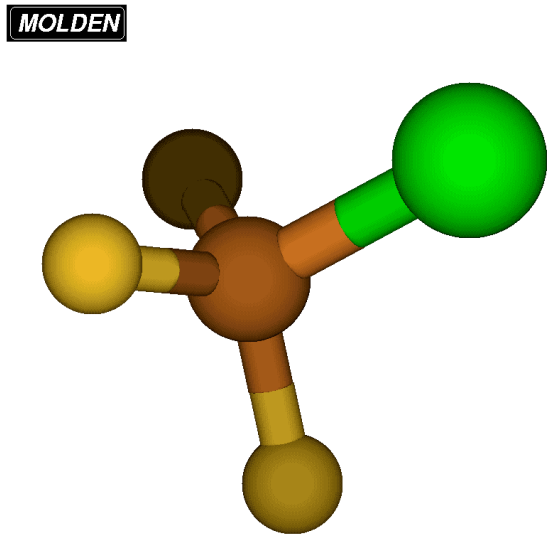
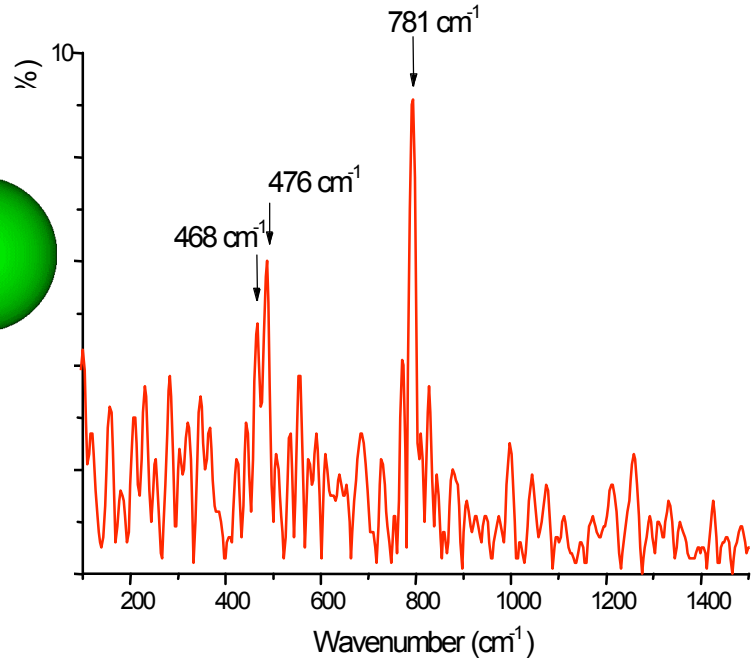




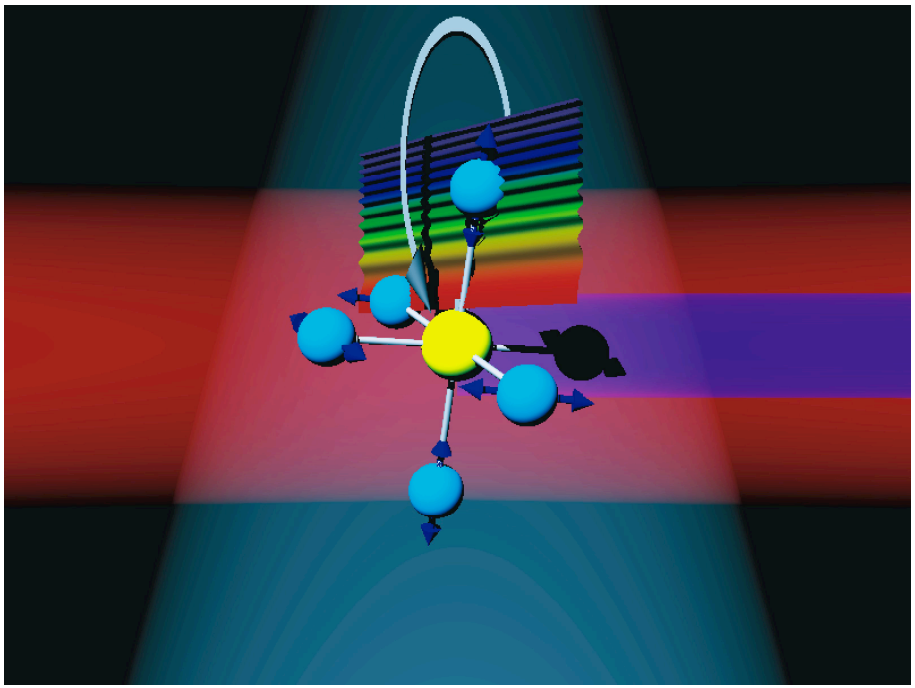


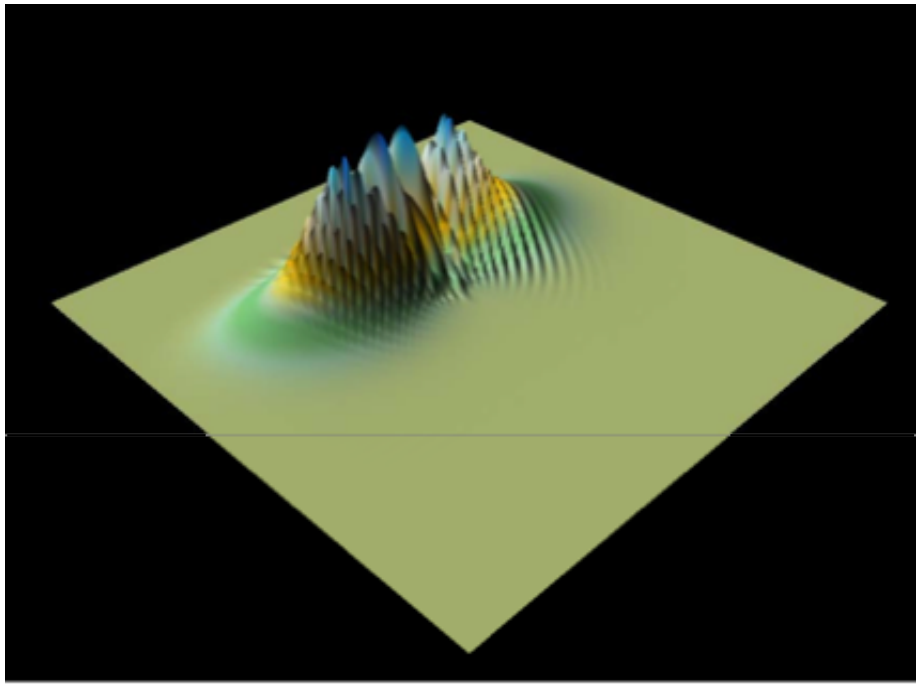
- **Observe two strongest Raman-active modes**
- **Likely due to signal-to-noise and pump pulse limitations**

Why does HHG probe of vibrations differ from ISRS?

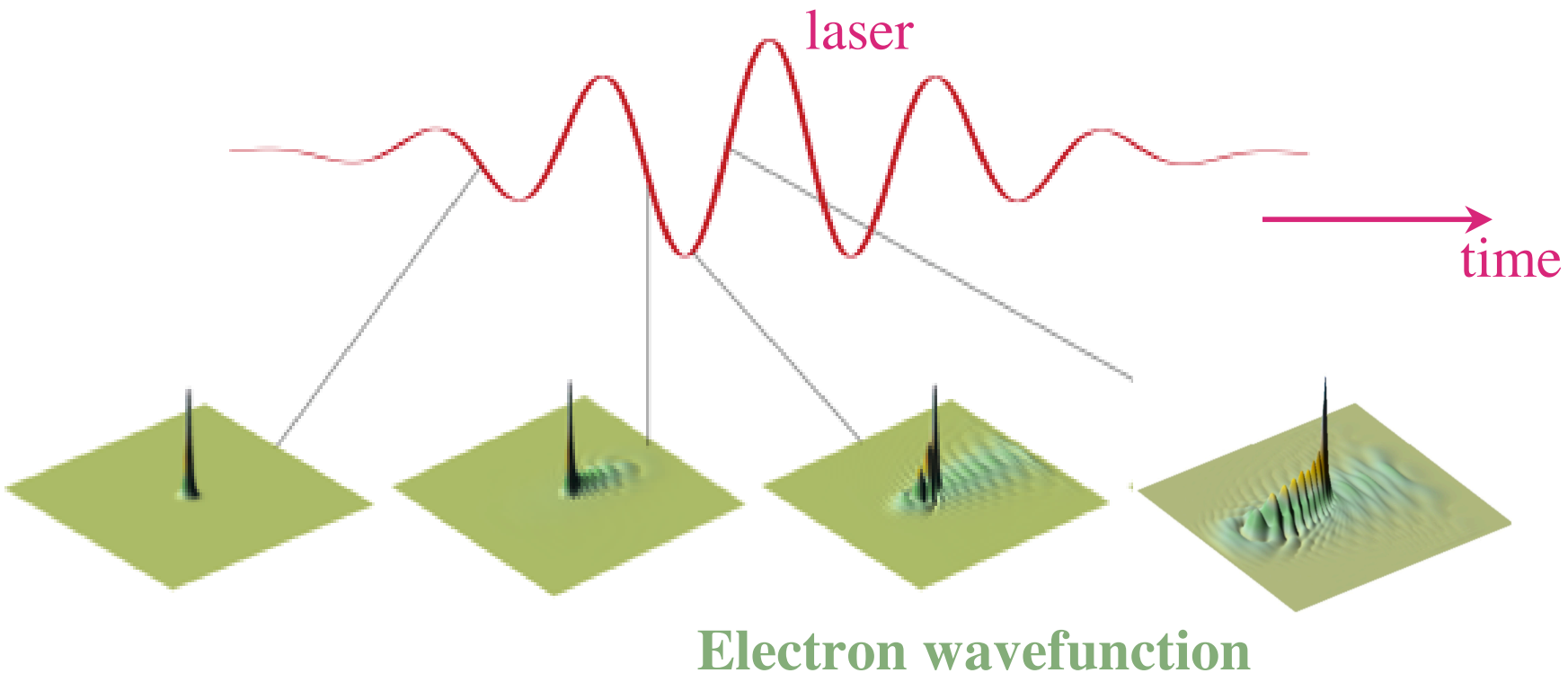
- **Not likely due to excitation - visible and x-ray experiment had same pump pulse**
- **Wavelength of recolliding electron comparable to molecular dimension**
- **Quantum interferences thus make HHG very sensitive to the *shape* of the molecule**

$$\lambda_e = h/p = h/\sqrt{2m_e E} = .15nm @ \quad H45 \quad (70eV)$$



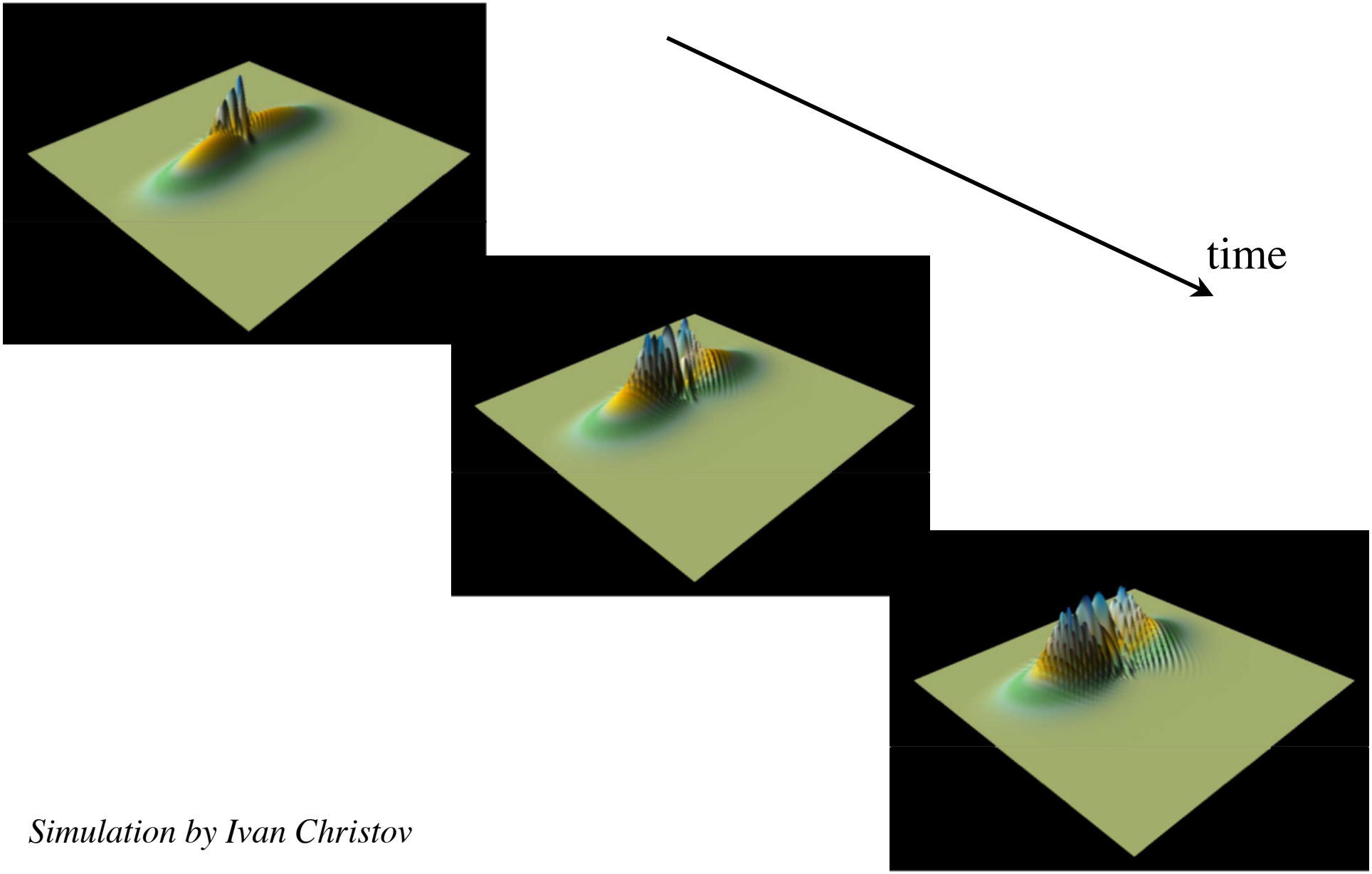


Quantum picture - electron being ripped from atom



Physics Today, Kapteyn et al. March 2005

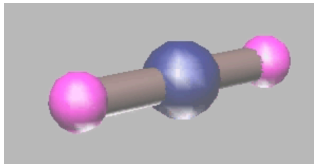
2D Plane wave electron recollision with SF_4

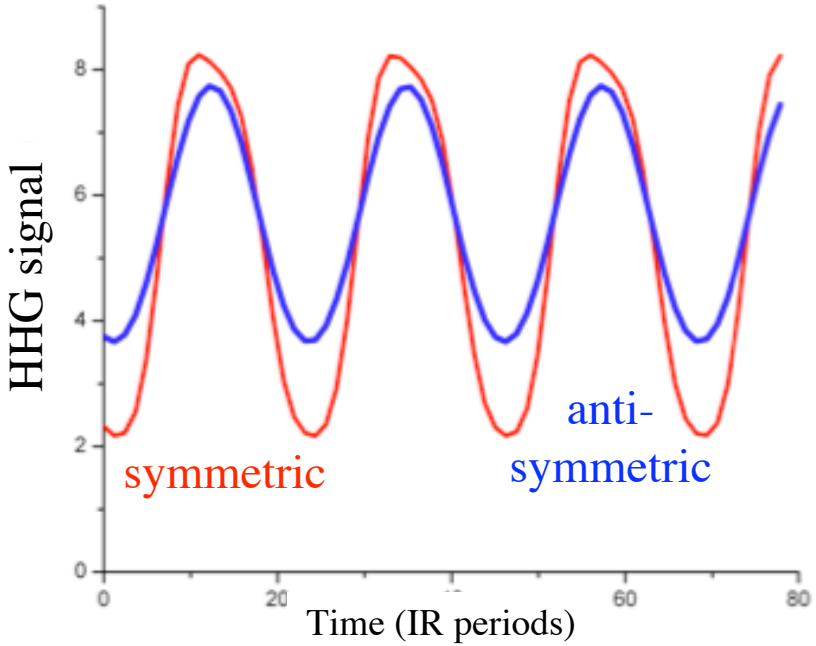


Simulation by Ivan Christov

Theoretical understanding to date

- **Fully quantum calculation of simple linear triatomic molecule** (*Ivan Christov)*
- **Predict that both symmetric and antisymmetric modes observable - harmonic generation should be sensitive to ALL modes, both Raman and IR-active**
- **Predict 2mÅ sensitivity for current experiment (0.1% modulation in bond length)**





Probing vibrational Raman-excited quantum beats

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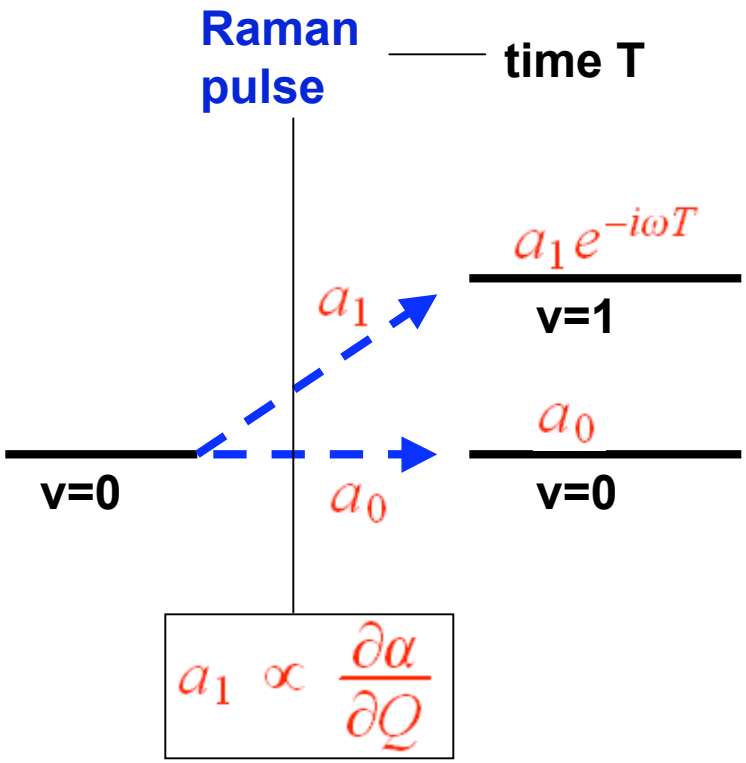

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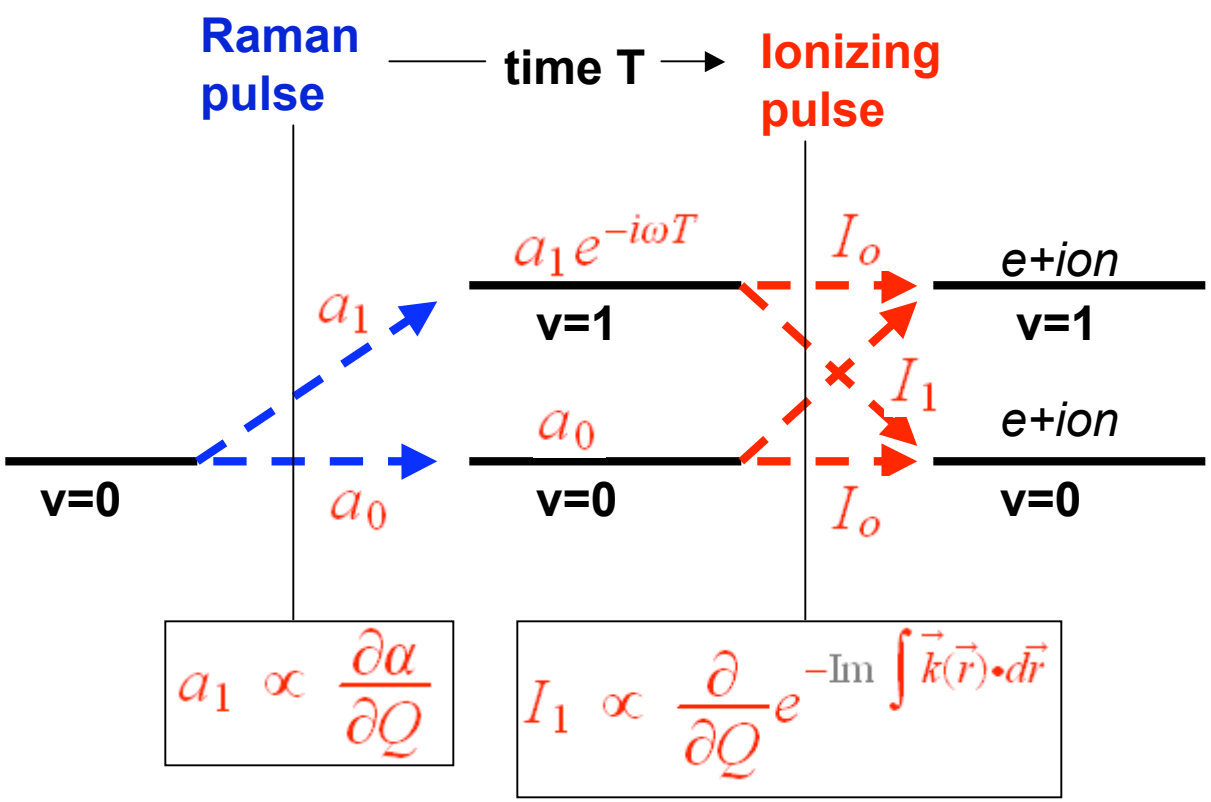

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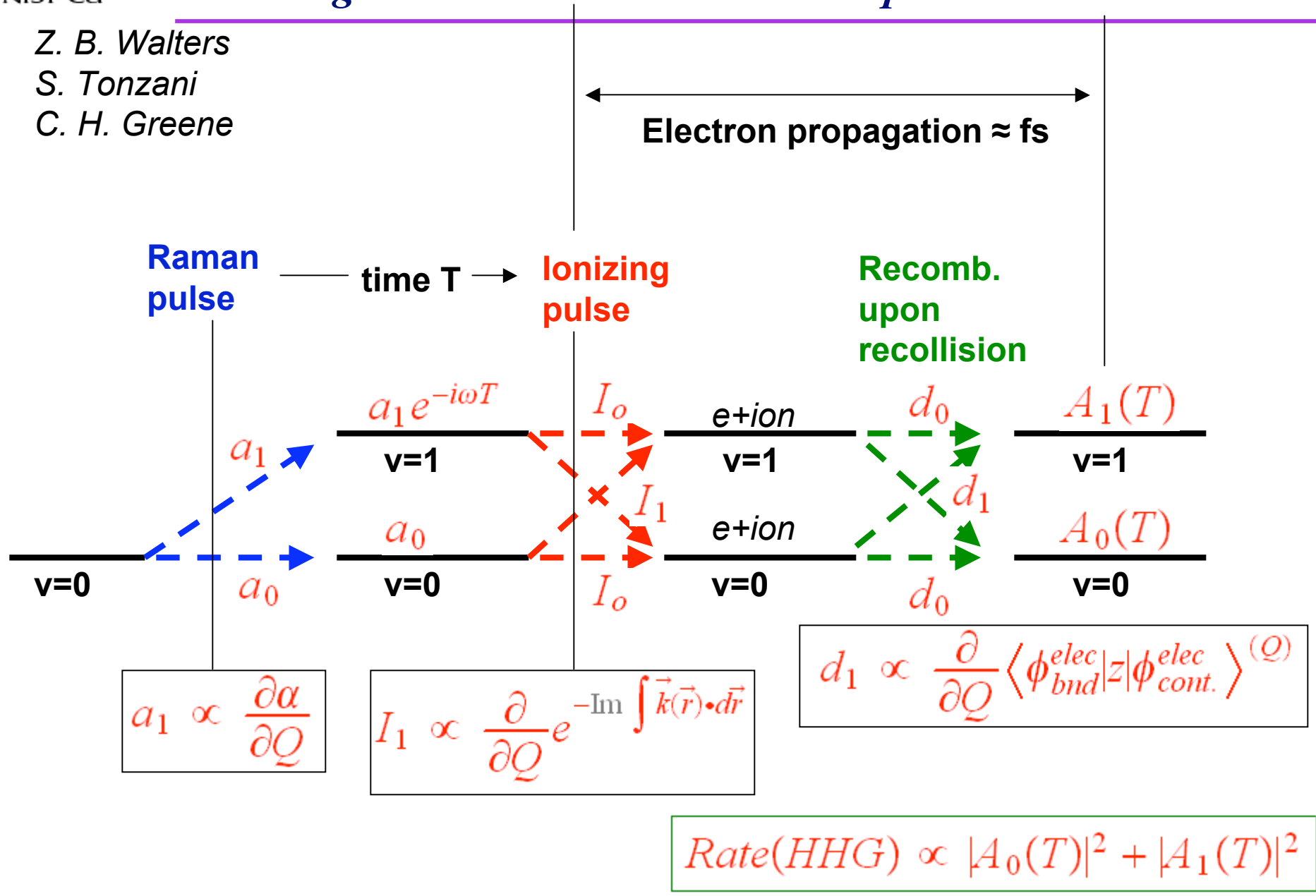
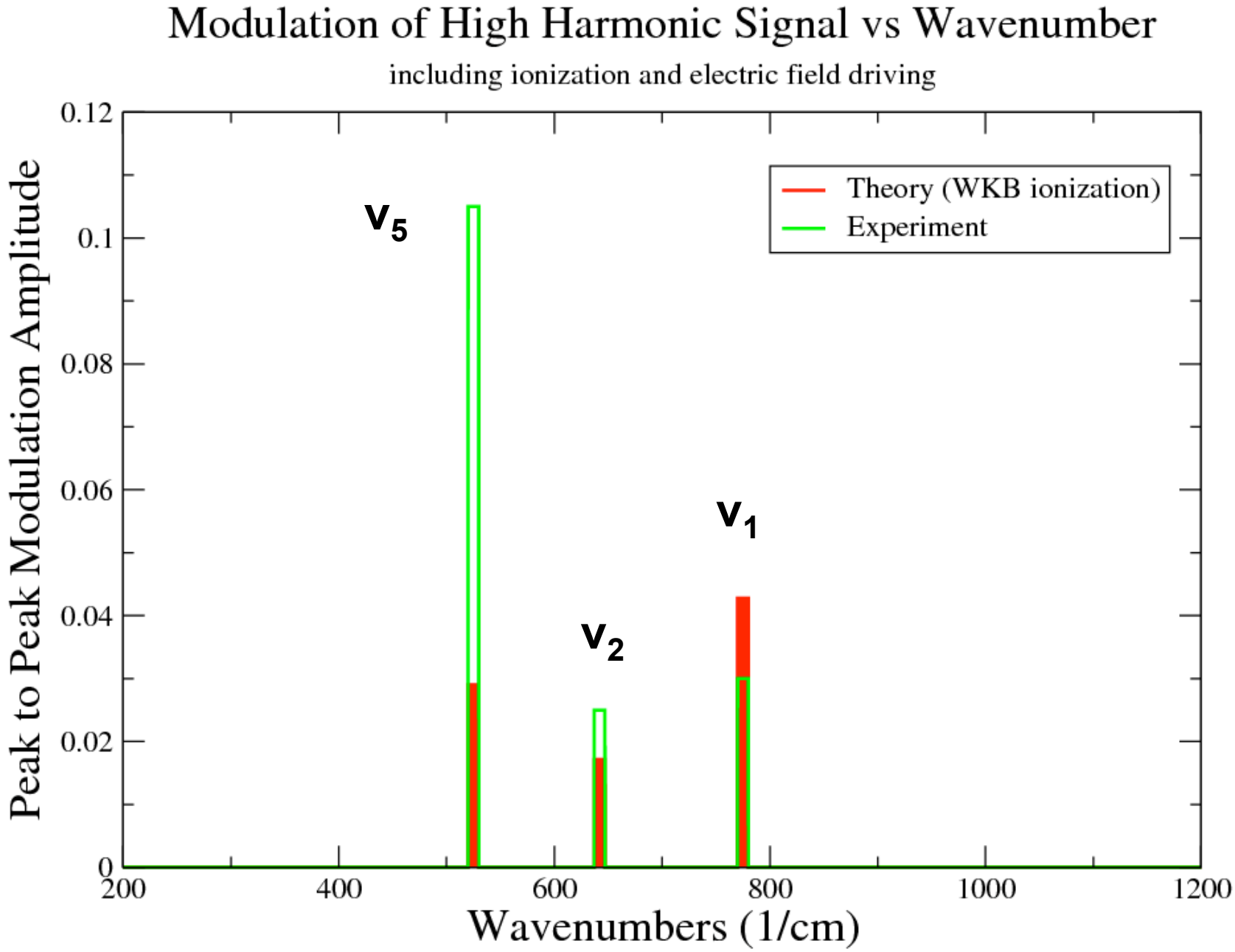
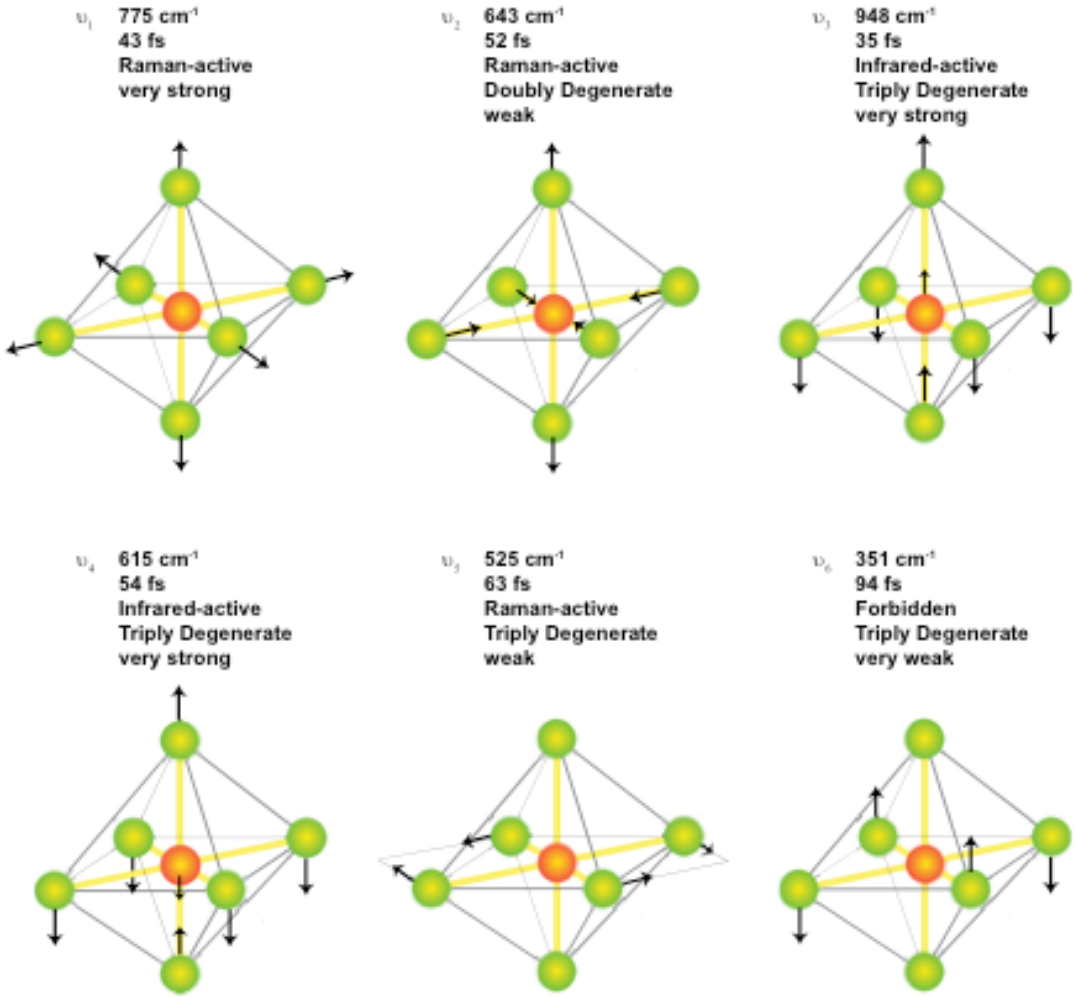
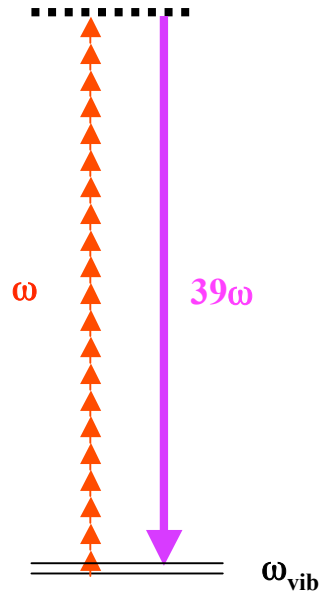



Modulation of High Harmonic Signal vs Wavenumber
including ionization and electric field driving
Peak to Peak Modulation Amplitude
Wavenumbers (1/cm)
Theory (WKB ionization)
Experiment
v_5
v_2
v_1
0.12
0.1
0.08
0.06
0.04
0.02
0
200
400
600
800
1000
1200

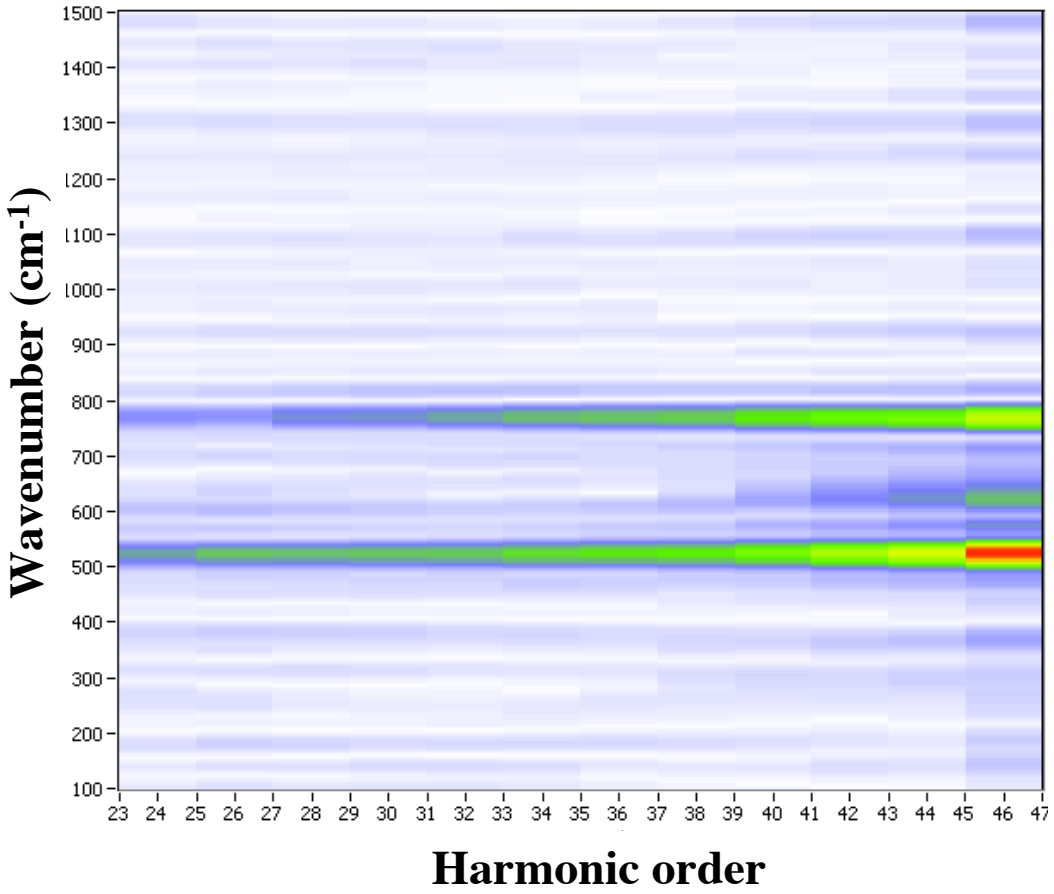
New spectroscopic high-order x-ray Raman probe?





XISRS?

Vibrations most visible in higher harmonics

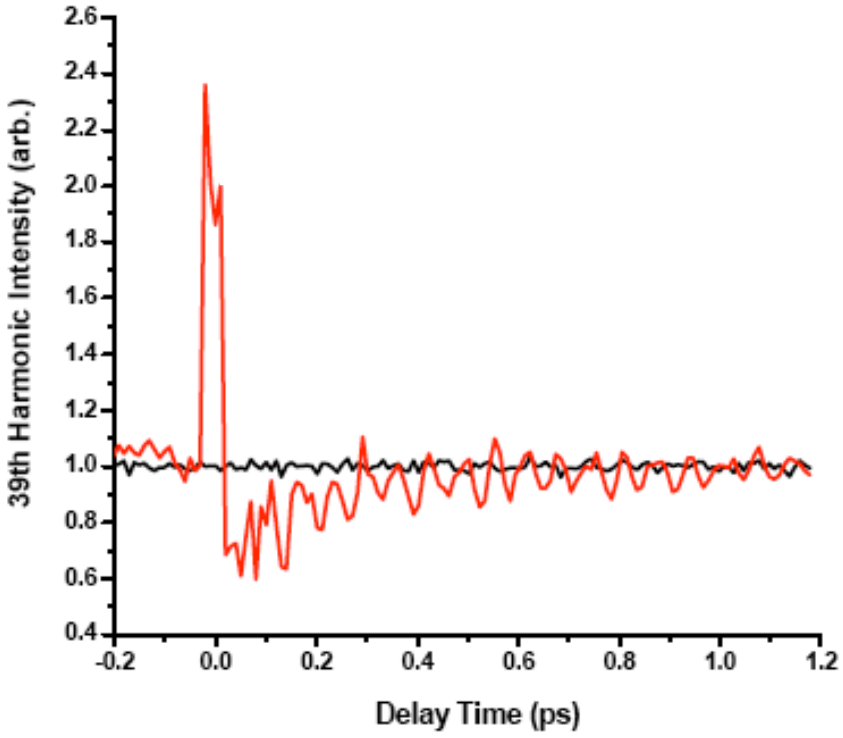


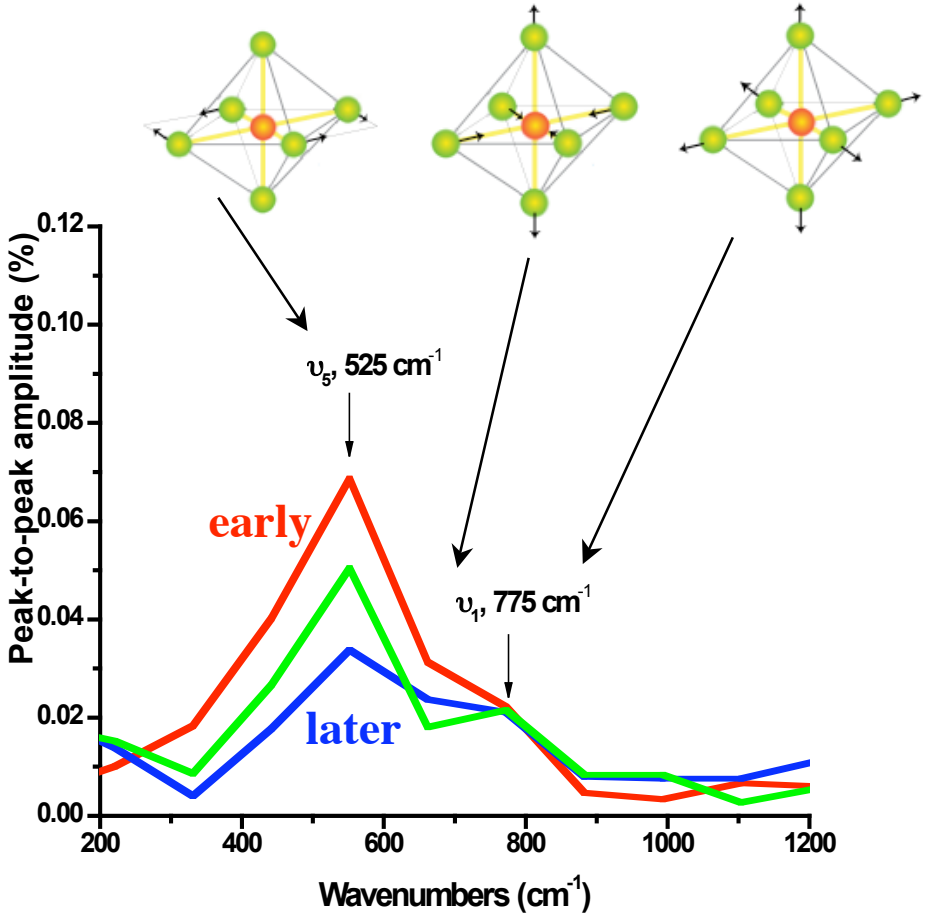
ν_1 symmetric
ν_2 asymmetric
ν_5 asymmetric

- **All vibrations more visible for higher harmonic orders**
- **Higher harmonic orders correspond to shorter wavelengths of the recolliding electrons and shorter duration x-ray pulses**

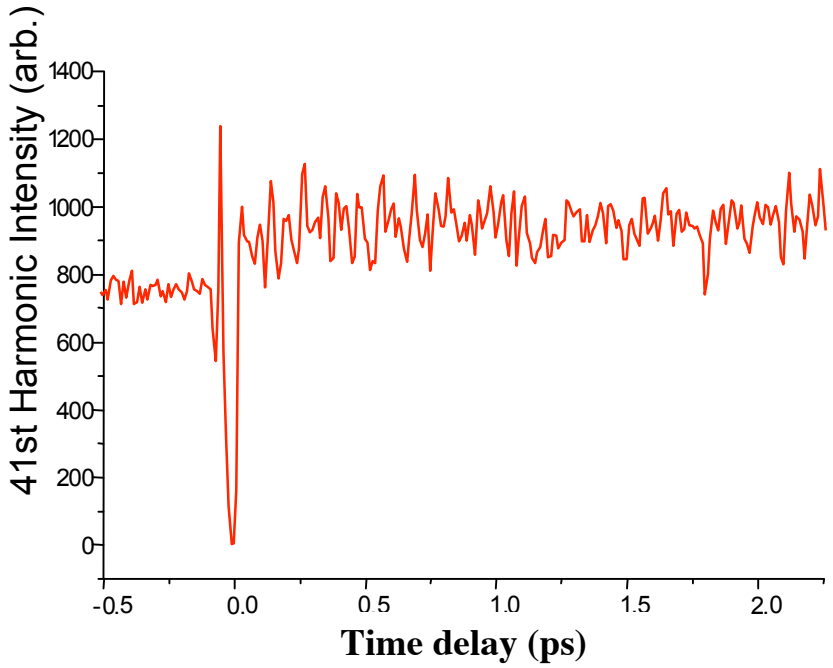
Observation of vibrational and reorientational relaxation

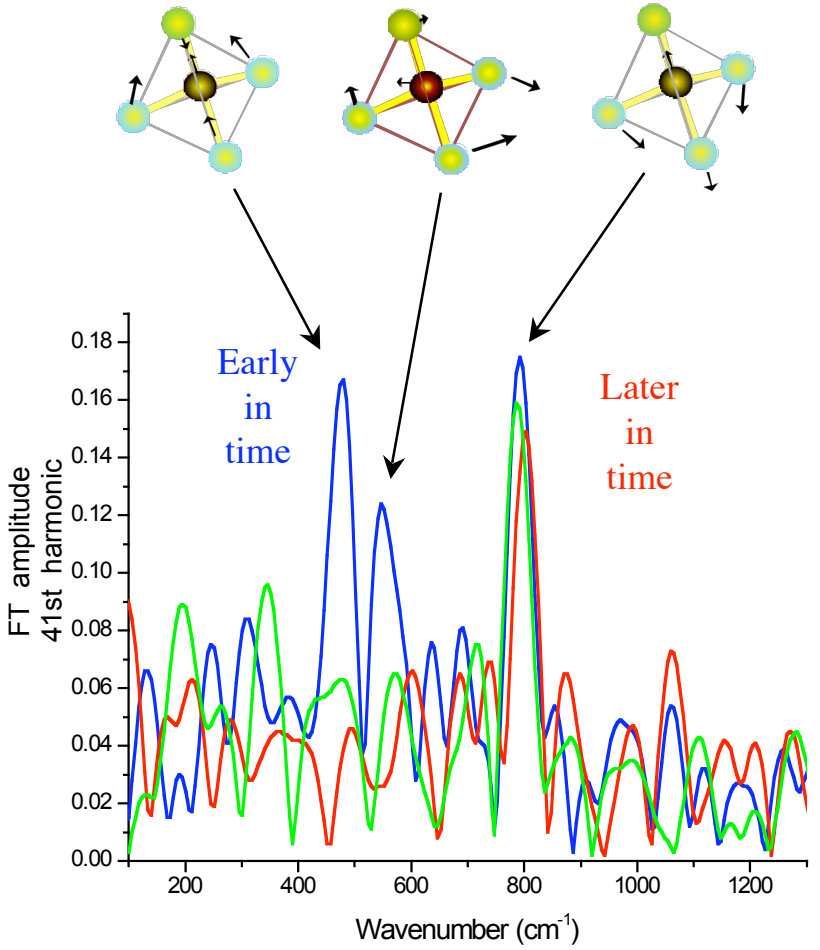
- **Asymmetric mode decays over time interval investigated, possibly due to reorientational dynamics**
- **Amplitude of symmetric mode remains constant**





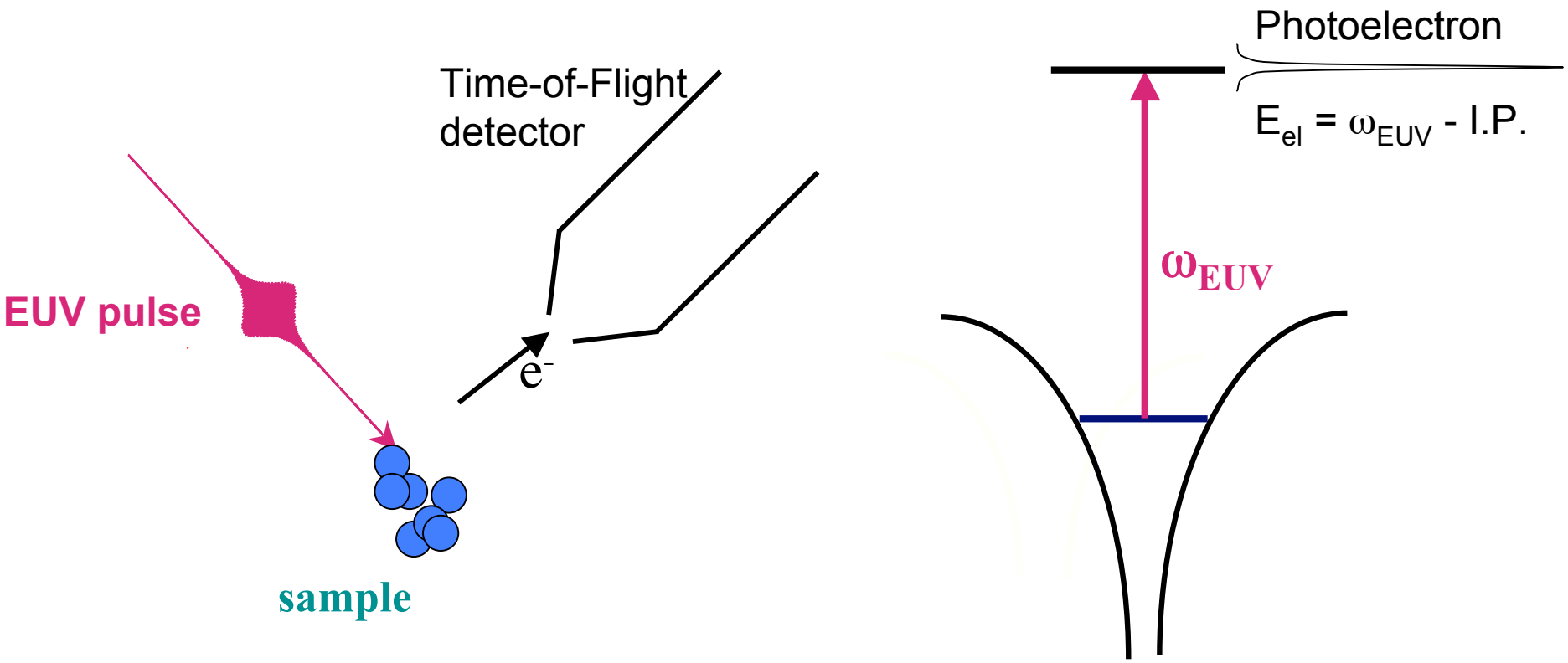
Vibrational dynamics in C Cl F_3





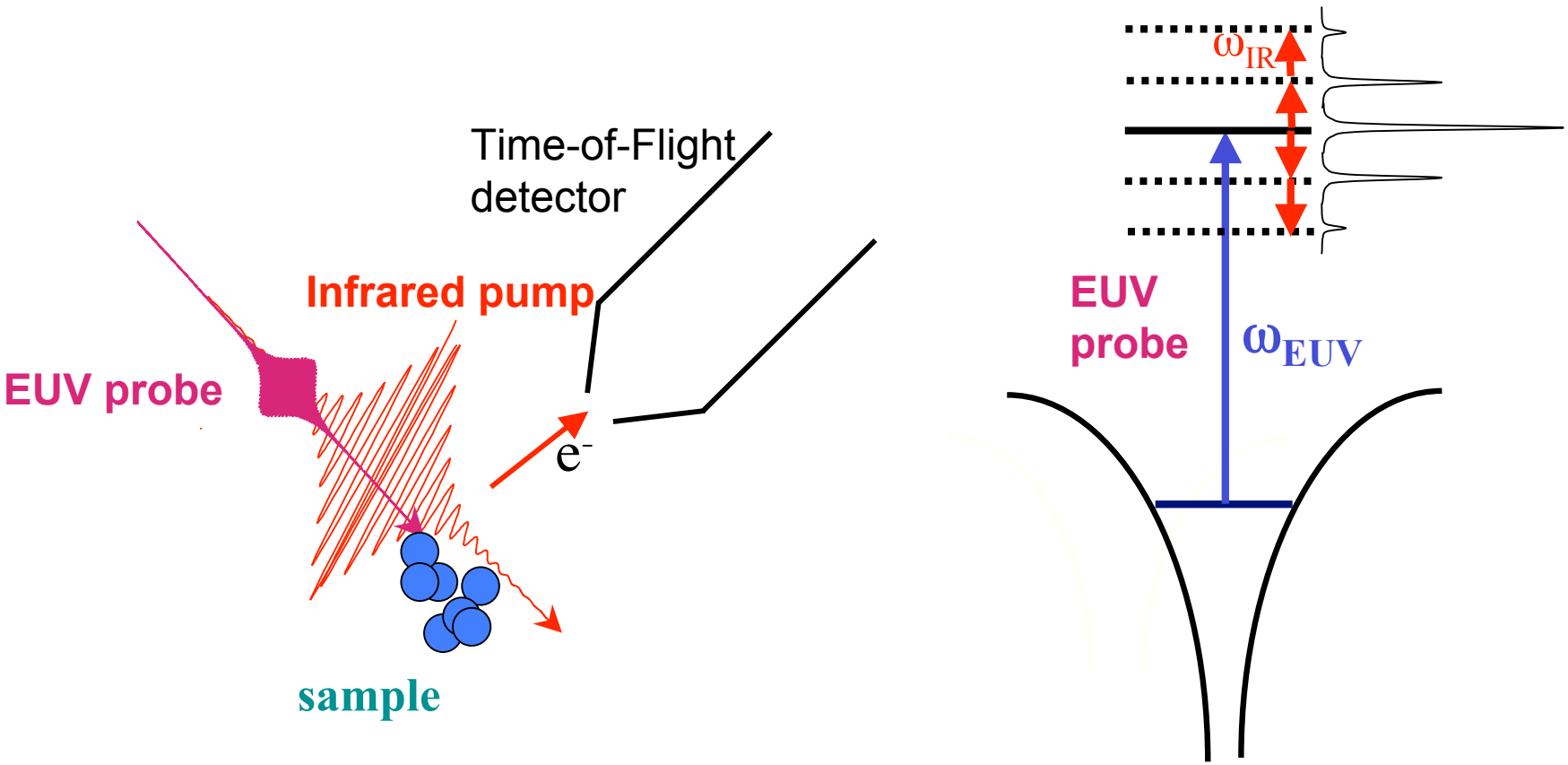
- **Observe rapid decay of 470cm^{-1} and 560cm^{-1} modes and persistence of 781cm^{-1} mode**

EUV Photoemission in the Presence of an Intense Laser



- **EUV pulse photoionizes the gas atoms**
- **Laser field modifies photoelectron energies** *(Glover et al. PRL 76, 2468 (1996)*

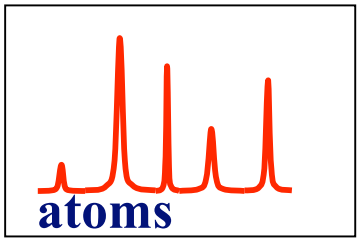
EUV Photoemission in the Presence of an Intense Laser



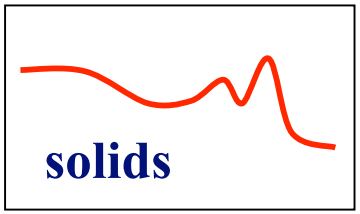
- **EUV pulse photoionizes the gas atoms**
- **Laser field modifies photoelectron energies** *(Glover et al. PRL 76, 2468 (1996)*

Can we see laser assisted photoemission from surfaces?

Photoelectron spectra



Dressed sideband PE peaks from atoms

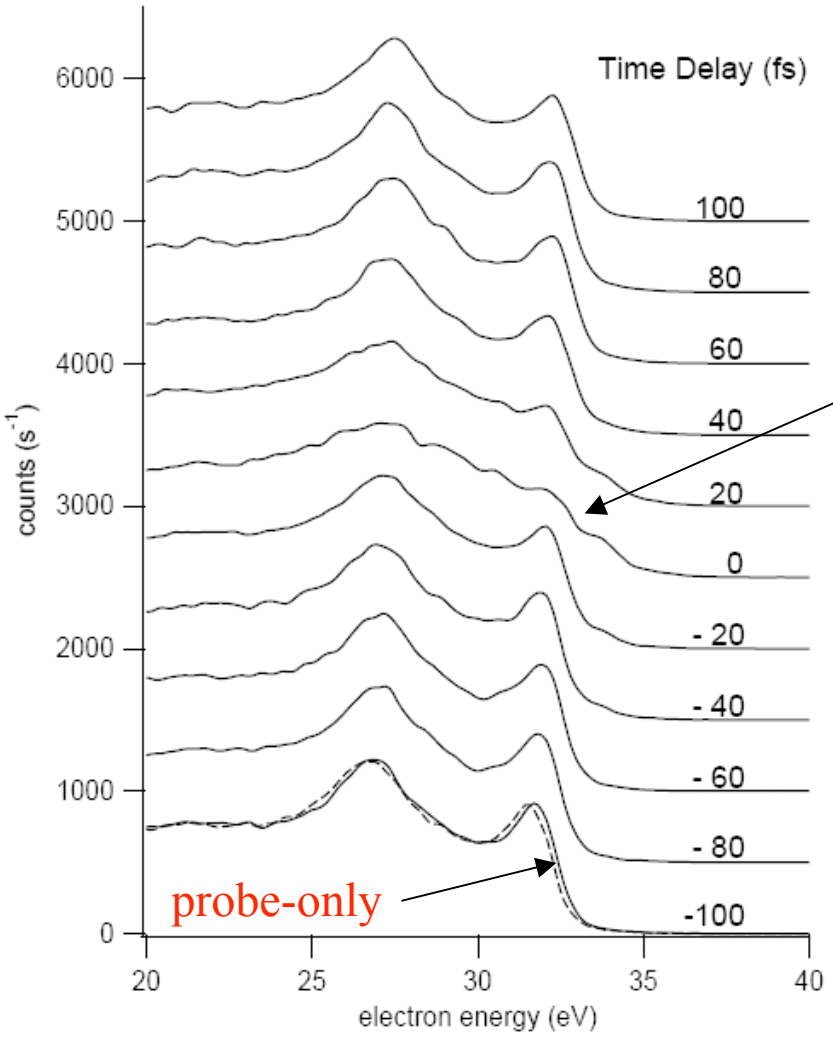


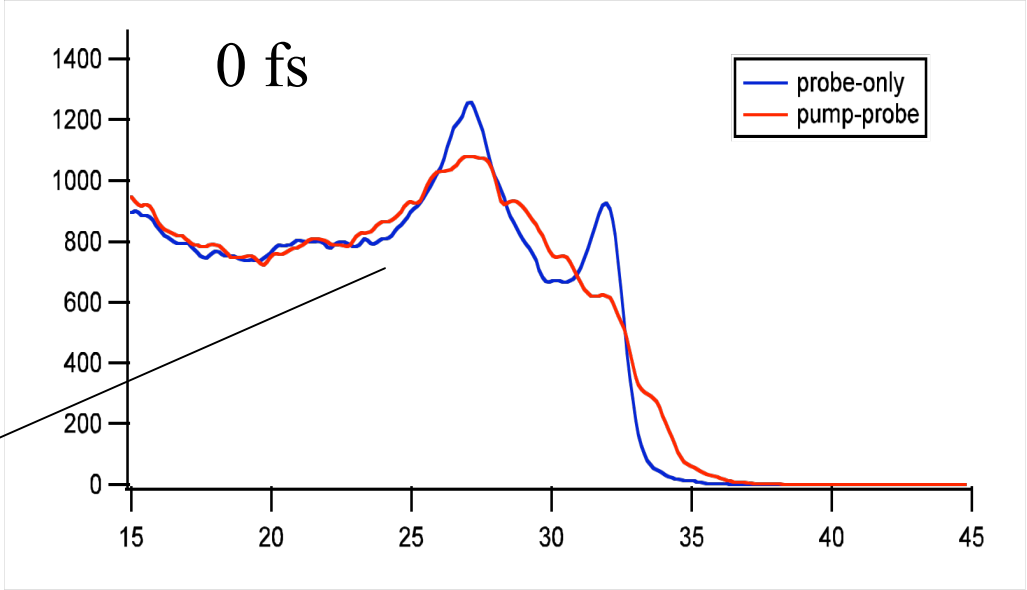
Continuous PE spectrum from solids

- **How to resolve sideband structure in laser-assisted photoemission from solids in order to observe attosecond dynamics in solids?**
- **The photoelectron spectra from clean Pt(111) exhibit a narrow d-band peak at the Fermi edge - that is ideal for the observation of sidebands**

Photoelectron spectra from Pt in presence of IR pump

p-polarized IR pump



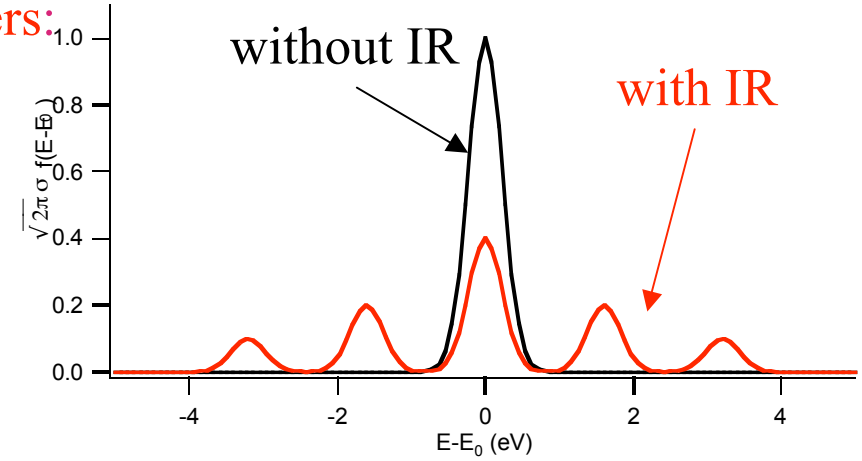


- **Photoelectron spectra dramatically modulated in the presence of an IR laser**
- **Not hot electrons!!**

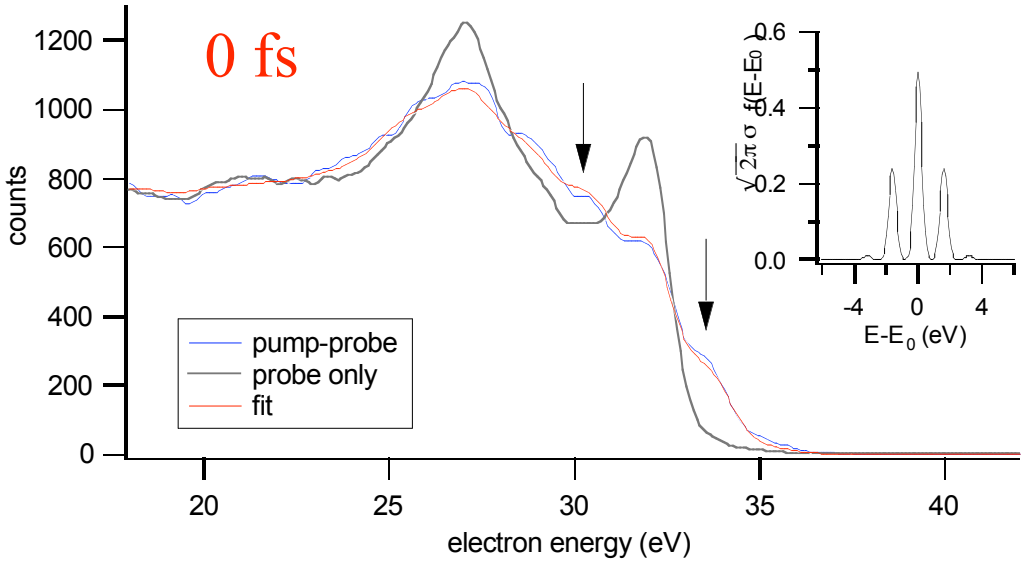
Modulation of photoemission consistent with dressing

Sideband response function with fit parameters:

$$f(E-E_0) = \frac{1-2A_1-2A_2}{\sqrt{2\pi}\sigma} e^{(E-E_0)^2/2\sigma^2} + \sum_{\pm} \frac{A_1}{\sqrt{2\pi}\sigma} e^{(E-E_0\pm\hbar\omega)^2/2\sigma^2} + \sum_{\pm} \frac{A_2}{\sqrt{2\pi}\sigma} e^{(E-E_0\pm 2\hbar\omega)^2/2\sigma^2}$$

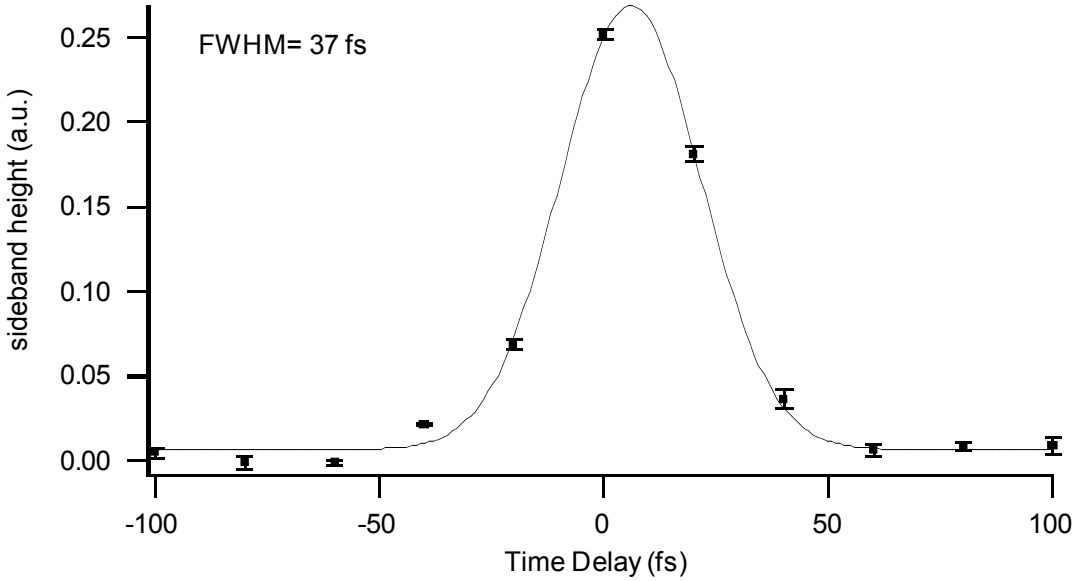


Sideband fit to d-band photoelectron peak explains data:



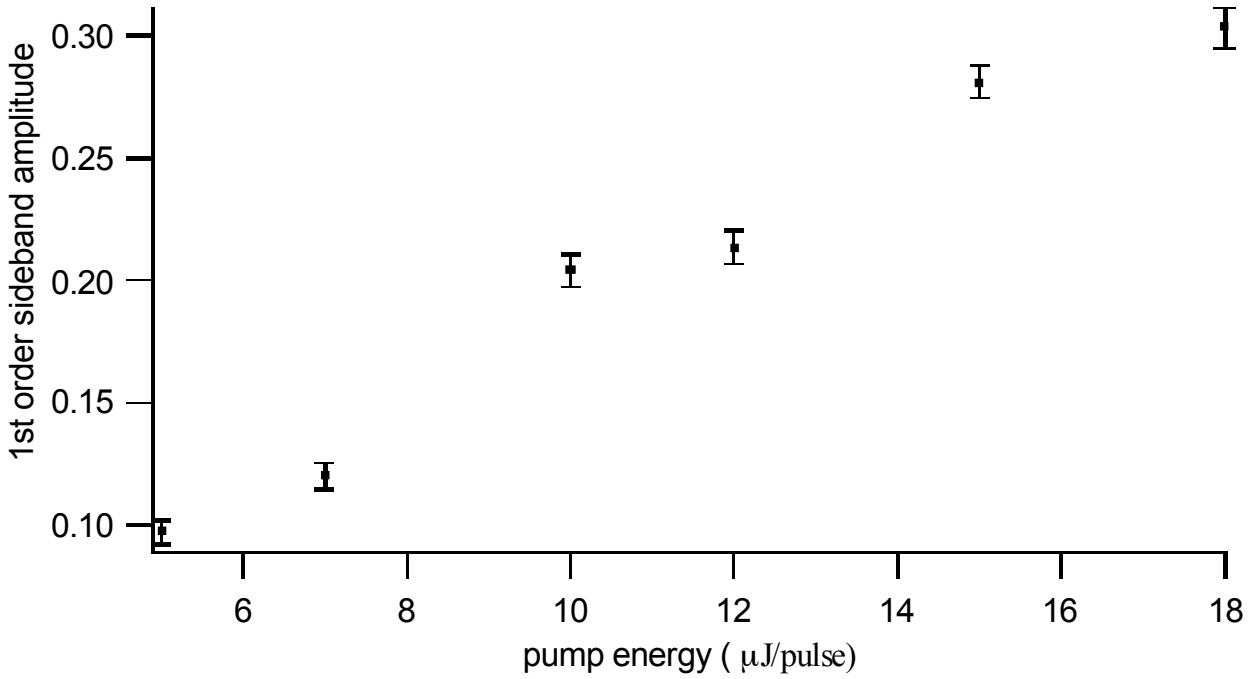
$$A_1 = 0.241 \pm 0.004$$
$$A_2 = 0.012 \pm 0.005$$
$$\sigma = 0.23 \pm 0.03 \text{ eV}$$
$$\hbar\omega = 1.59 \pm 0.02 \text{ eV}.$$

Cross-correlation of EUV and IR beams



- **Magnitude of sidebands yields FWHM of EUV pulse at 37 ± 3 fs (limited by IR pulse duration)**
- **Sub-femtosecond time resolution is feasible - opening up measurements of complex, attosecond, electron dynamics in solids and adsorbates**
- **Method useful to characterize high energy harmonics, where atomic medium would have too low a cross section**

This REALLY is laser-assisted photoemission from surfaces



- **No sidebands observed for perpendicular polarization**
- **Sideband intensity proportional to laser intensity**
- **Generation and observation of hot electrons occurs at higher laser intensity**
- **Excellent agreement of fit to experimental data**

Conclusion and Future Plans

- **Utility of harmonic generation as a new high-order Raman probe of intra-molecular dynamics is immediately apparent**
  - **High-order x-ray Raman scattering sensitive to ALL vibrational modes**
  - **SIMPLE fourier transform of data yields vibrational modes**
  - **> 1000 times more sensitive than conventional impulsive Raman spectroscopy**
  - **Sensitive to < 0.1% changes in bond**
  - **Coherent, time resolved probe of intramolecular relaxation on ground state potential surface**

- **Future work**
  - **Resonant excitation and dissociation using ultrashort VUV pulses**
  - **Non-adiabatic transitions (i.e. internal conversion and intersystem crossing)**
  - **Attosecond dynamics in molecules**

- **Thanks to DOE and NSF!**