# Ultrafast X-ray and Molecular Diffraction

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**PHB**

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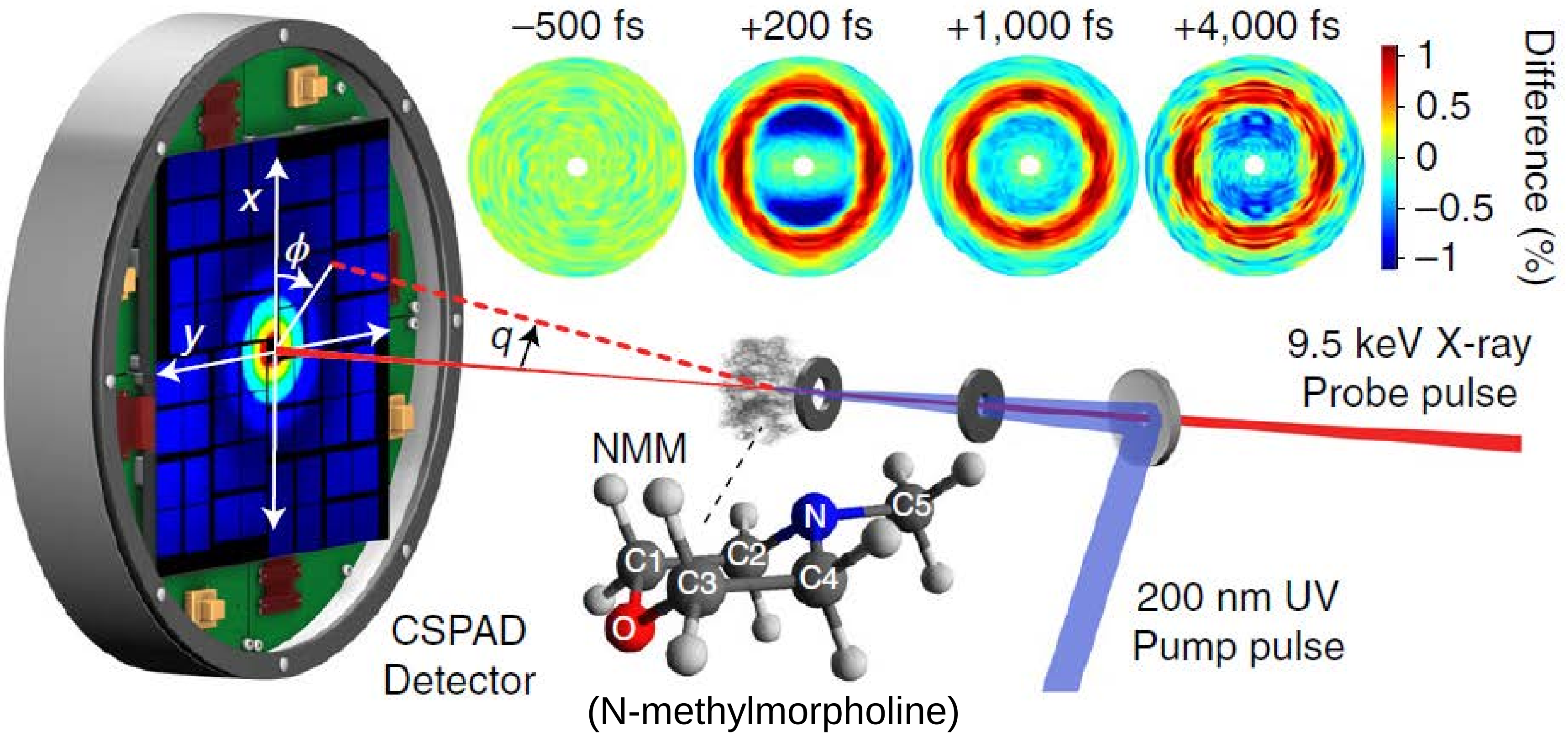
# Several groups are now making femtosecond movies of intramolecular dynamics:



(N-methylmorpholine)

B. Stankus, H. Yong, N. Zotev, J. M. Ruddock, D. Bellshaw, T. J. Lane, M. Liang, S. Boutet, S. Carbajo, J. S. Robinson, W. Du, N. Goff, Y. Chang, J. E. Koglin, M. P. Minitti, A. Kirrander, and P. M. Weber, Nat. Chem. 11, 716 (2019).

# Hard X-ray Elastic Scattering

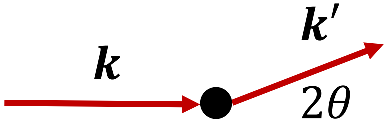
Interaction Hamiltonian:
Elastic Nonresonant scattering

$$H_I = \frac{e}{m}\mathbf{p}\cdot\mathbf{A} + \frac{e}{m}\mathbf{S}\cdot\mathbf{B} + \boxed{\frac{e^2}{2m}\mathbf{A}^2}$$

Scattering theory: Lowest order
Single scattering (Born) approximation

$$Field\ Amplitude = e^{ikz} + f(\theta)\frac{e^{ikr}}{r}$$

$$|\boldsymbol{Q}| = |\boldsymbol{k} - \boldsymbol{k}'| = 2k sin\theta$$



Scattering
matrix element:

$$f\left(\vec{Q}\right) = \epsilon\cdot\epsilon'\sum_n \left\langle\varphi_n\middle|e^{i\vec{Q}\cdot\vec{r}_n}\middle|\varphi_n\right\rangle$$

Scattered intensity:
(matrix element)$^2$

$$\left|f(\vec{Q})\right|^2 = \sigma_{Th}(\Omega)\left|\sum_n \left\langle\varphi_n\middle|e^{i\vec{Q}\cdot\vec{r}_n}\middle|\varphi_n\right\rangle\right|^2$$

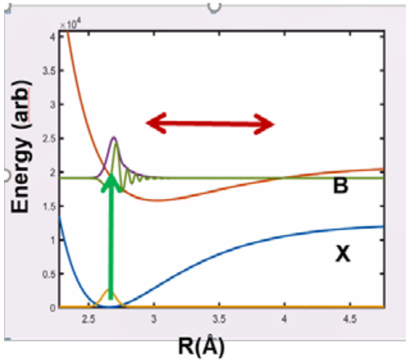
$$= \sigma_{Th}(\Omega)\sum_{i,j}\left\langle\psi_m(\vec{r}_i \ldots \vec{r}_j)\middle|e^{i\vec{Q}\cdot(\vec{r}_i-\vec{r}_j)}\middle|\psi_m(\vec{r}_i \ldots \vec{r}_j)\right\rangle$$

**Scattering measures the relative position of pairs of electrons.**

# Approximations to simplify this further

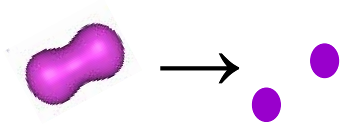
**Born-Oppenheimer approximation…**

**Nuclei move on potential energy surfaces** $\chi_n\left(\vec{R},\tau\right)$



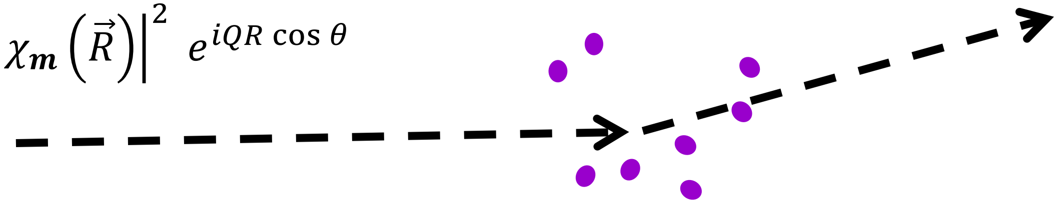
**Independent atom approximation…**

**X-rays scatter from these atomic locations** $\chi_n\left(\vec{R},\tau\right)$



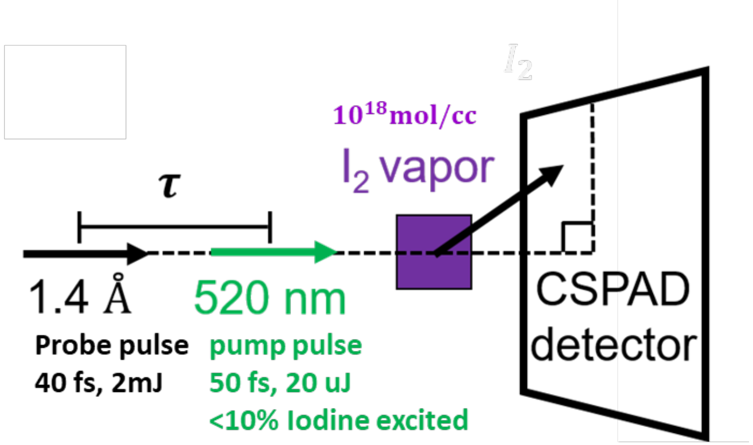
**Homonuclear diatomic molecule in an eigenstate…**

$$\left\langle \psi_m \middle| \hat{S}\left(\vec{Q}\right) \middle| \psi_m \right\rangle = 2|f_I(Q)|^2 \int d\vec{R}\, \left|\chi_{\boldsymbol{m}}\left(\vec{R}\right)\right|^2 e^{iQR\cos\theta}$$



$\boldsymbol{\rho_m(r)}$ **is the cosine transform of** $\left\langle \hat{\boldsymbol{S}}\left(\vec{\boldsymbol{Q}}\right)\right\rangle$**.**

# Here's the real thing:



$10^{18}$mol/cc

$I_2$ vapor

$\tau$

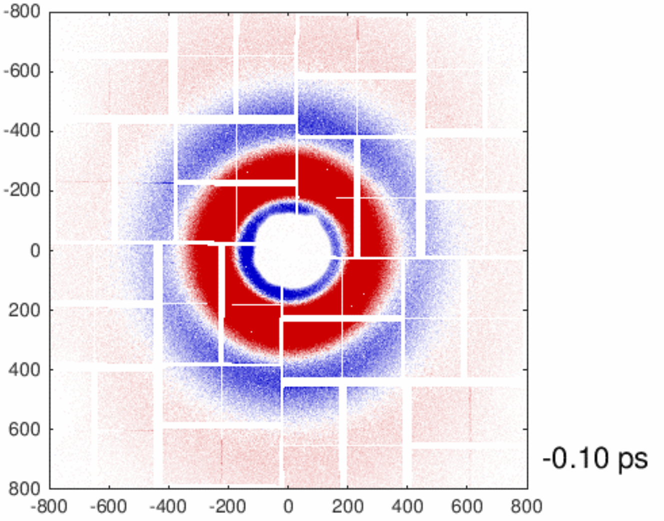
1.4 Å

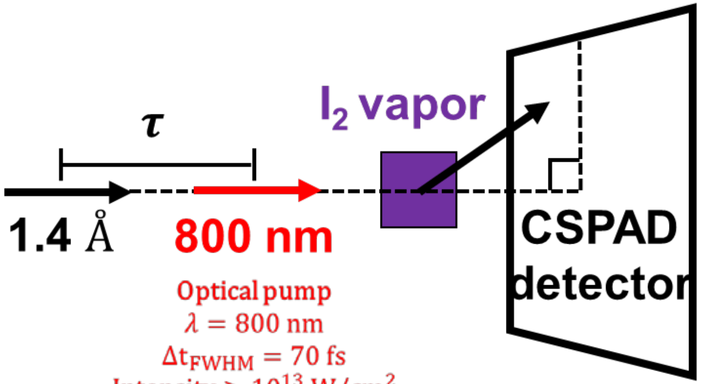
520 nm

**Probe pulse**
**40 fs, 2mJ**

**pump pulse**
**50 fs, 20 uJ**
**<10% Iodine excited**

CSPAD detector





**$I_2$ vapor**

$\tau$

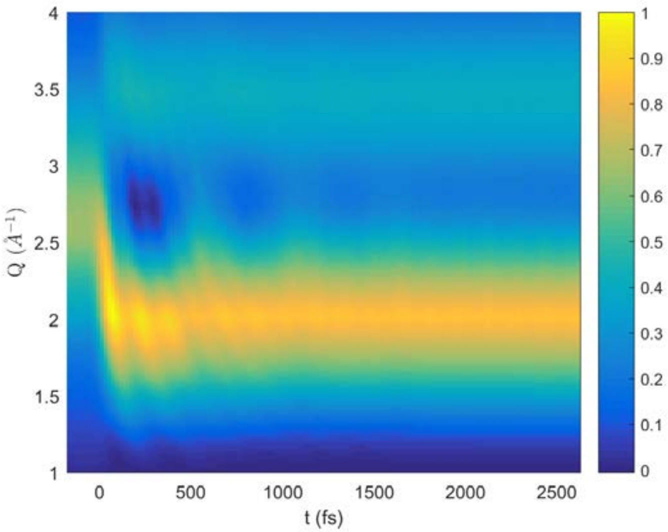
**1.4 Å**

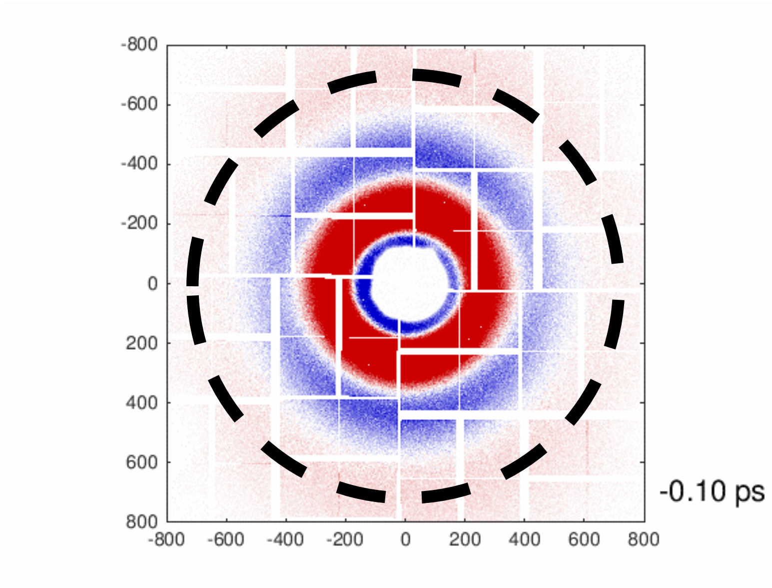
**800 nm**

**CSPAD detector**

Optical pump
$\lambda = 800$ nm
$\Delta t_{FWHM} = 70$ fs
Intensity $> 10^{13}$ W/cm$^2$
Vertical polarization

# Making movies: Angle-integrated signal





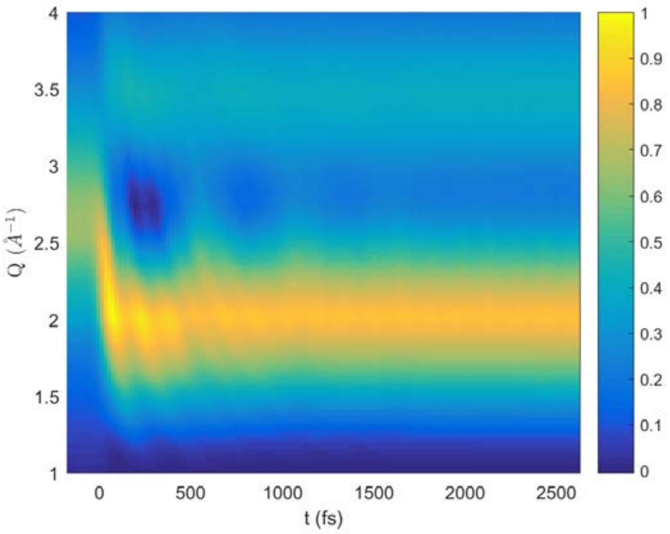
**(t<0) signal partly subtracted to keep signal non-negative everywhere**

$$\boldsymbol{Q(R) = \oint Q(R,\phi)\, d\phi}$$

Mike Glownia, Adi Natan, James Cryan, et al., Phys. Rev. Lett. 117, 153003 (2016); Reply to SM Comment, 119, 069302 (2017).

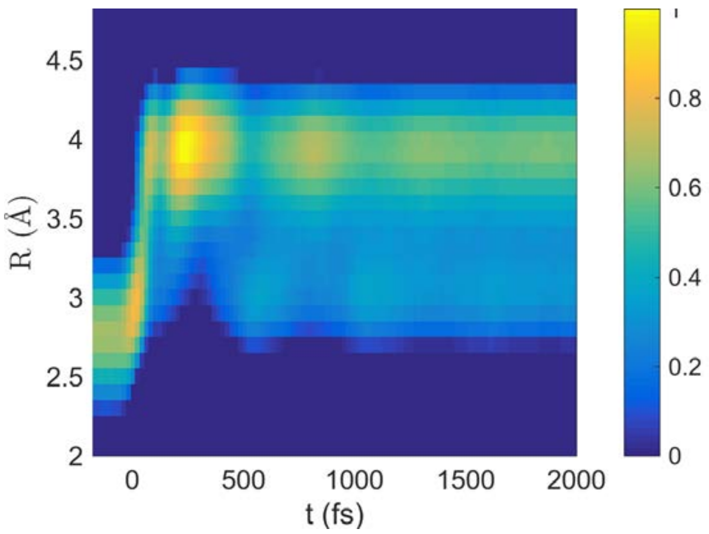
Natan, Ware

# Making movies:
# Angle-integrated signal



**(t<0) signal partly subtracted to keep signal non-negative everywhere**

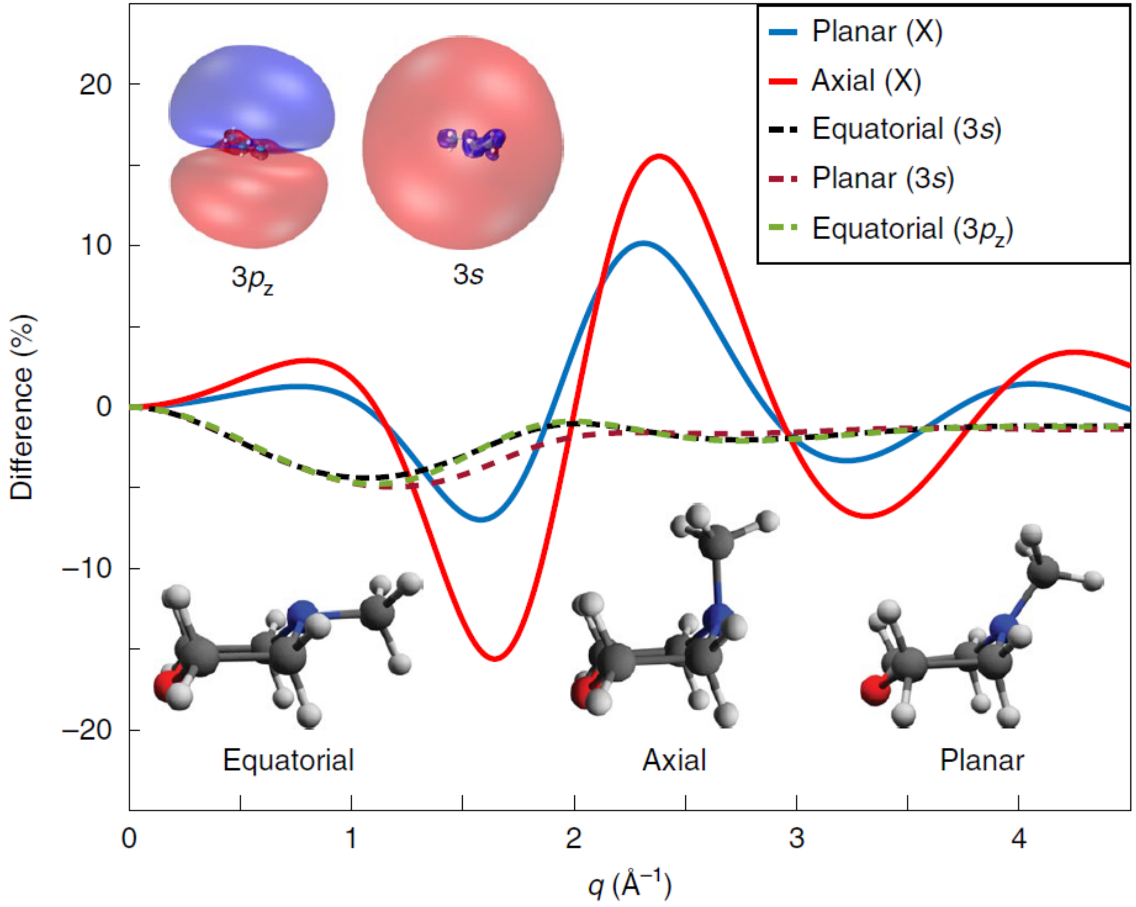
Mike Glownia, Adi Natan, James Cryan, et al., Phys. Rev. Lett. 117, 153003 (2016); Reply to SM Comment, 119, 069302 (2017).



**R-space movie.**
**The signal at t<0 is the fraction of the X state that was excited at t=0.**

Natan, Ware

# Polyatomic molecules are more challenging: First, there are lots of conformers:



**Calculated difference scattering for this molecule (N-methylmorpholine)**

**Blue solid line: Planar vs Equitorial in the ground state.**

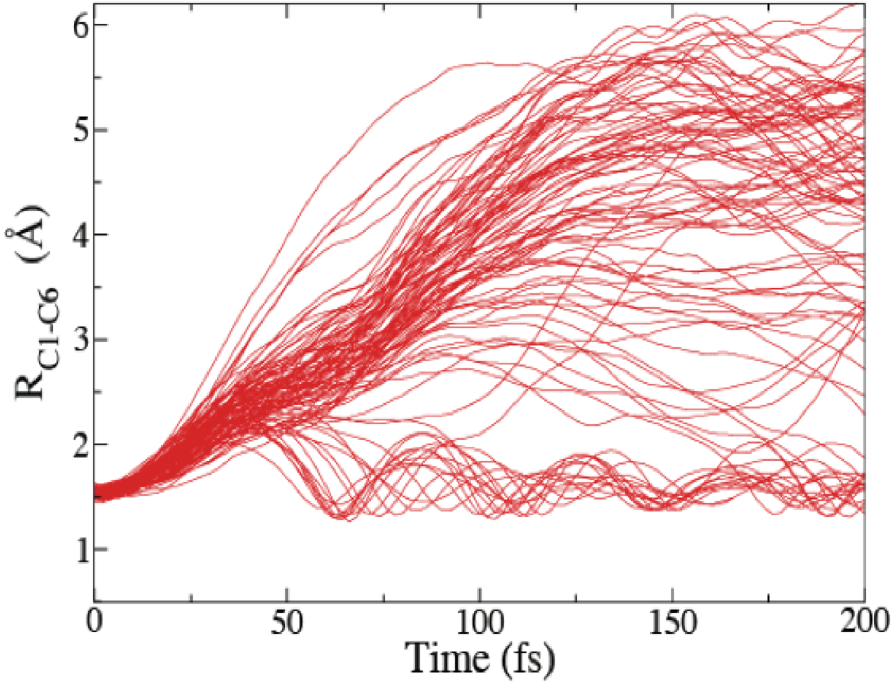
**Red solid line: axial vs. equatorial in the ground state,**

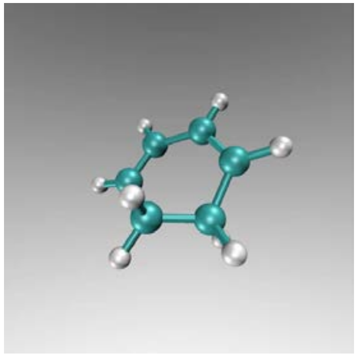
**Dotted lines: Excitation of 3s and 3p orbitals**

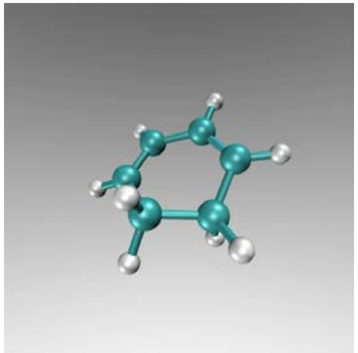
B. Stankus, H. Yong, N. Zotev, J. M. Ruddock, D. Bellshaw, T. J. Lane, M. Liang, S. Boutet, S. Carbajo, J. S. Robinson, W. Du, N. Goff, Y. Chang, J. E. Koglin, M. P. Minitti, A. Kirrander, and P. M. Weber, Nat. Chem. 11, 716 (2019).

# Also lots of trajectories.

Cyclohexadiene

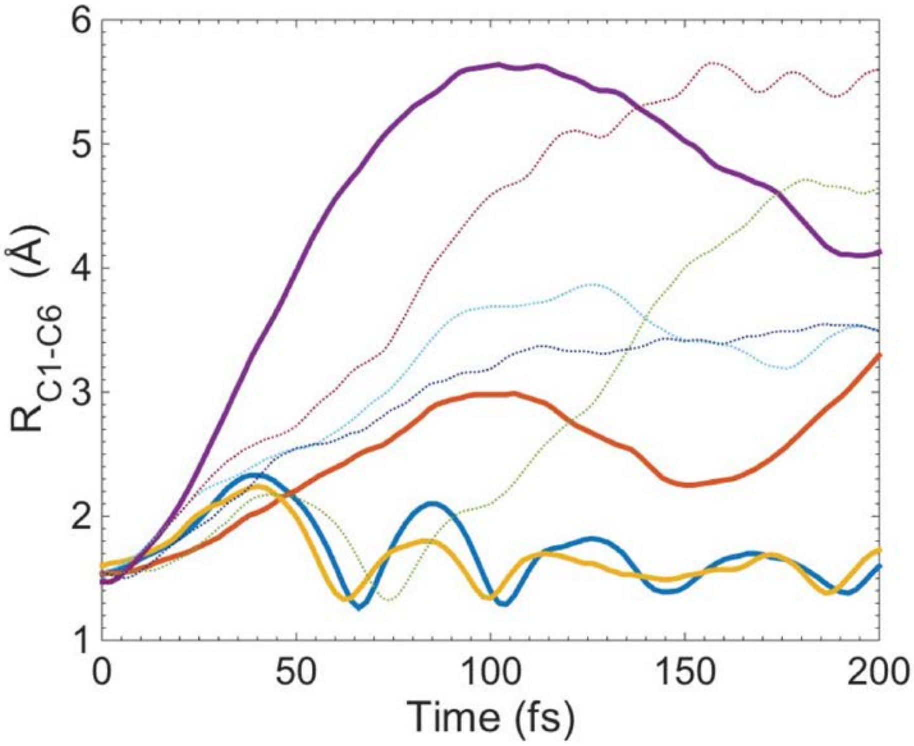




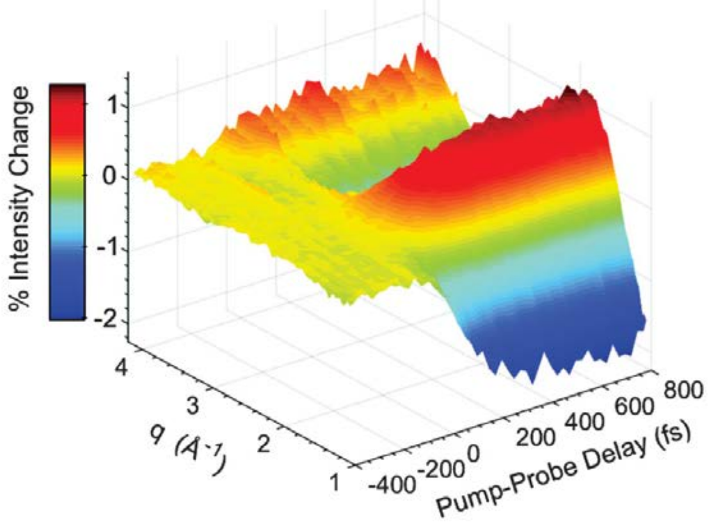


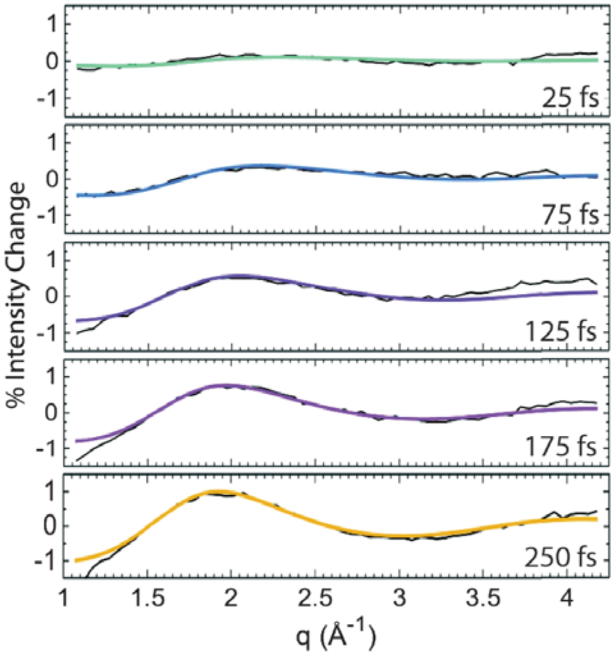
M. P. Minitti, J. M. Budarz, A. Kirrander, J. S. Robinson, D. Ratner, T. J. Lane, D. Zhu, J. M. Glownia, M. Kozina, H. T. Lemke, M. Sikorski, Y. Feng, S. Nelson, K. Saita, B. Stankus, T. Northey, J. B. Hastings, and P. M. Weber, Phys. Rev. Lett. **114**, 255501 (2015).

# A current approach: Find trajectories that fit the data best:



Minitti, M. P. *et al. Phys. Rev. Lett.* 114, 255501 (2015).

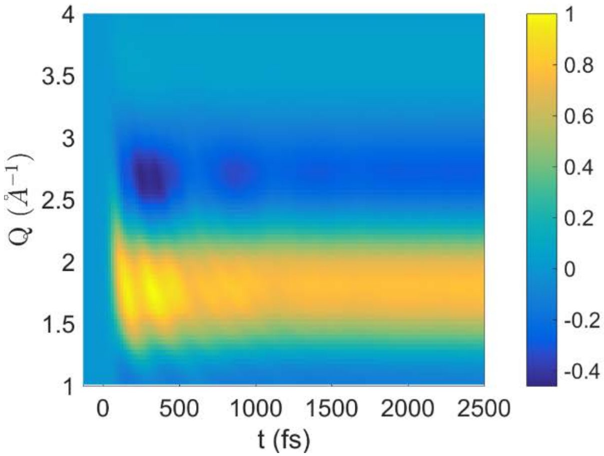




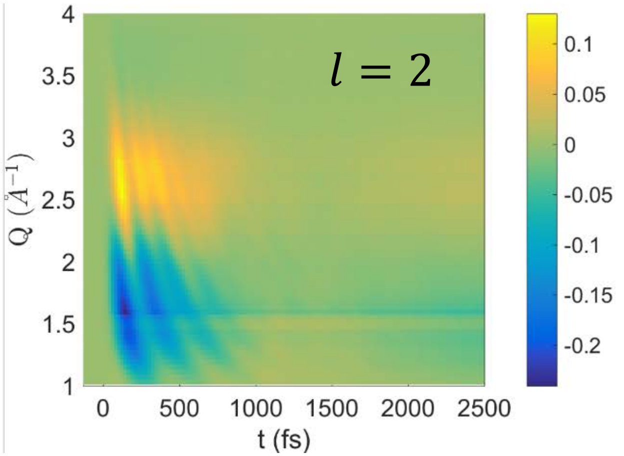
# Another approach: Align the molecule to the lab frame, for example using dipole selection rules:

$$S_N(Q,\theta,\tau) = \sum_{l=0,2,\ldots} \sqrt{\frac{2\pi}{2l+1}} P_l(\cos\theta) S_{N,l}(Q,\tau).$$

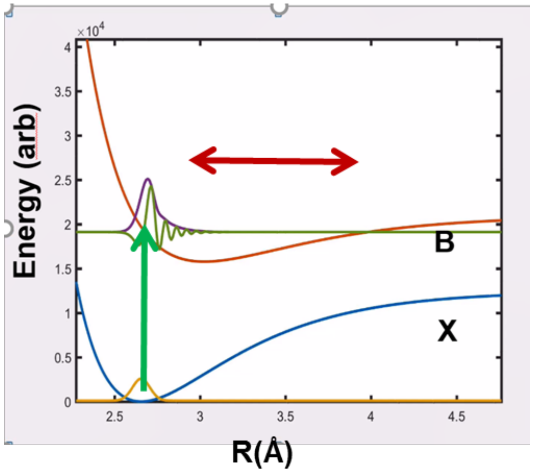
$S_0(Q,t)$



$S_2(Q,t)$

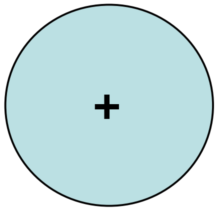


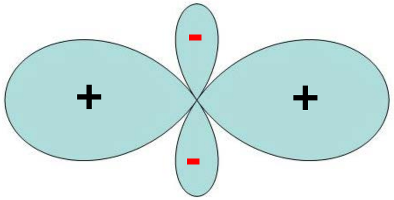
Linear polarization



$S_X(Q,t) \sim isotropic \sim S_0$

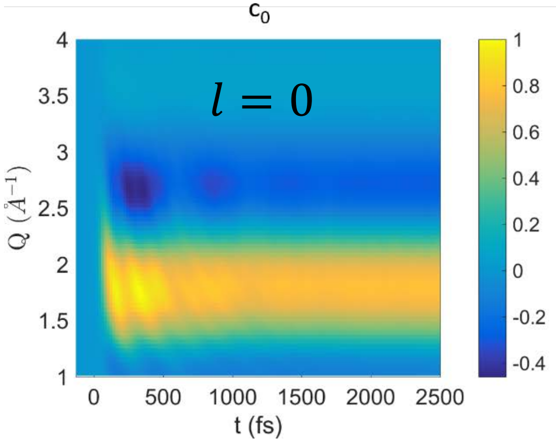
$S_B \sim \cos^2\theta \sim S_0 + 2S_2$

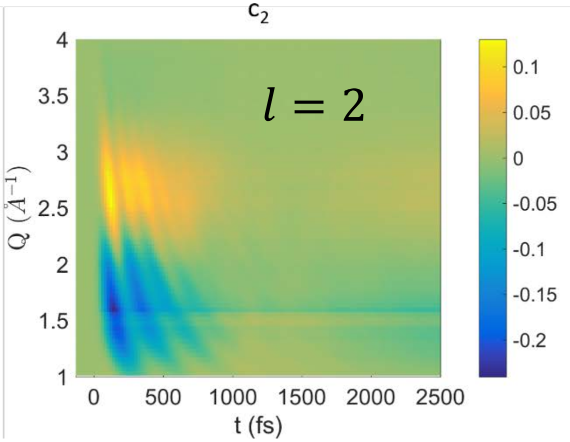


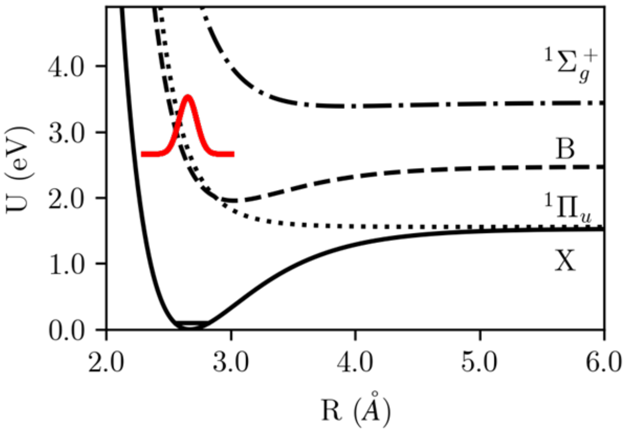


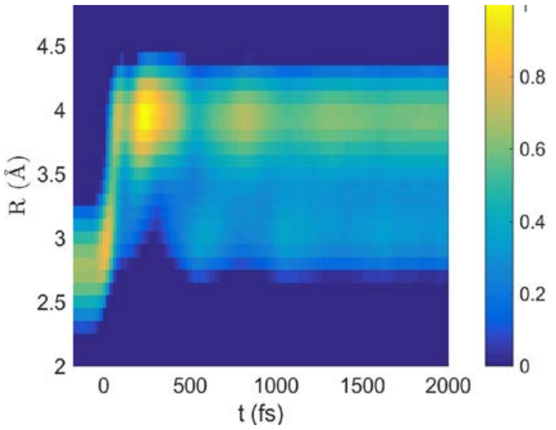
Mike Glownia, Adi Natan, James Cryan, et al., Phys. Rev. Lett. 117, 153003 (2016); Reply to SM Comment, 119, 069302 (2017).

# Reconstructions emphasize different aspects of the wave packet

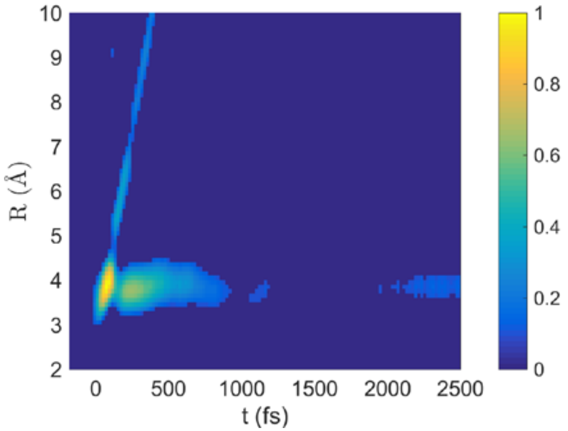








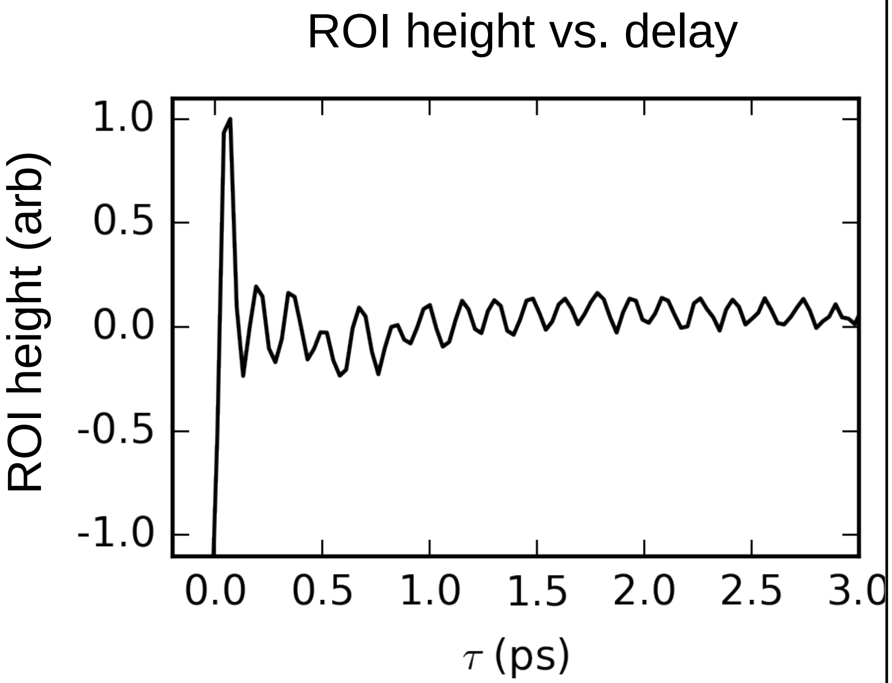
**X-state subtracted**



**B'' dissociation**

Mike Glownia, Adi Natan, James Cryan, et al., Phys. Rev. Lett. 117, 153003 (2016); Reply to SM Comment, 119, 069302 (2017).

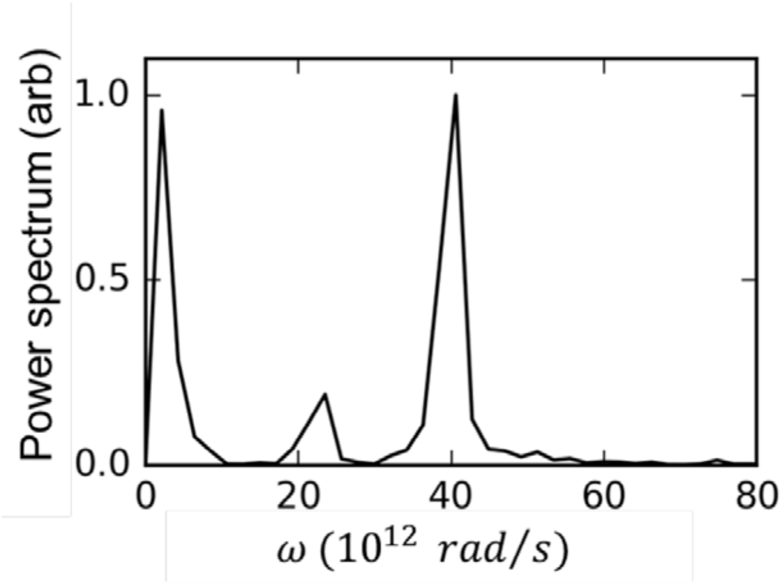
# A third approach: Each angle has its own special time-dependence:

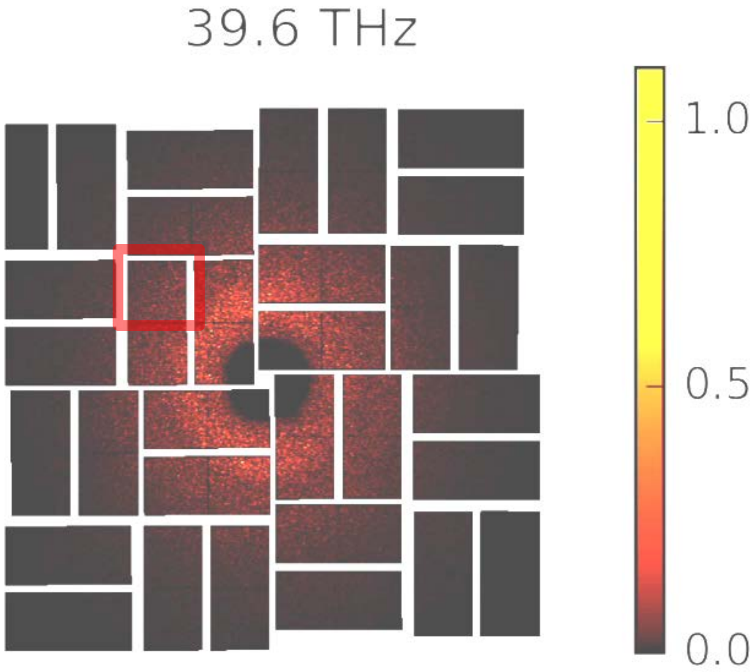

ROI height vs. delay

M. R. Ware, J. M. Glownia, A. Natan, J. P. Cryan, and P. H. Bucksbaum, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 377, 20170477 (2019).

**Matt Ware**

# Frequency-resolved x-ray scattering (FRXS) from molecular iodine



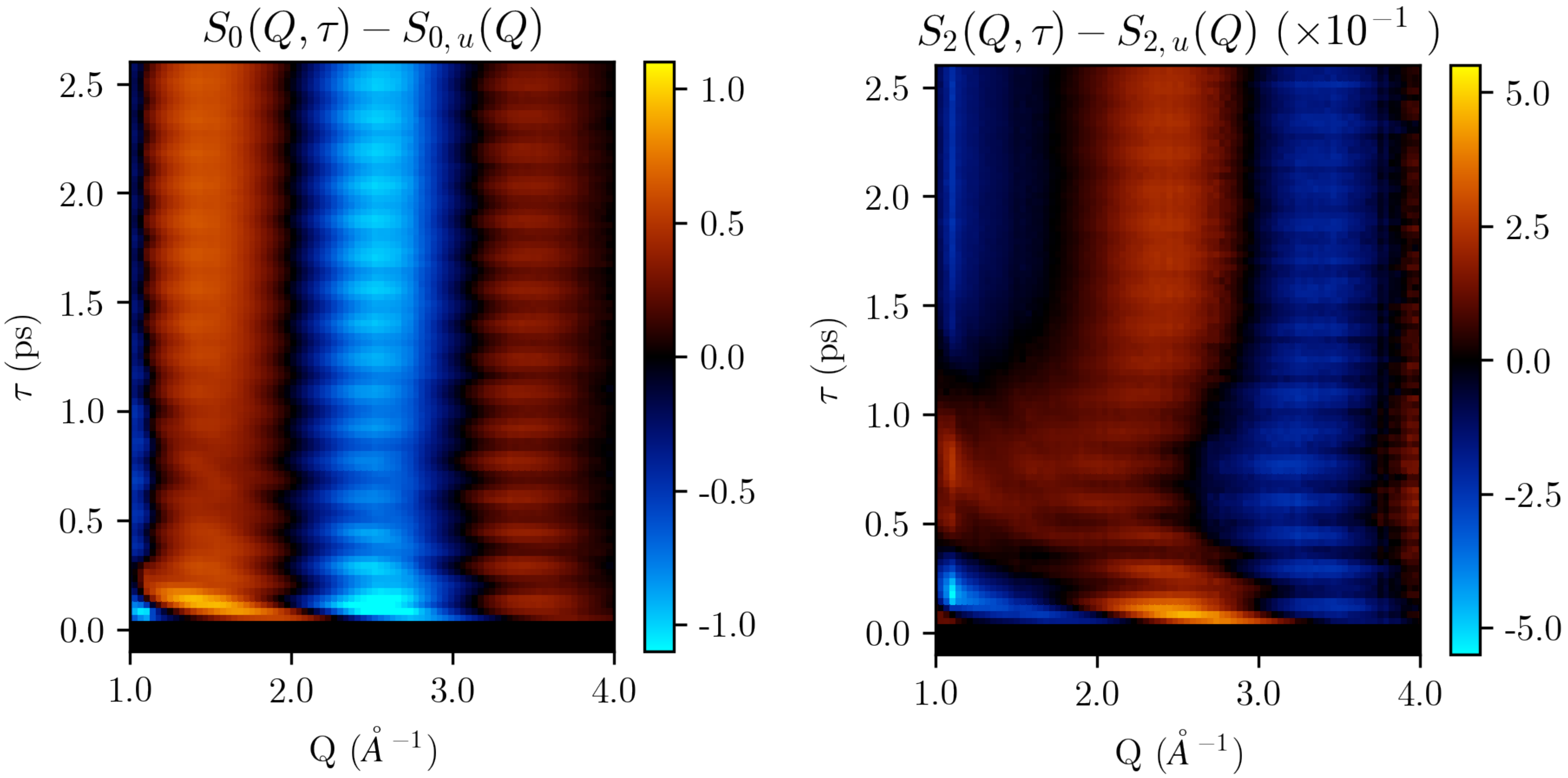


$$\left|\tilde{S}(x,y,\omega)\right|^2 = \left|\int_{-\infty}^{+\infty} d\tau\, e^{-i\omega\tau}\, S(x,y,\tau)\right|^2$$

$$\Delta\omega = \frac{2\pi}{\tau_{Range}} \qquad \omega_{max} = \frac{2\pi}{\Delta\tau}$$

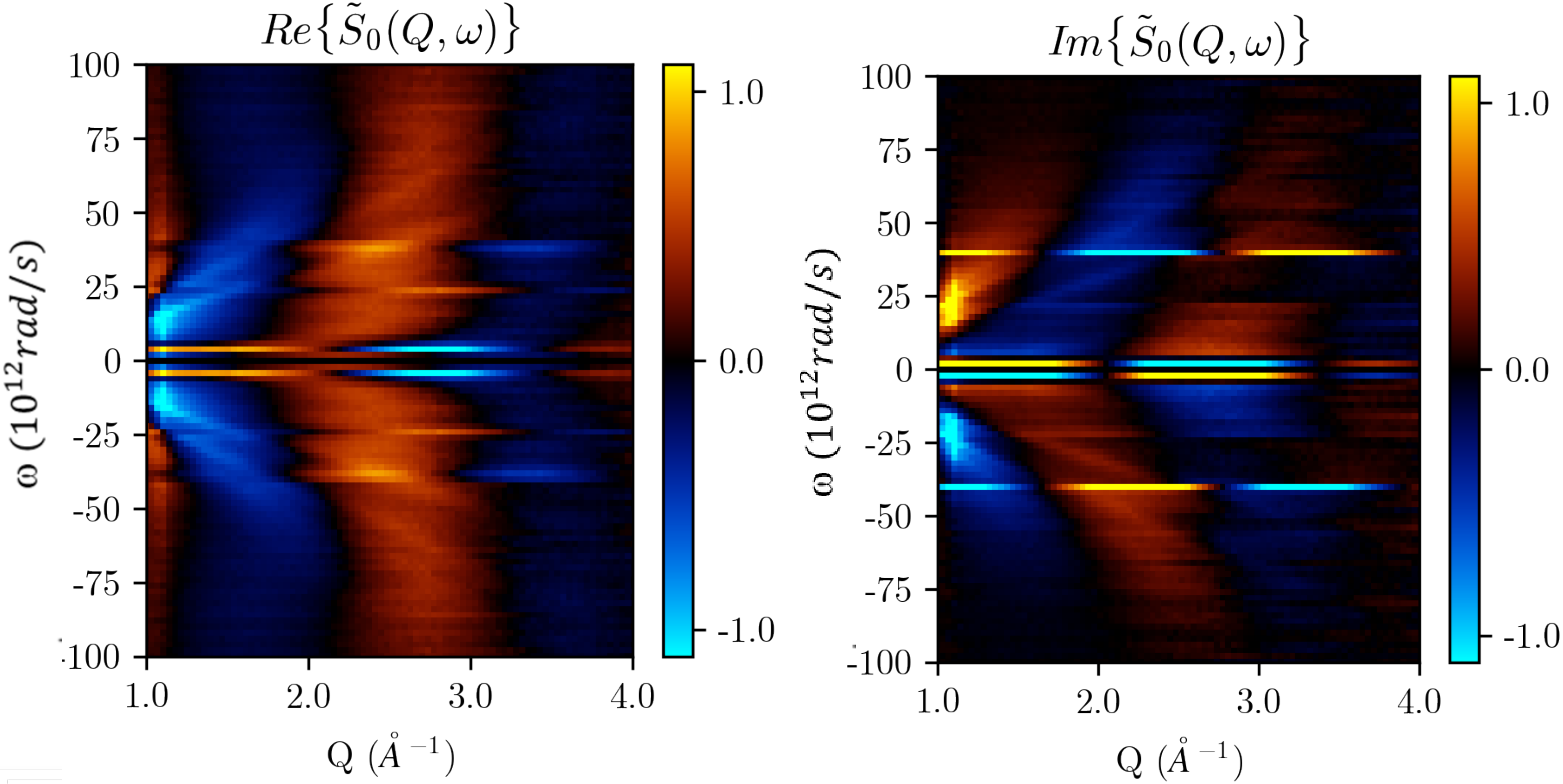
M. R. Ware, J. M. Glownia, A. Natan, J. P. Cryan, and P. H. Bucksbaum, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 377, 20170477 (2019).

# Apply this to Legendre decompositions.



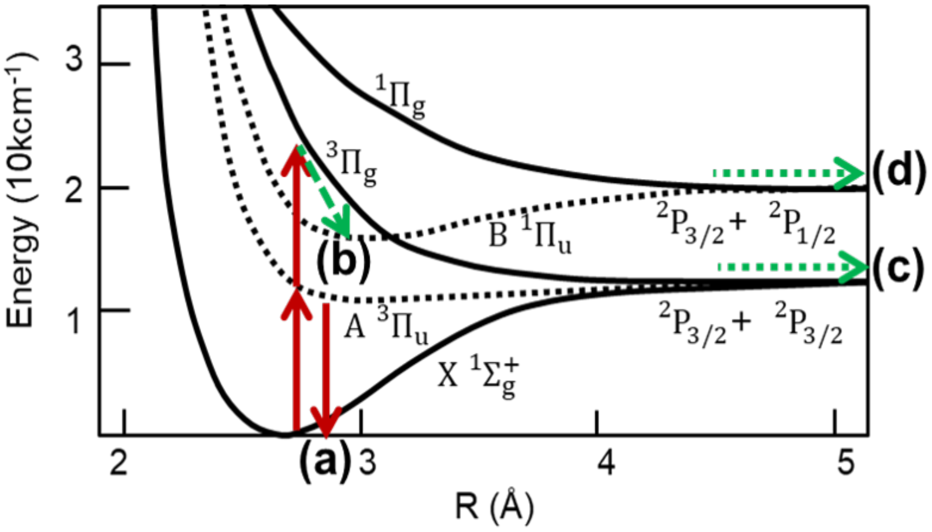
$$S_n(Q,\tau) = \int dR\, R^2\, j_n(QR)\, \rho_n(R,\tau)$$

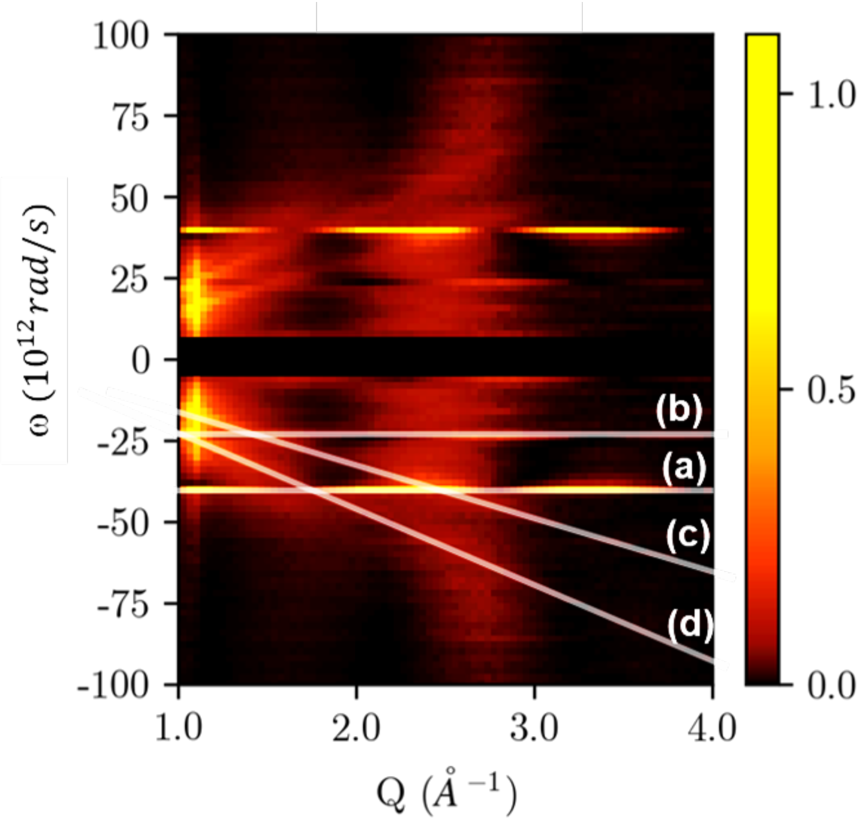
# Frequency-resolved x-ray scattering spectral amplitudes



P. H. Bucksbaum, M. R. Ware, A. Natan, J. P. Cryan, and J. M. Glownia, ArXiv:1911.01323 [Physics] (2019).

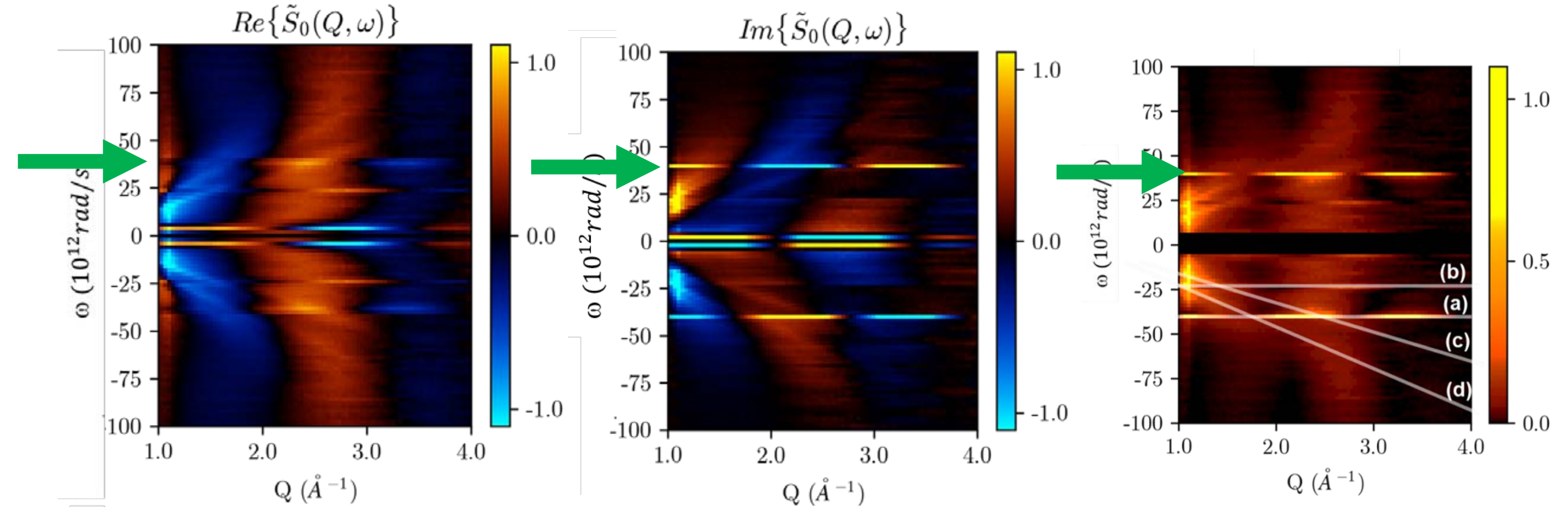
# Power spectrum isolates different modes

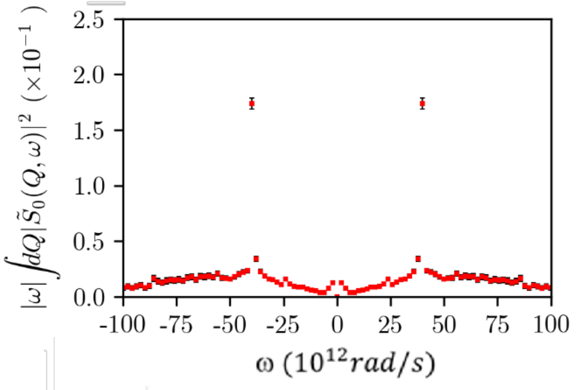


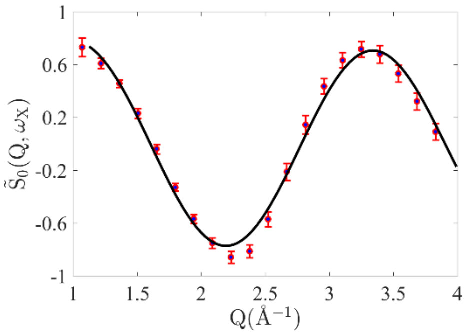


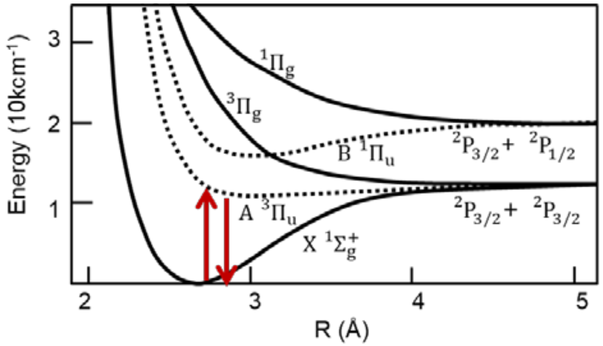
P. H. Bucksbaum, M. R. Ware, A. Natan, J. P. Cryan, and J. M. Glownia, ArXiv:1911.01323 [Physics] (2019).

# Impulsive Stimulated Raman Scattering





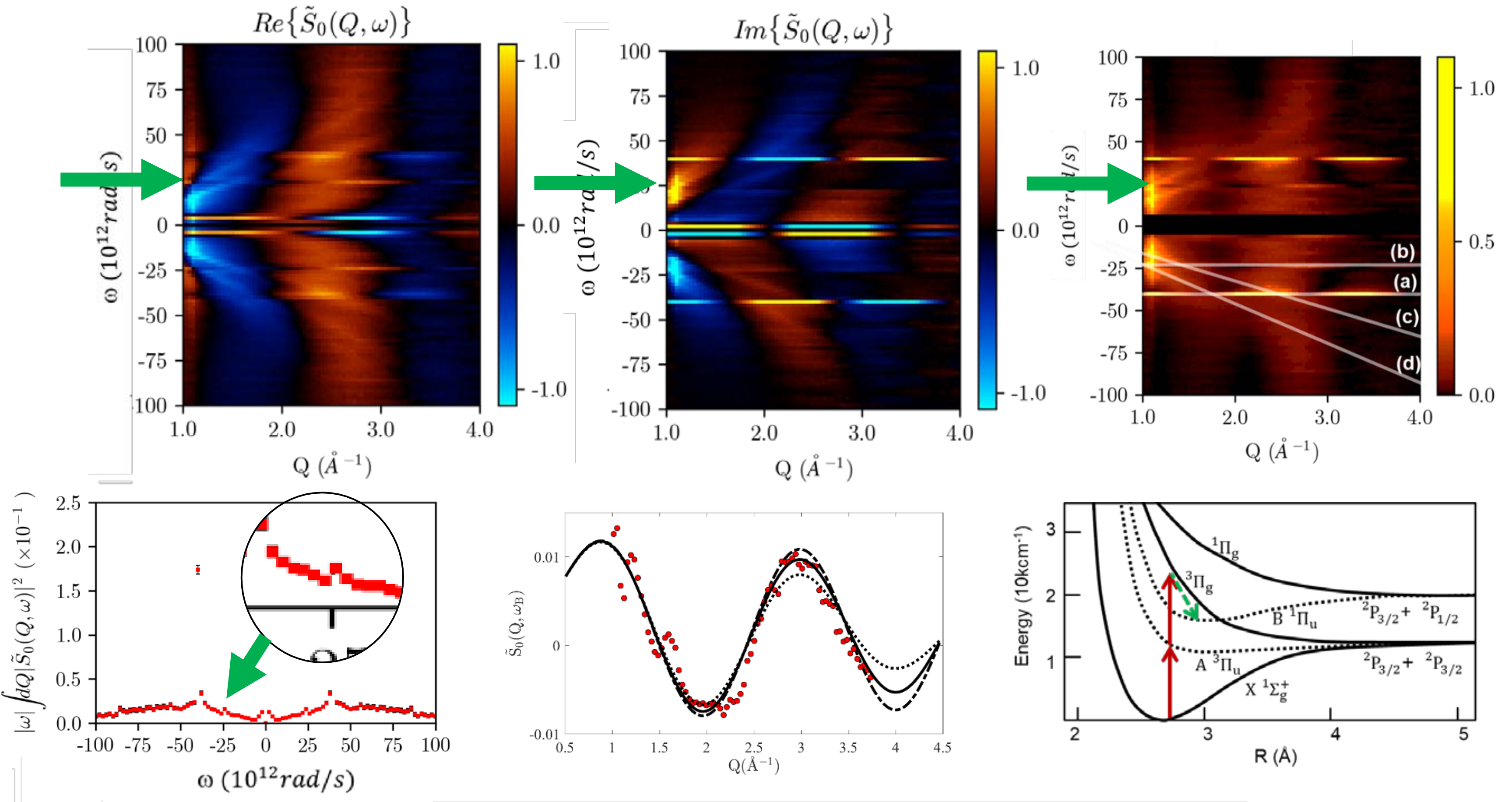




|  |  |
|---|---|
| Center of oscillation | $2.79 \pm 0.07$ Å |
| Oscillation frequency $\omega$ | $40.3 \pm 1.0 \times 10^{12}$rad/s |
| Oscillation amplitude | $0.164 \pm 0.009$ Å |
| Oscillation phase $\delta$ | $290^o$ |

P. H. Bucksbaum, M. R. Ware, A. Natan, J. P. Cryan, and J. M. Glownia, ArXiv:1911.01323 [Physics] (2019).

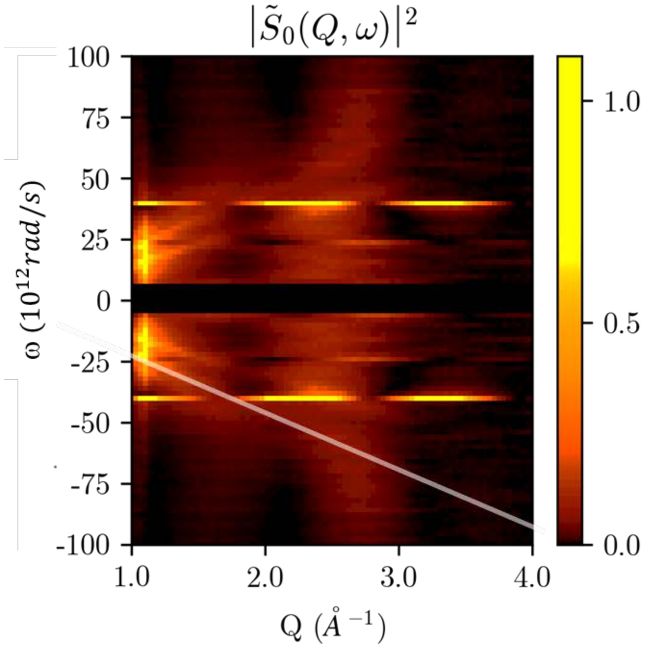
# Spontaneous Hyper-Raman Scattering



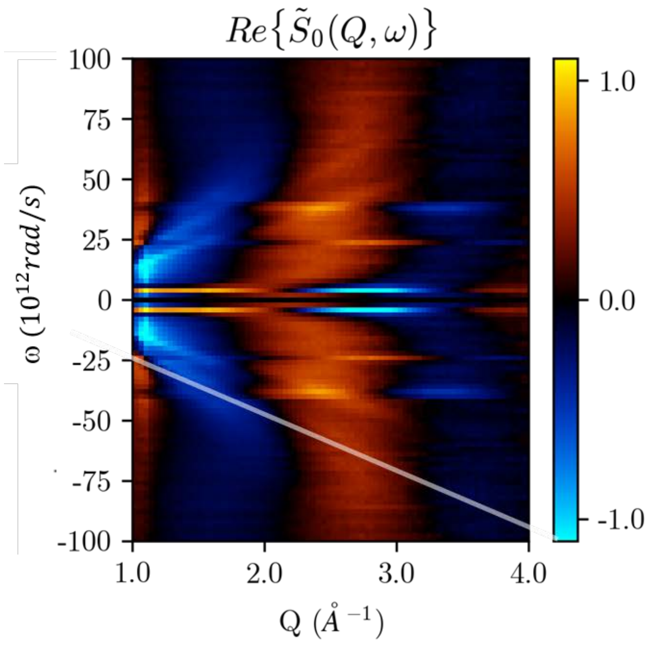
|  |  |
|---|---|
| Center of oscillation | $3.10 \pm 0.15$ Å |
| Oscillation frequency $\omega$ | $24 \pm 2 \times 10^{12}$rad/s |
| Oscillation amplitude | $0.4 \pm 0.4$ Å |
| Oscillation phase $\delta$ | $0^o$ |

P. H. Bucksbaum, M. R. Ware, A. Natan, J. P. Cryan, and J. M. Glownia, ArXiv:1911.01323 [Physics] (2019).

# Two photon dissociation

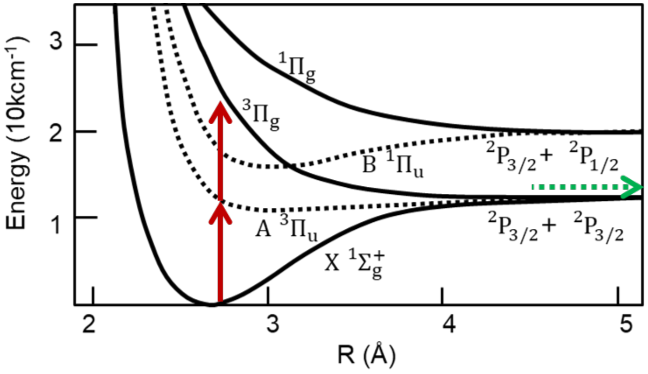


$v = \omega/Q =$
dissociation speed



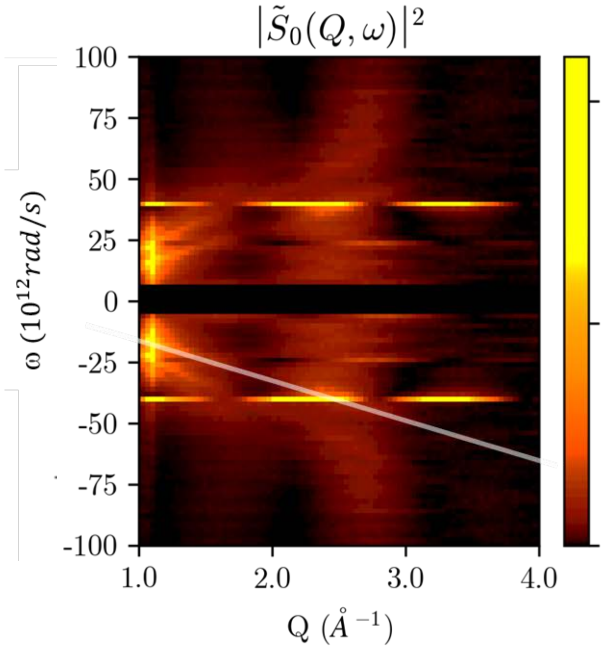
$\tau_i = \theta/(Qv)$ =
dissociation time shift

| | |
|---|---|
| Separation velocity $v_{(d)}$ | $23 \pm 1$ Å/ps |
| Dissociation Time Shift $\tau_{i(d)}$ | $+124 \pm 20$fs |



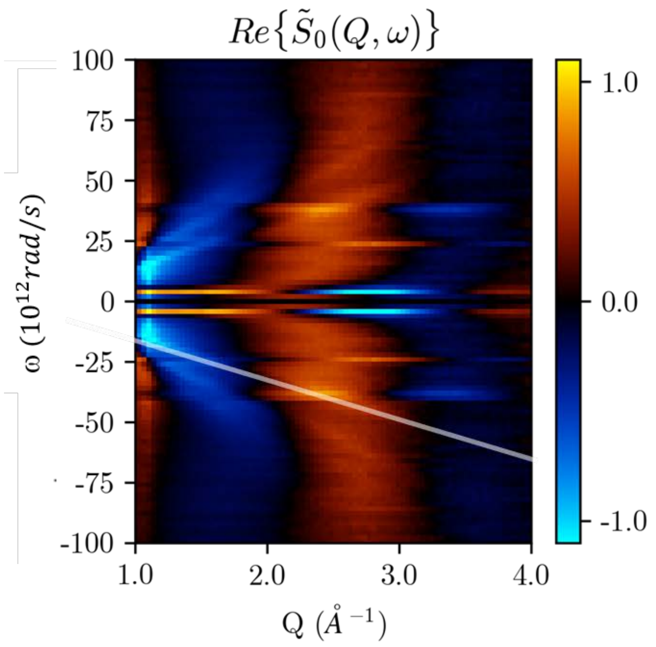
P. H. Bucksbaum, M. R. Ware, A. Natan, J. P. Cryan, and J. M. Glownia, ArXiv:1911.01323 [Physics] (2019).

# Two photon curve-crossing dissociation



$v = \omega / Q =$

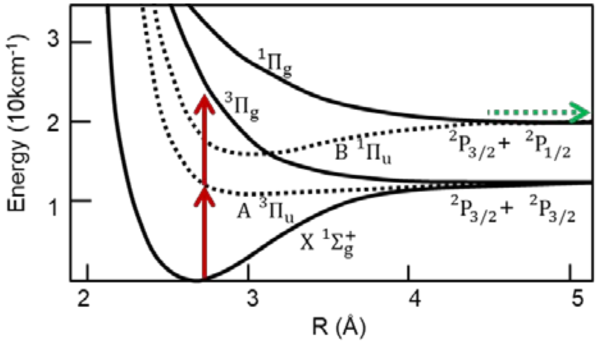
dissociation speed



$\tau_i = \theta/(Qv)$ =

dissociation time shift

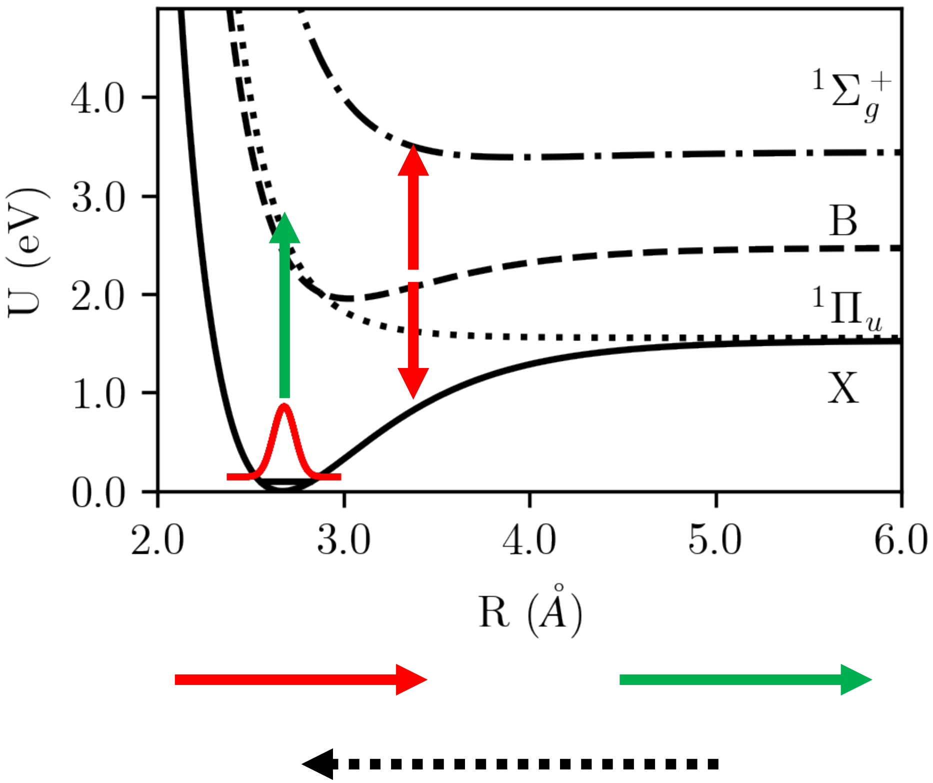
|  |  |
|---|---|
| Separation velocity $v_{(c)}$ | $14 \pm 1$ Å/ps |
| Dissociation time shift $\tau_{i(c)}$ | $+250 \pm 20$fs |



P. H. Bucksbaum, M. R. Ware, A. Natan, J. P. Cryan, and J. M. Glownia, ArXiv:1911.01323 [Physics] (2019).

# Coherent control:
# The experiment

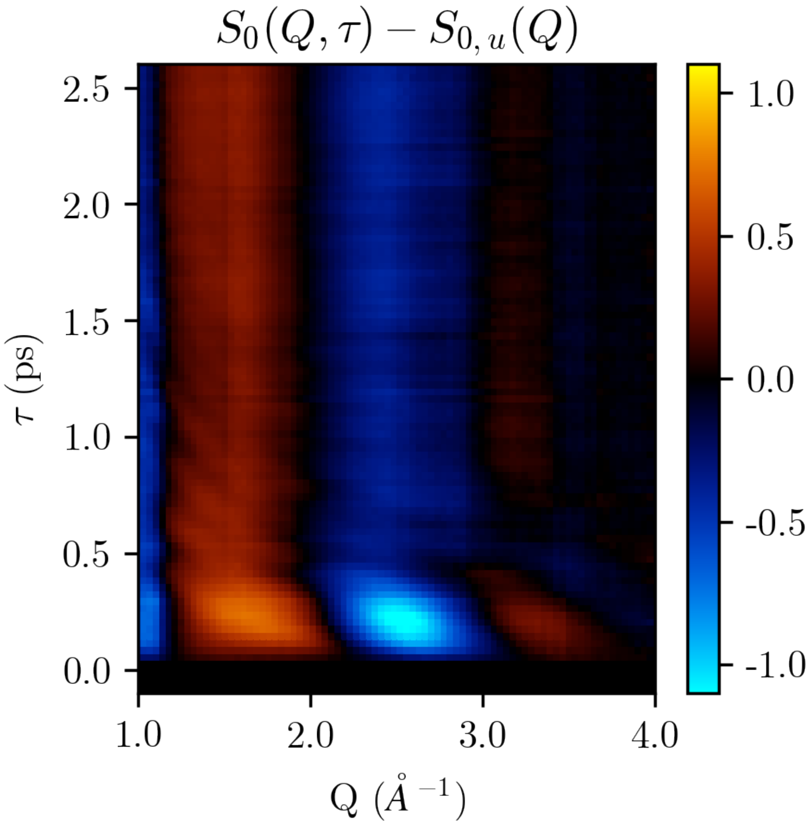
### Potential energy curves



$\boldsymbol{\tau_d}$

M.R. Ware

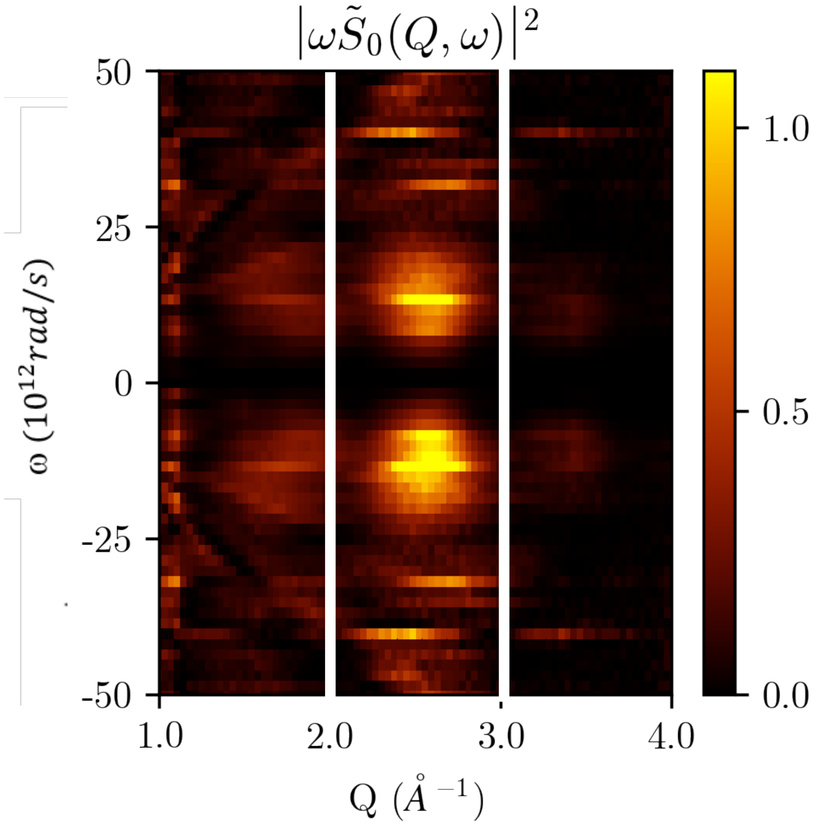
### Measurement



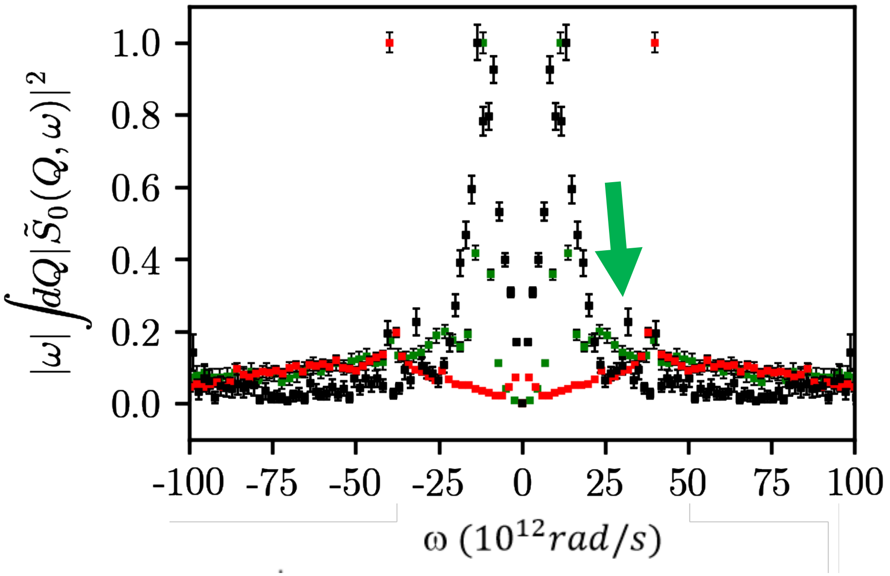
$\boldsymbol{\tau_d = 0.45}$ **ps**

# Coherent control: Identifying the dumped population

**FRXS**



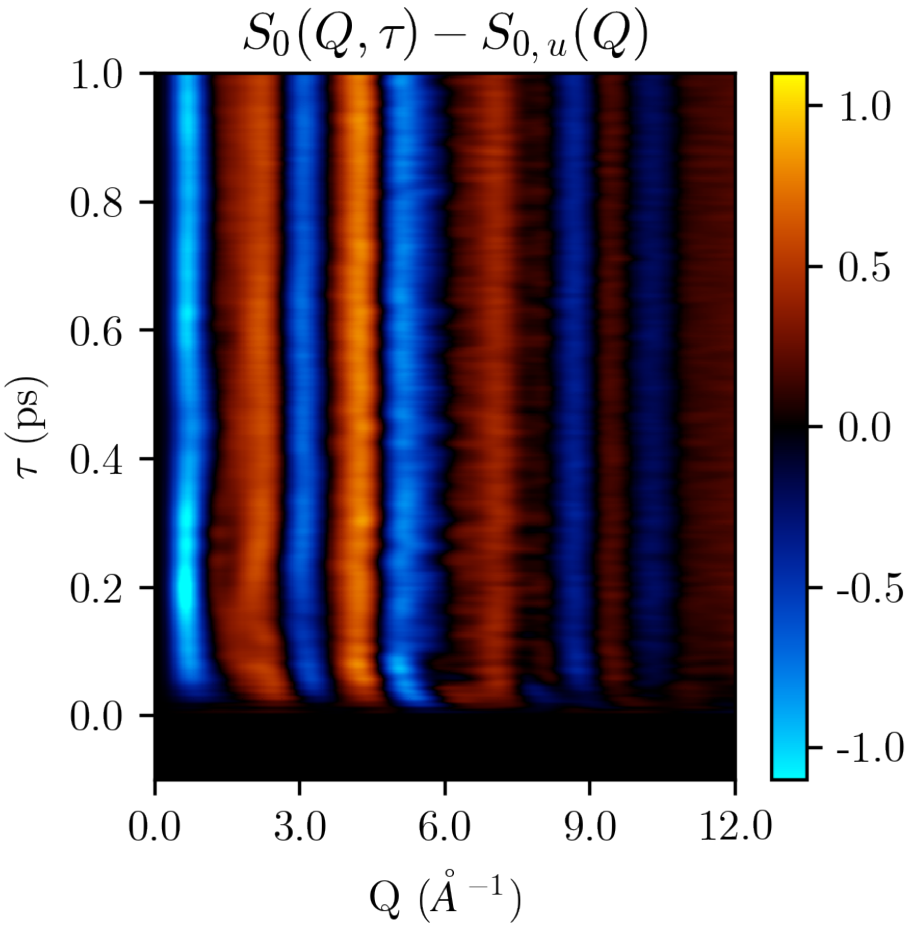
**Integrated spectrum**



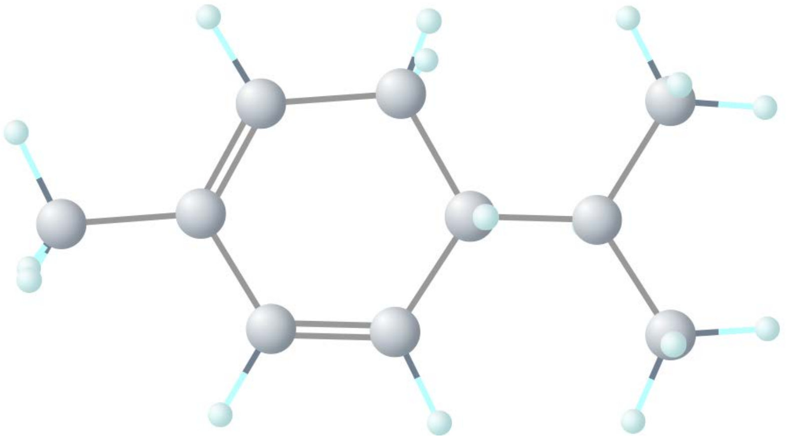
$\omega_d = 31.8 \pm 0.9$ THz
as compared to $\omega_{lit} = 31.9$ THz

M.R. Ware

# Finding the essential modes of motion in a polyatomic molecule with many modes:

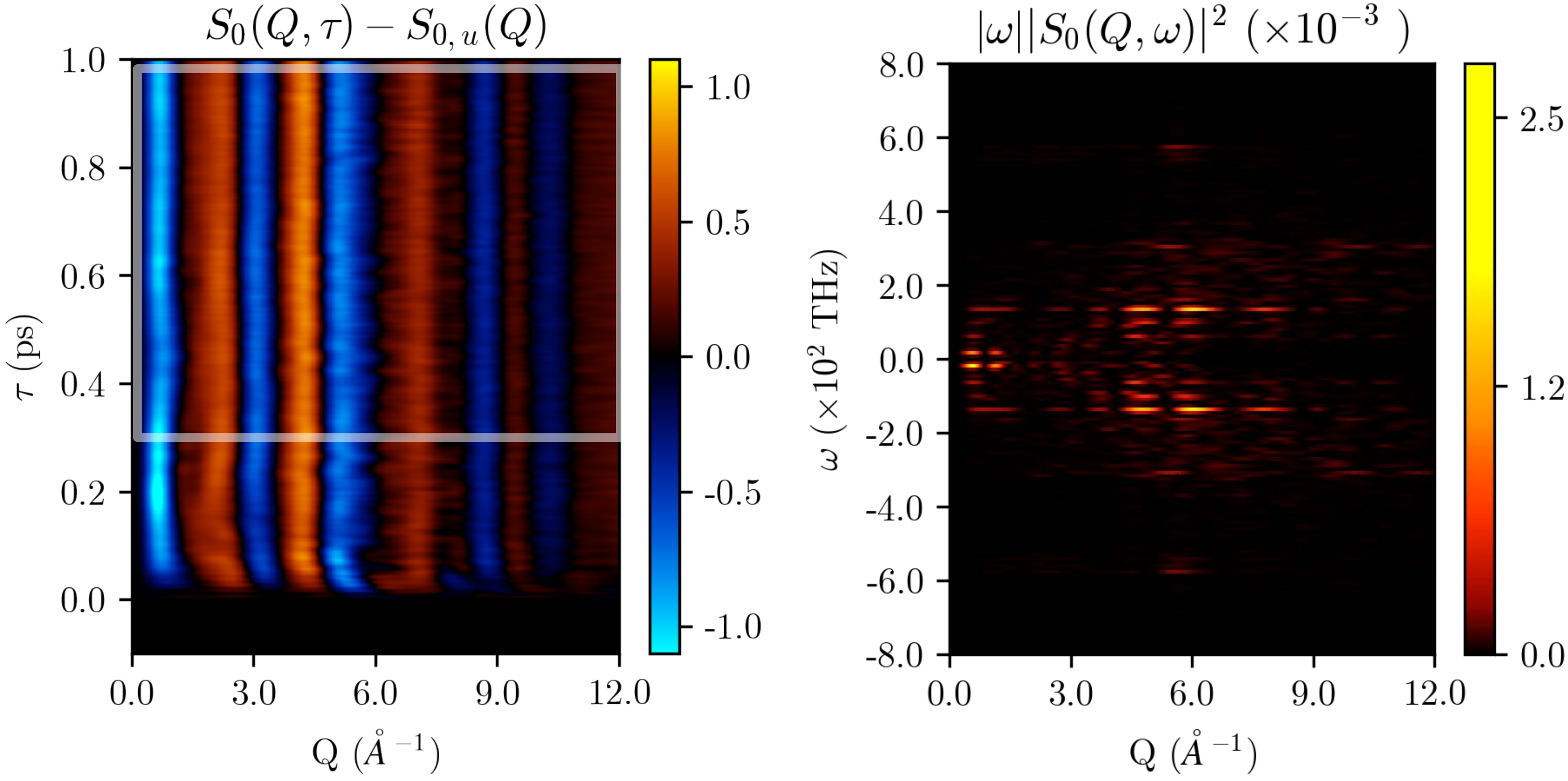


Simulation courtesy of
David Sanchez, Martinez group



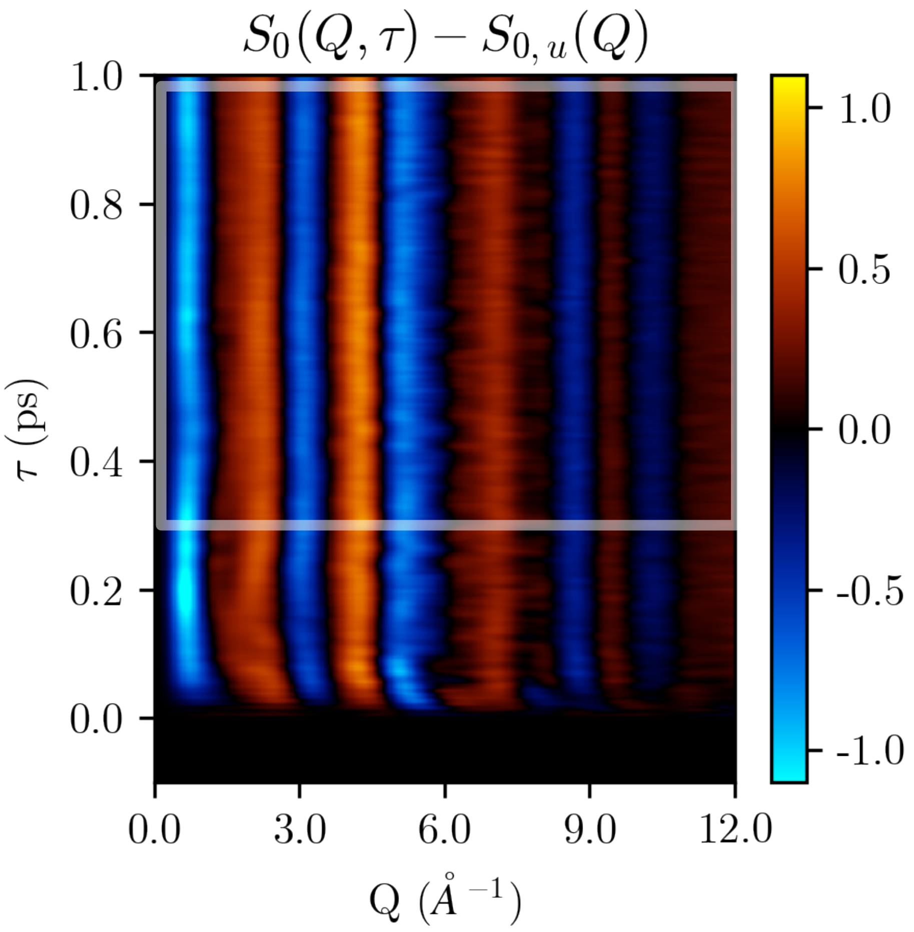
alpha-Phellandrene

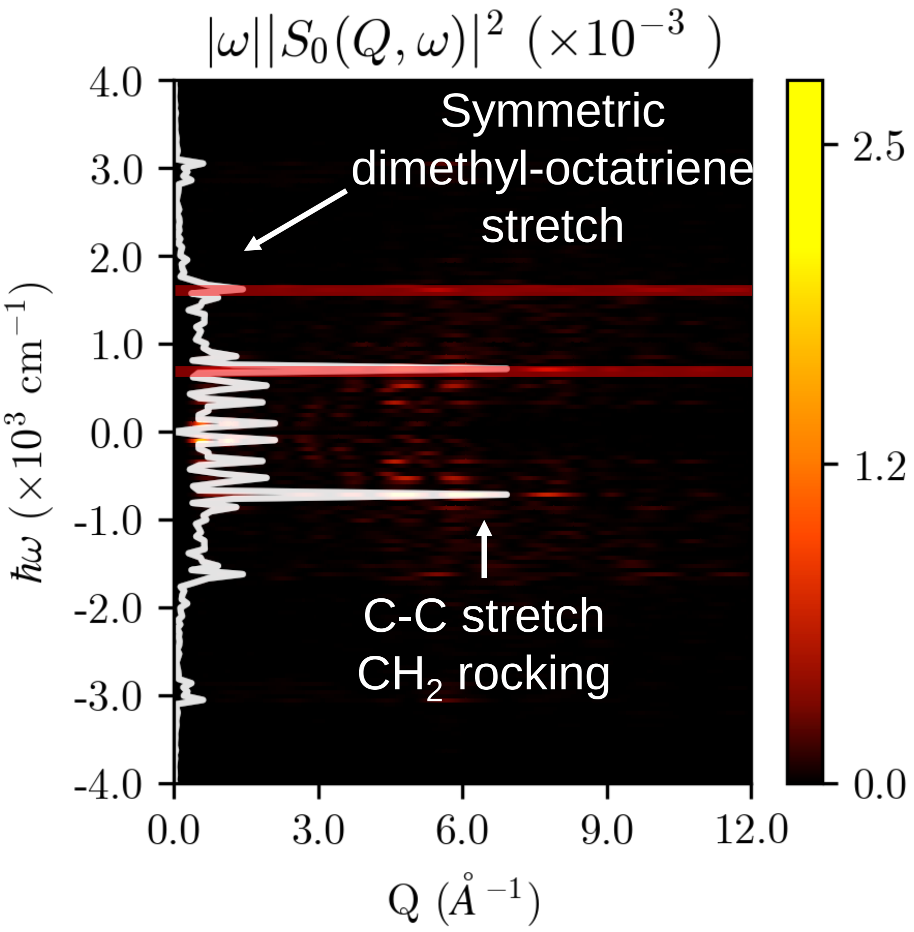
# Finding the essential modes of motion



Simulation courtesy of
David Sanchez, Martinez group

# Finding the essential modes of motion





Symmetric dimethyl-octatriene stretch

C-C stretch
$CH_2$ rocking

Simulation courtesy of
David Sanchez, Martinez Group

Reid, P.J, et. al. J. Phys. Chem. 1990.
Reid, P.J, et. al. J. Am. Chem. Soc. 1993.

# Conclusion:

- **Optics-based methods cannot measure sub-Angstrom displacement and femtosecond motion in molecules.**
- **Femtosecond X-ray laser scattering fills this gap, and can answer questions about the dynamics of motion:**
  - **How long does it take the atoms to move?**
  - **Where is the motion within the molecule?**
  - **What is the amplitude of this motion?**
  - **What is the phase, i.e. when initially excited, do the molecular bonds first contract or first expand?**
- **Taken together, these are molecular movies that provide new insights about mechnisms in molecular physics and chemistry.**

# Credits

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