Ultrafast Molecular Dynamics Probed by Coherent Electrons and X-Rays

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Ivan Christov, Chris Greene, Margaret Murnane and Henry Kapteyn
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
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 87 18 (18) (2001))
Can we observe intramolecular dynamics?

- Is harmonic generation sensitive to small amplitude vibrational motions in a molecule? What modes can we observe?
What happens when we hit a molecule with a short light pulse?

I. Molecule can align along the field

II. Excite Raman-active vibrations

Experiment

- IR pump pulse excites vibrations using Impulsive Stimulated Raman excitation (ISRS) with $T_{\text{pump}} < T_{\text{vib}}$
- IR probe pulse excites harmonics from vibrational wavepacket with $T_{\text{probe}} < T_{\text{vib}}$
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 $SF_6$

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

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$_6$
- $T_{\text{pump}} < T_{\text{vib}}$ -- Impulsive Raman excitation (ISRS)
- $T_{\text{probe}} < T_{\text{vib}}$ -- measure Raman scattered narrow band visible

Short, impulsive, pump pulse at $\omega$

Long, weak, probe pulse at $2\omega$
Direct comparison with visible-probed ISRS

- Conventional ISRS ONLY sees symmetric breathing mode
  - 100x stronger than other modes

- 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$_3$**

- CClF$_3$ is a non-spherically symmetric molecule with six normal modes.
- Observe larger modulation of the HHG signal due to vibrations than SF$_6$.
Observe dynamics in non-spherically symmetric molecule - $\text{CCIF}_3$

- $\text{CCIF}_3$ is a non-spherically symmetric molecule with six normal modes
- Observe larger modulation of the HHG signal due to vibrations than $\text{SF}_6$
Vibrational modes in CClF$_3$

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<tr>
<td>350</td>
<td>e fundamental</td>
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<tr>
<td>468</td>
<td>a$_1$ fundamental</td>
<td>71</td>
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<tr>
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<tr>
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<td>a$_1$ fundamental</td>
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</tr>
<tr>
<td>1217</td>
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- 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
Vibrational modes in $\text{CCIF}_3$

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- Observe two strongest Raman-active modes
- Likely due to signal-to-noise and pump pulse limitations
Vibrational modes in $\text{CClF}_3$

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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

$$\lambda_e = \frac{h}{p} = \frac{h}{\sqrt{2m_eE}} = .15\text{nm} @ \ H45 \ (70\text{eV})$$
Quantum picture - electron being ripped from atom

Electron wavefunction

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

Z. B. Walters
S. Tonzani
C. H. Greene

\[ a_1 e^{-i\omega T} \]

\[ a_1 \propto \frac{\partial \alpha}{\partial Q} \]
Probing vibrational Raman-excited quantum beats

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\[ a_1 \propto \frac{\partial a}{\partial Q} \]

\[ I_1 \propto \frac{\partial}{\partial Q} e^{-\text{Im} \int k(\vec{r}) \cdot d\vec{r}} \]
Probing vibrational Raman-excited quantum beats

Raman pulse \( \rightarrow \) time \( T \) \( \rightarrow \) Ionizing pulse

Electron propagation \( \approx \) fs

Recomb. upon recollision

\[
\begin{align*}
I_o & \quad e^{+\text{ion}} \\
I_0 & \quad v=0 \\
I_1 & \quad v=1
\end{align*}
\]

\[
\begin{align*}
d_0 & \quad v=0 \\
d_0 & \quad v=0 \\
d_1 & \quad v=1 \\
A_1(T) & \quad v=1 \\
A_0(T) & \quad v=0
\end{align*}
\]

Electron propagation \( \approx \) fs

\[
a_1 \propto \frac{\partial \alpha}{\partial Q}
\]

\[
I_1 \propto \frac{\partial}{\partial Q} e^{-\text{Im} \int \overrightarrow{k(r)} \cdot d\overrightarrow{r}}
\]

\[
d_1 \propto \frac{\partial}{\partial Q} \langle \phi_{\text{bnd}}(z) | \phi_{\text{cont.}}^{(Q)} \rangle
\]

Rate(HHG) \( \propto |A_0(T)|^2 + |A_1(T)|^2 \)
Modulation of High Harmonic Signal vs Wavenumber

including ionization and electric field driving

Peak to Peak Modulation Amplitude

Wavenumbers (1/cm)

V5

V1

V2

Theory (WKB ionization)
Experiment
New spectroscopic high-order x-ray Raman probe?
Vibrations most visible in higher harmonics

- 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\text{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))
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- 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

- Photoelectron spectra dramatically modulated in the presence of an IR laser
- Not hot electrons!!
Sideband response function with fit parameters:

\[
\begin{align*}
    f(E - E_0) &= \frac{1 - 2A_1 - 2A_2}{\sqrt{2\pi}\sigma} e^{(E - E_0)^2 / 2\sigma^2} \\
    &+ \sum_{\pm} \frac{A_1}{\sqrt{2\pi}\sigma} e^{(E - E_0 \pm \hbar\omega)^2 / 2\sigma^2} \\
    &+ \sum_{\pm} \frac{A_2}{\sqrt{2\pi}\sigma} e^{(E - E_0 \pm 2\hbar\omega)^2 / 2\sigma^2}
\end{align*}
\]

Sideband fit to d-band photoelectron peak explains data:

\[0 \text{ fs}\]

\[
\begin{align*}
    A_1 &= 0.241 \pm 0.004 \\
    A_2 &= 0.012 \pm 0.005 \\
    \sigma &= 0.23 \pm 0.03 \text{ eV} \\
    \hbar\omega &= 1.59 \pm 0.02 \text{ eV}
\end{align*}
\]
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!