Imaging electron dynamics in water with a 41.3 attosecond time resolution

or *What does inelastic x-ray scattering tell us about dynamics?*

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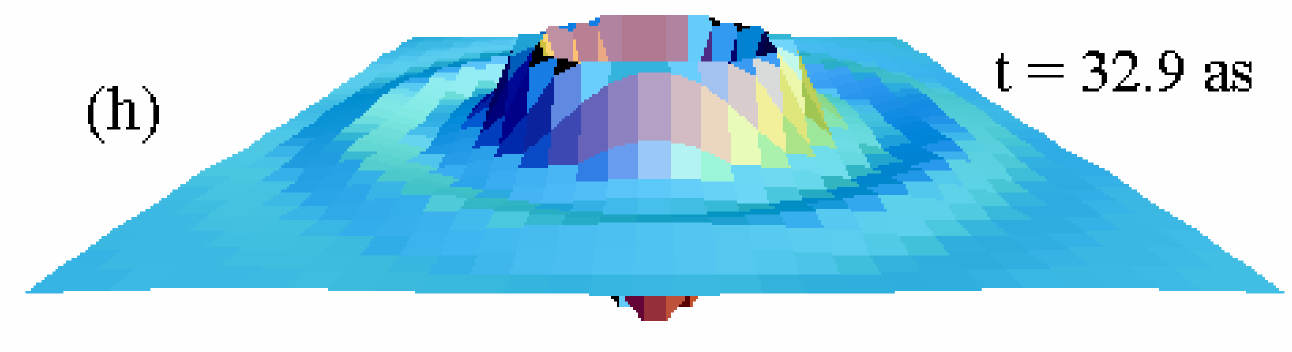

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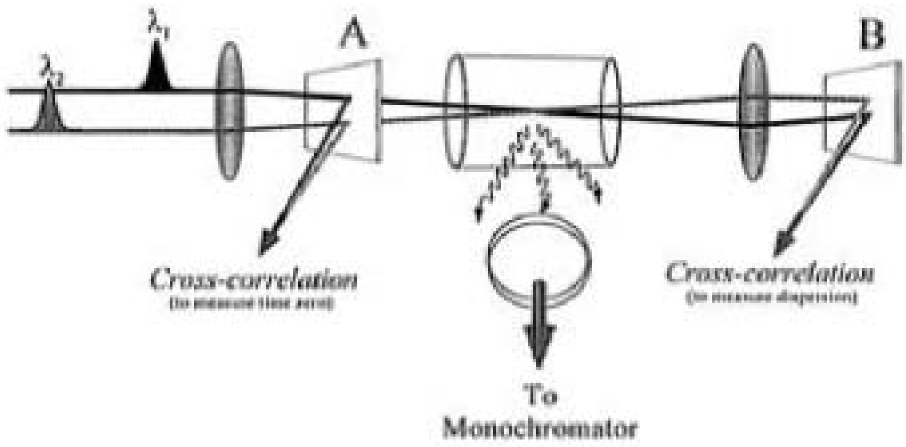
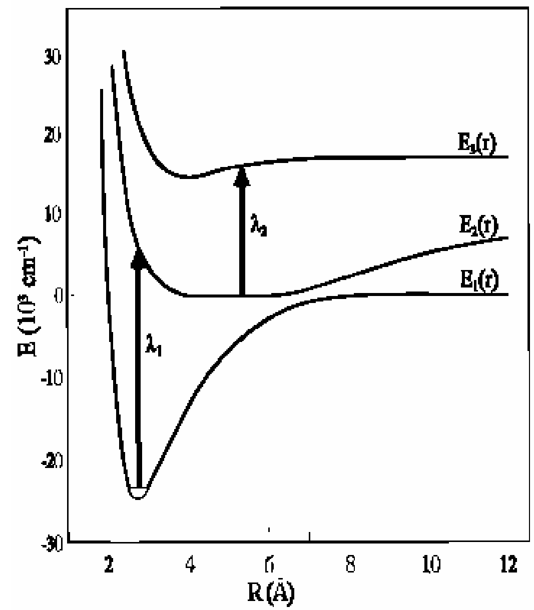
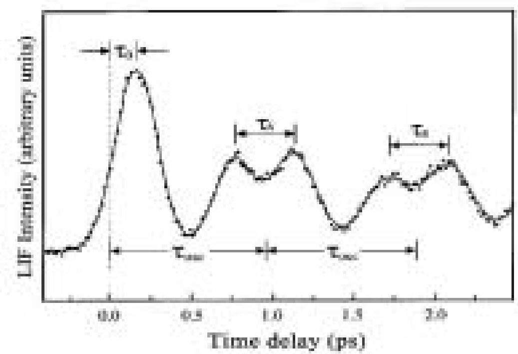
Ultrafast spectroscopy / femtochemistry

$$\mathrm{NaI}(^1\Sigma_0) \rightarrow [\mathrm{Na}\cdots\mathrm{I}]^* \rightarrow \mathrm{Na}(^2S_{1/2}) + \mathrm{I}(^2P_{3/2})$$



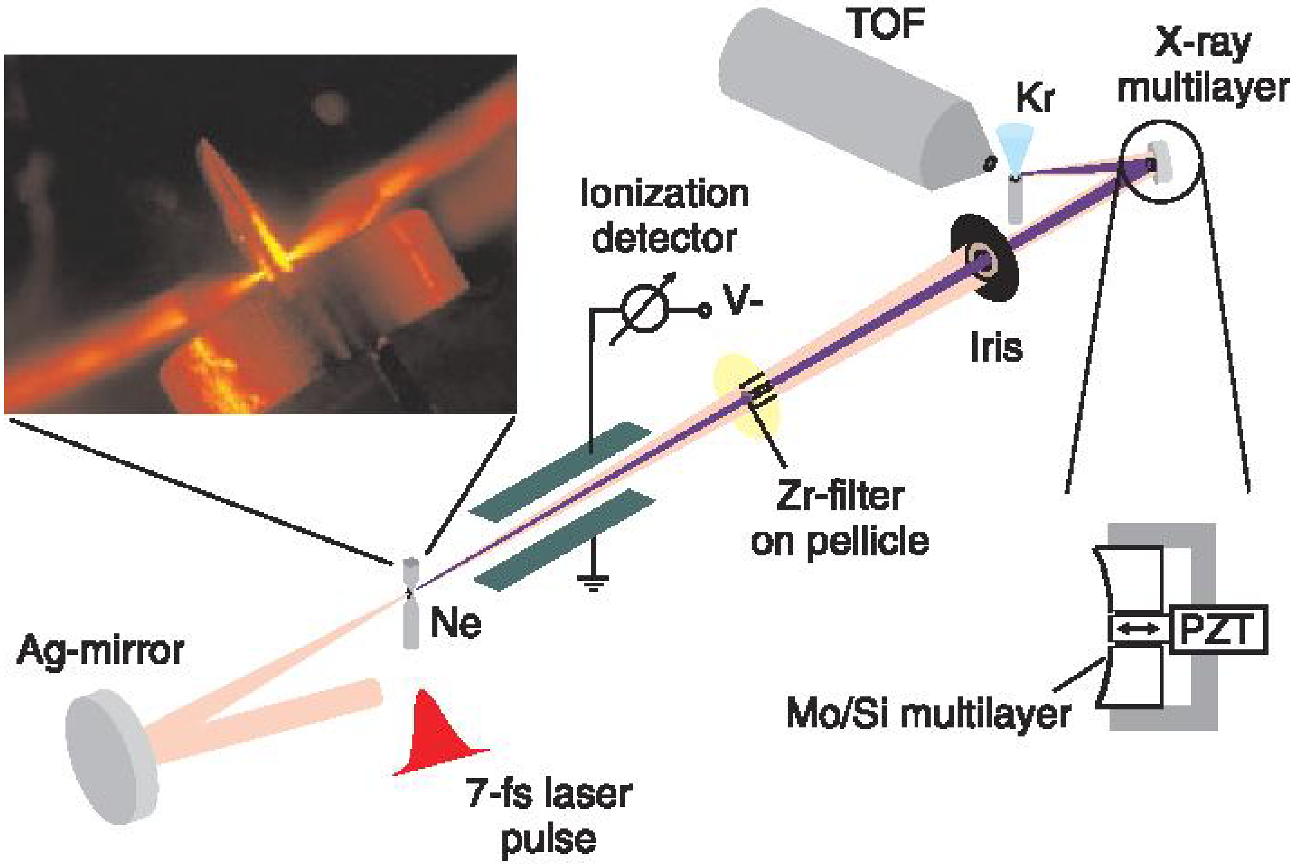




*P. Cong, et. al., J. Phys. Chem., **100**, 7832 (1996)*

"Is there another domain in which the race against time can continue to be pushed? Sub-femtosecond or attosecond (10^{-18} s) resolution may one day allow for the direct observation of the electron's motion. … In the coming decades we may view electron rearrangement, say, in the benzene molecule, in real time." – Ahmed Zewail, 2000 Nobel Address

Attosecond spectroscopy



Reproduced from Drescher, *et. al.*, *Science*, **291** 1923 (2001)

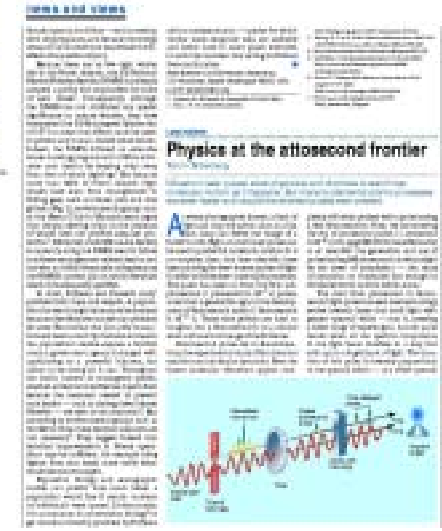
- Events *preceding* photofragmentation
- Quasiparticle "birth" in Si
- Inner shell processes (shape resonances)
- Electron transfer chemistry

Press

2002 in context

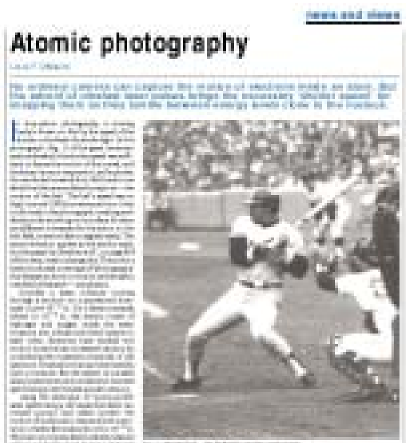
The fast show

Tanked up and ready for action



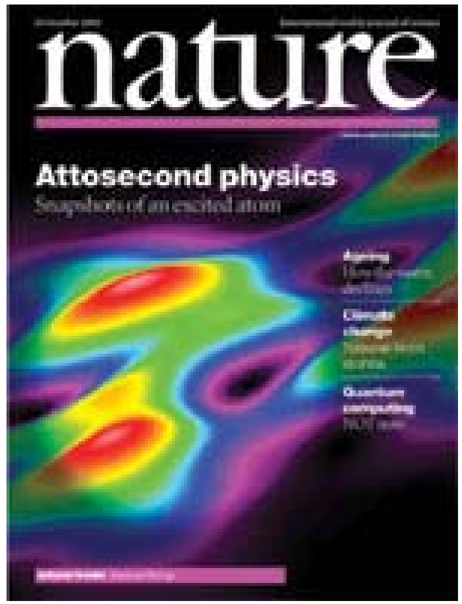
news and views

Physics at the attosecond frontier



news and views

Atomic photography



nature

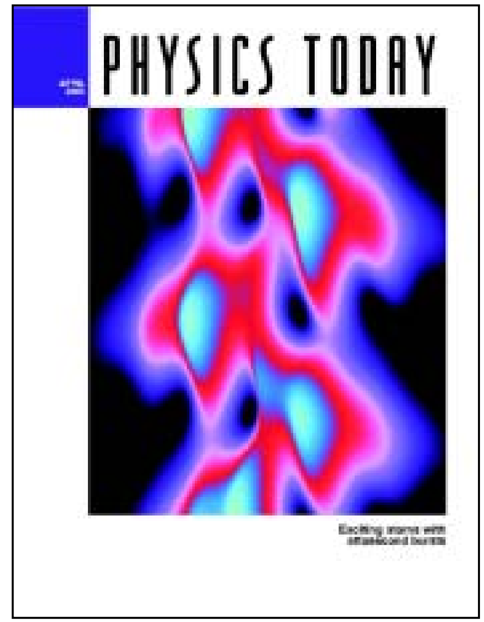
Attosecond physics

Snapshots of an excited atom

Ageing

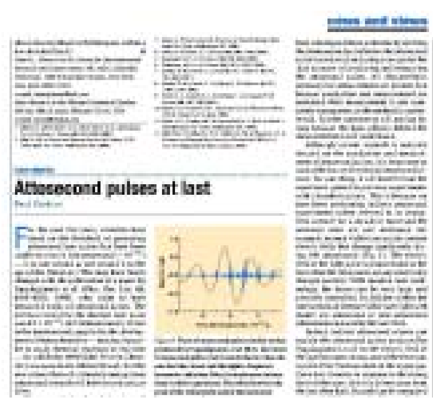
Climate change

Quantum computing



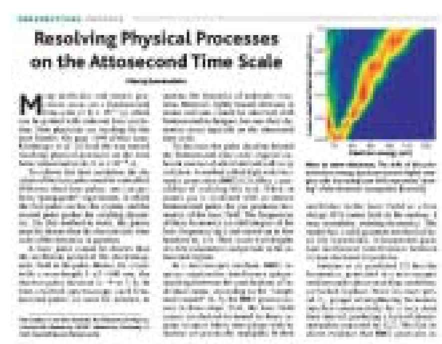
PHYSICS TODAY

Exciting atoms with attosecond bursts



news and views

Attosecond pulses at last



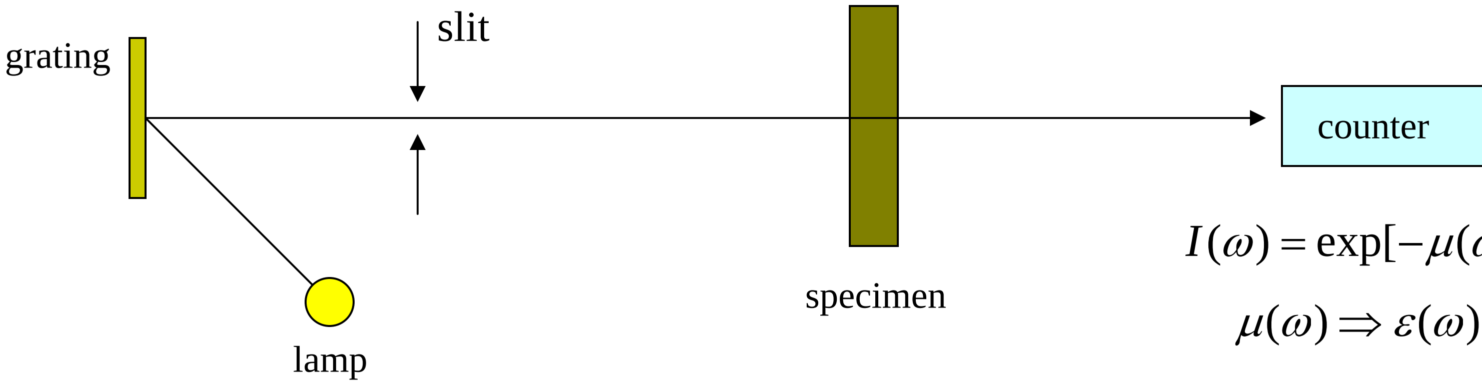
Resolving Physical Processes on the Attosecond Time Scale

news and views

Ultrafast control

Why not energy domain? - photoabsorption

Δt = 100 attosecond, $\Delta E \cdot \Delta t = \hbar \Rightarrow \Delta E = 6.58$ eV



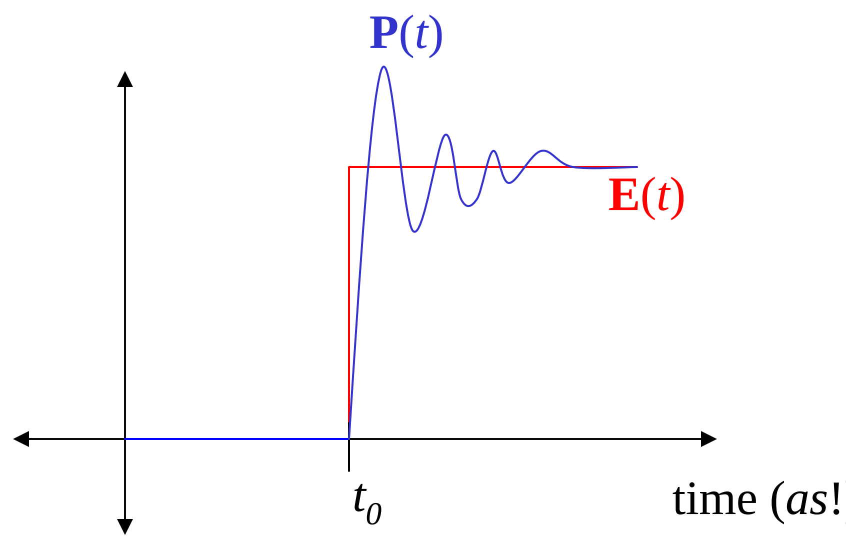
$$I(\omega) = \exp[-\mu(\omega)L]$$

$$\mu(\omega) \Rightarrow \varepsilon(\omega)$$

$$\chi_e(\omega) = \frac{\varepsilon(\omega)-1}{4\pi}$$

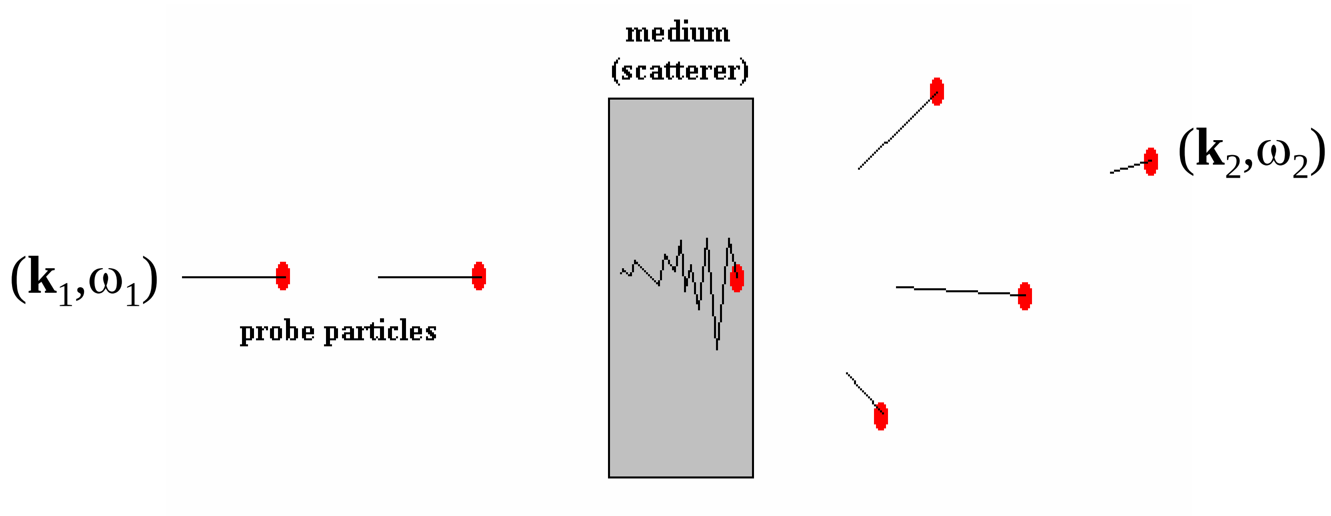
$$\mathbf{P}(\omega) = \chi_e(\omega)\mathbf{E}(\omega)$$

$$\mathbf{P}(t) = \int_{-\infty}^{\infty} dt' \chi_e(t-t')\mathbf{E}(t')$$



"…energy-domain measurements on their own are – in general – unable to provide detailed insight into the evolution of multi-electron dynamics." – M. Drescher, *et. al.*, *Nature* (2002)

Momentum-resolved *spectroscopy: IXS* *(or INS or EELS)*

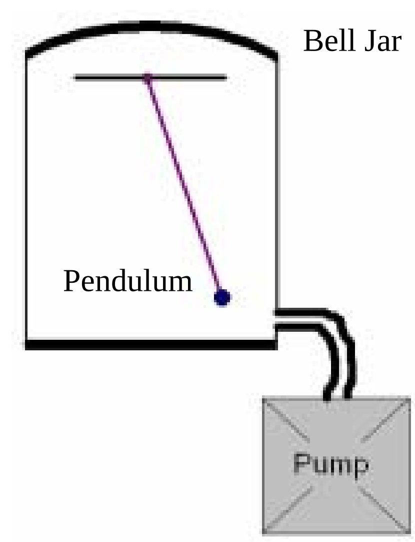


Fluctuation-Dissipation theorem:

$$I(\mathbf{k},\omega) \sim -\,\mathrm{Im}[\chi(\mathbf{k},\omega)]$$

$$\mathbf{k} = \mathbf{k}_1 - \mathbf{k}_2$$

$$\omega = \omega_1 - \omega_2$$



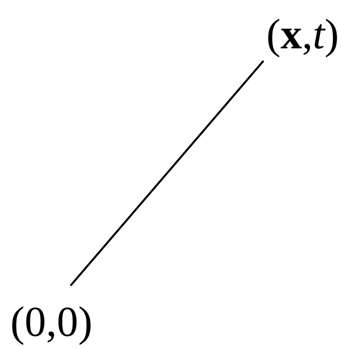
What is $\chi(\mathbf{k},\omega)$?

$\chi(\mathbf{k},\omega)$:

- density Green's function
- density propagator
- susceptibility
- (old) influence function

Describes how disturbances in electron density travel about the medium.

$$\chi(\mathbf{x},t) = -i < 0|\ \hat{n}(\mathbf{x},t)\ \hat{n}(0,0)\ |0> \theta(t)$$



Causality

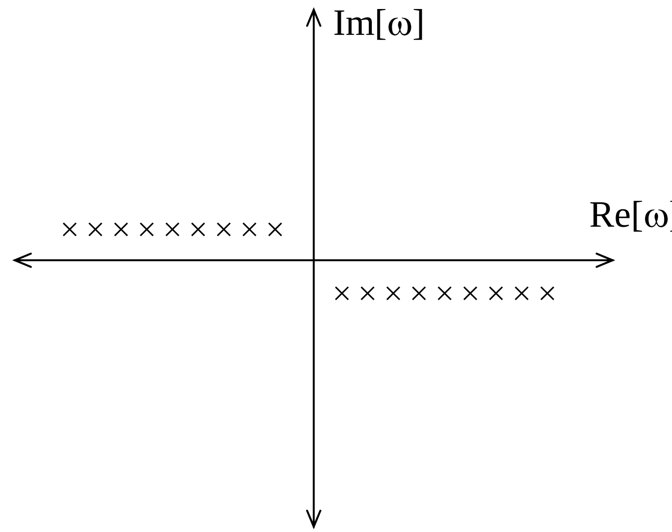
Same as a pump-probe experiment.

Dynamics is dynamics

"Phase problem" and the arrow of time

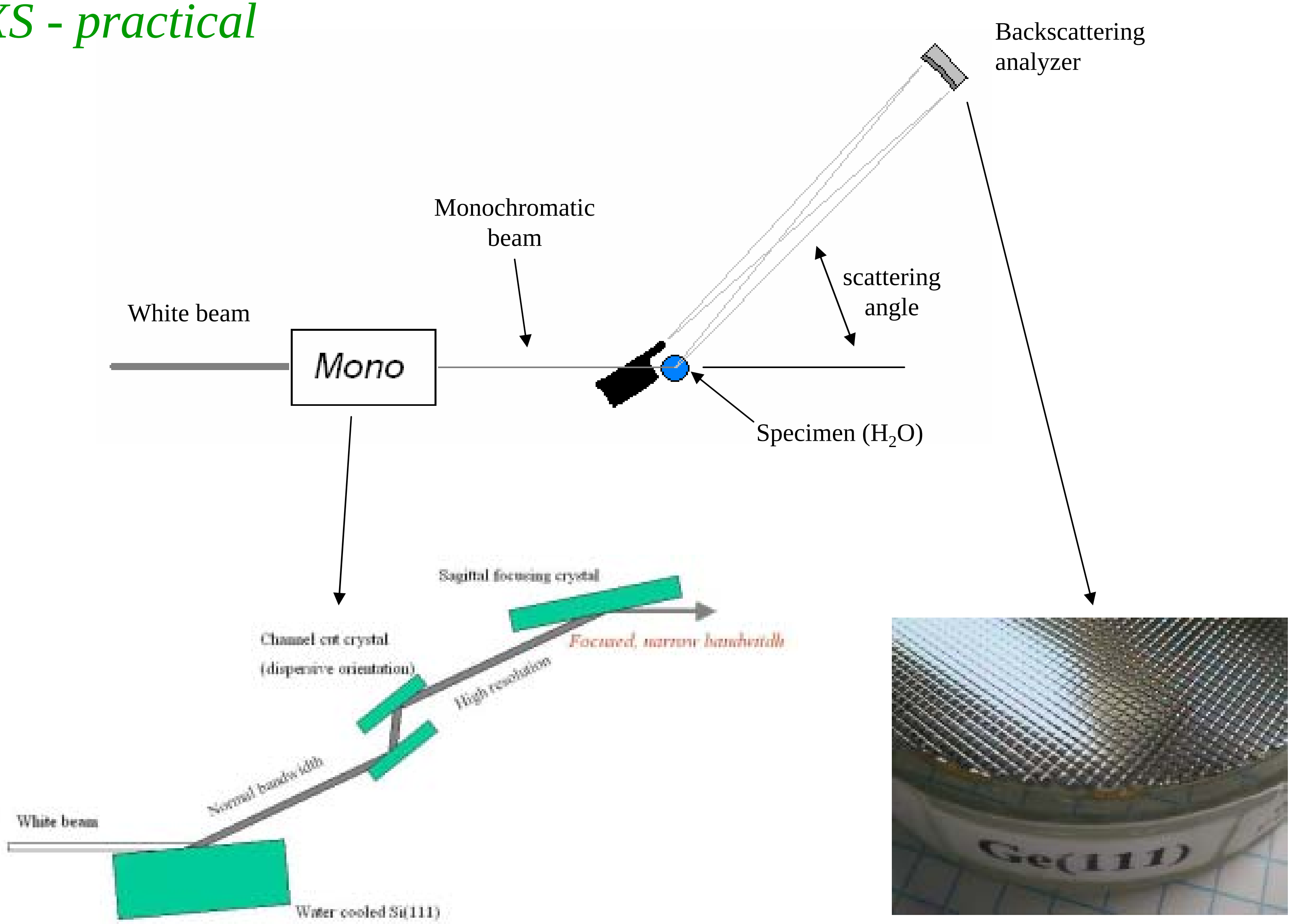
Cannot invert with only Im[$\chi(\mathbf{k},\omega)$]

$$Re\left[\chi(\mathbf{k},\omega)\right] = \frac{2}{\pi} P \int_0^\infty d\omega' \frac{Im\left[\chi(\mathbf{k},\omega)\right]}{\omega' - \omega}$$



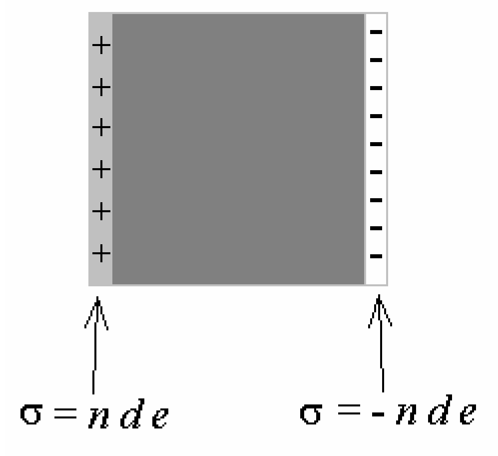
- $\chi(\mathbf{x},t) = 0$ for $t < 0$
- Raw spectra do not really describe dynamics – no causal information
- Must assign an *arrow of time* to the problem. Permits retrieval of $\chi(\mathbf{x},t)$ – view dynamics explicitly.

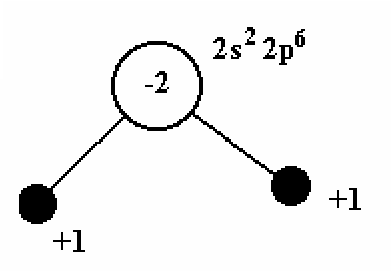
IXS - practical



K. D. Finkelstein, P. Abbamonte, V. O. Kostroun, *Proc. SPIE Int. Soc. Opt. Eng.* **4783**, 139 (2002)

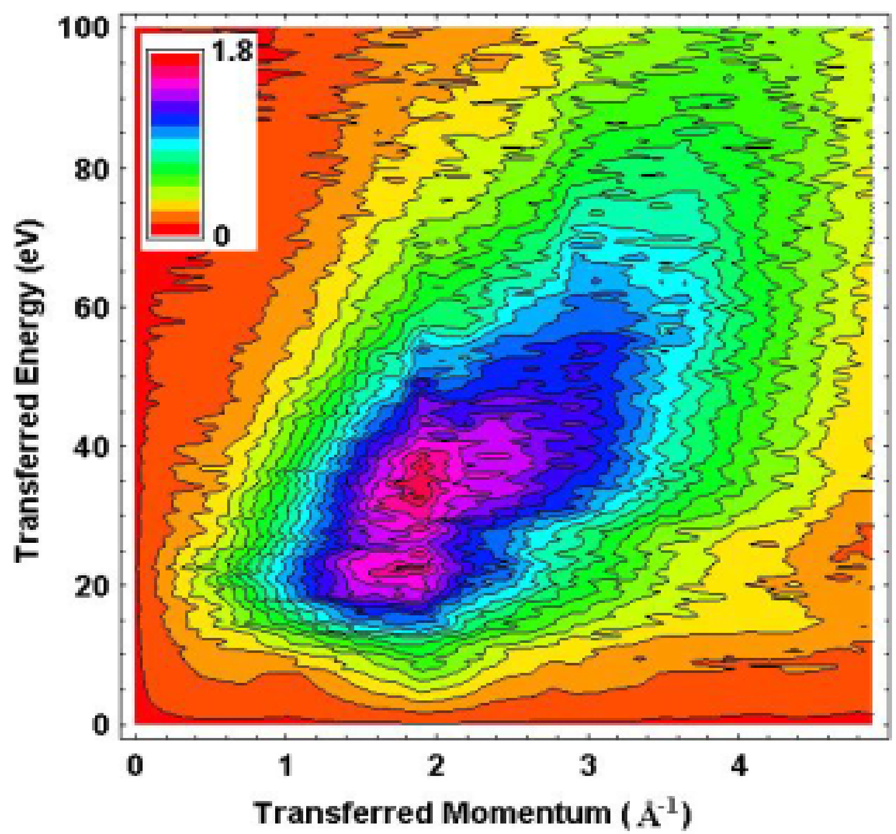
Plasma oscillations in water





- 8 valence electrons / molecule
- $\rho = 1$ g/cm^3 $\Rightarrow n = 0.20\ e/\text{Å}^3$
- $\omega_p = \sqrt{(4\pi ne^2/m)} = 16.6$ eV
- $k_{max} = 4.95$ Å$^{-1} \Rightarrow$ dx = 1.27 Å
- $\omega_{max} = 100$ eV $\Rightarrow$ dt = 41.3 *as*

$-\,\mathrm{Im}[\chi(k,\omega)]\quad (as/\text{Å}^3)$

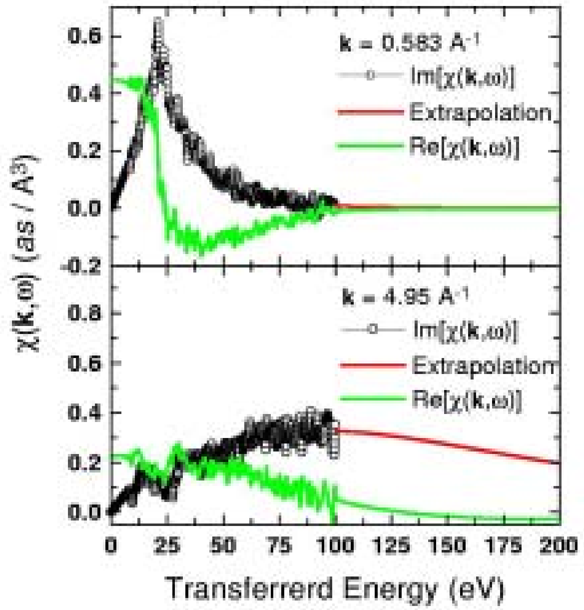


Retaining causality with real data

Problem #1:
Im[$\chi(\mathbf{k},\omega)$] must be defined on *infinite* ω interval for KK transform

Solution:
Extrapolate.

Side Effects:
$\chi(\mathbf{x},t)$ defined at all times (infinitely narrow Δt)



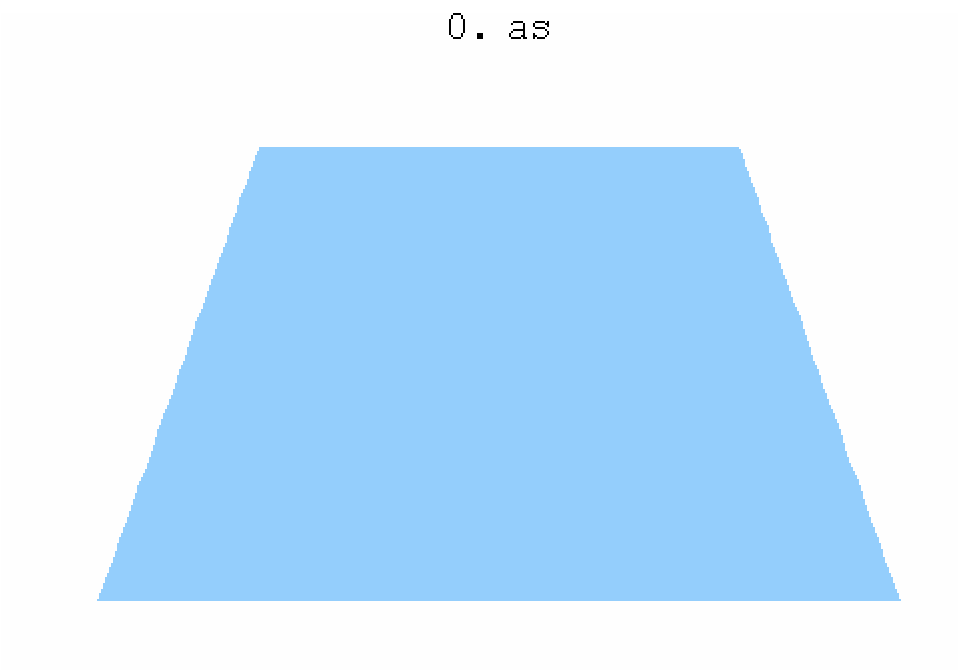
Problem #2:
Discrete points violate causality
Im[$\chi(\mathbf{k},\omega)$] must be defined on continuous ω interval.

Solution:
Analytic continuation (interpolate)

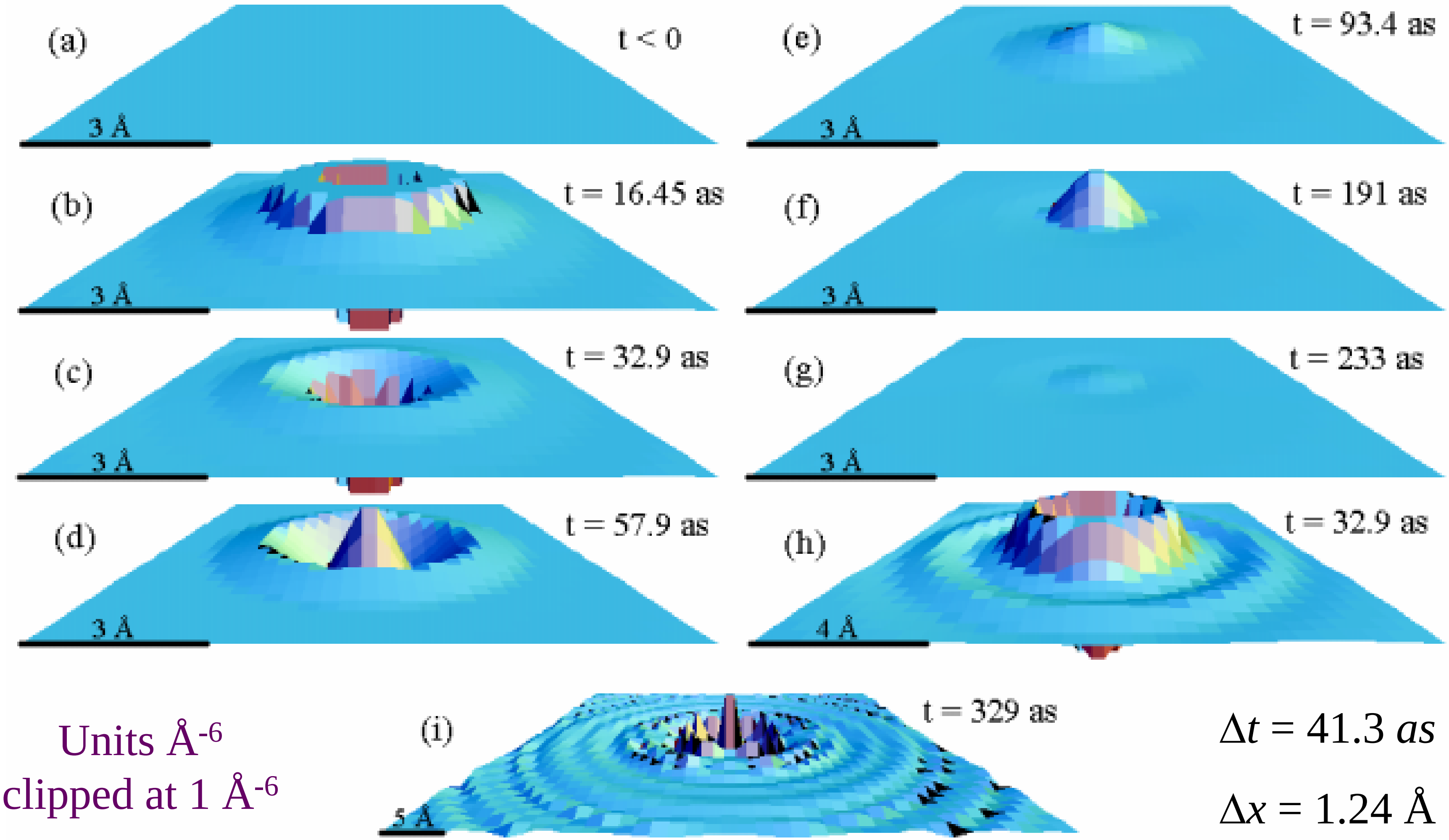
$$\chi(\mathbf{k},t) = \int_0^\infty \frac{d\omega}{\pi}\left[\sin(\omega t)\, Im\chi(\mathbf{k},\omega) + \cos(\omega t)\, Re\chi(\mathbf{k},\omega)\right]$$

Side effects:
$\chi(\mathbf{x},t)$ defined forever, vanishes for $t < 0$, but repeats with period $T = 13.8$ femtoseconds

Disturbance from a point perturbation.



Disturbance from a point perturbation – frame-by-frame



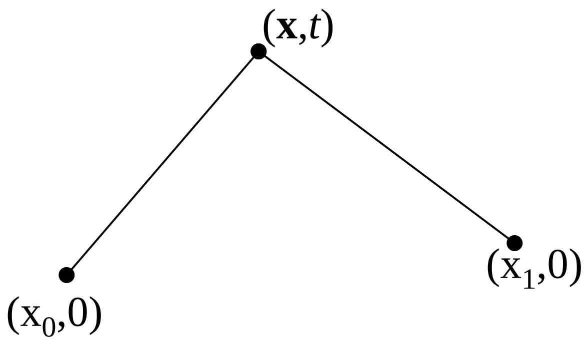
Units $Å^{-6}$
clipped at 1 $Å^{-6}$

$\Delta t = 41.3\ as$

$\Delta x = 1.24$ Å

Causality ⇔ Rise of entropy ⇔ Arrow of time

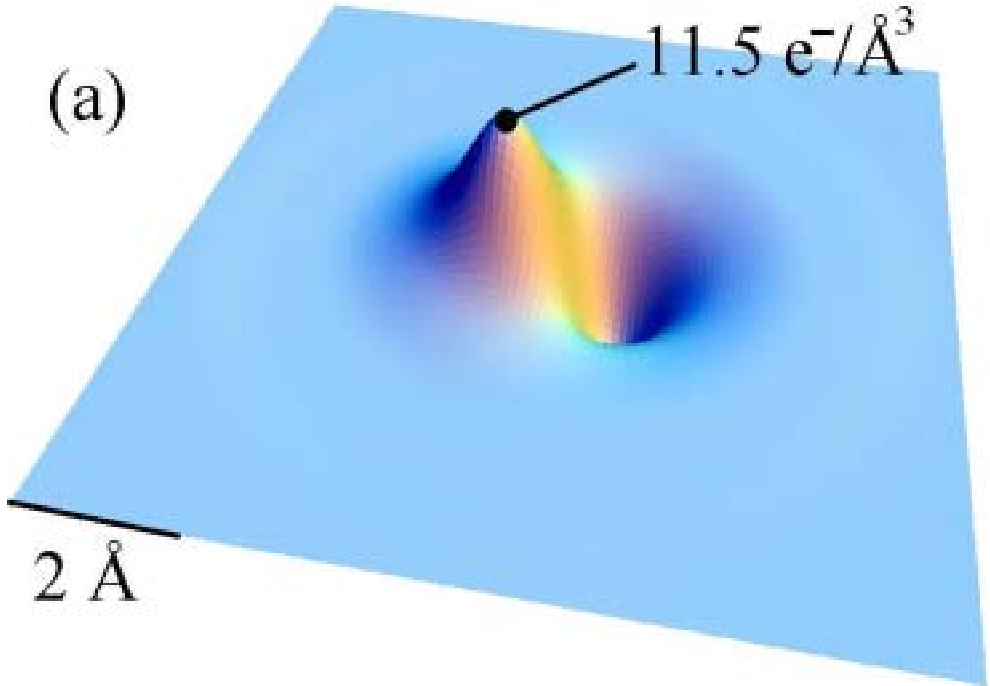
Compound sources



$$n_{ind}(\mathbf{k},\omega) = -\frac{4\pi e^2}{\hbar k^2}\,\chi(\mathbf{k},\omega)\;n_{free}(\mathbf{k},\omega)$$

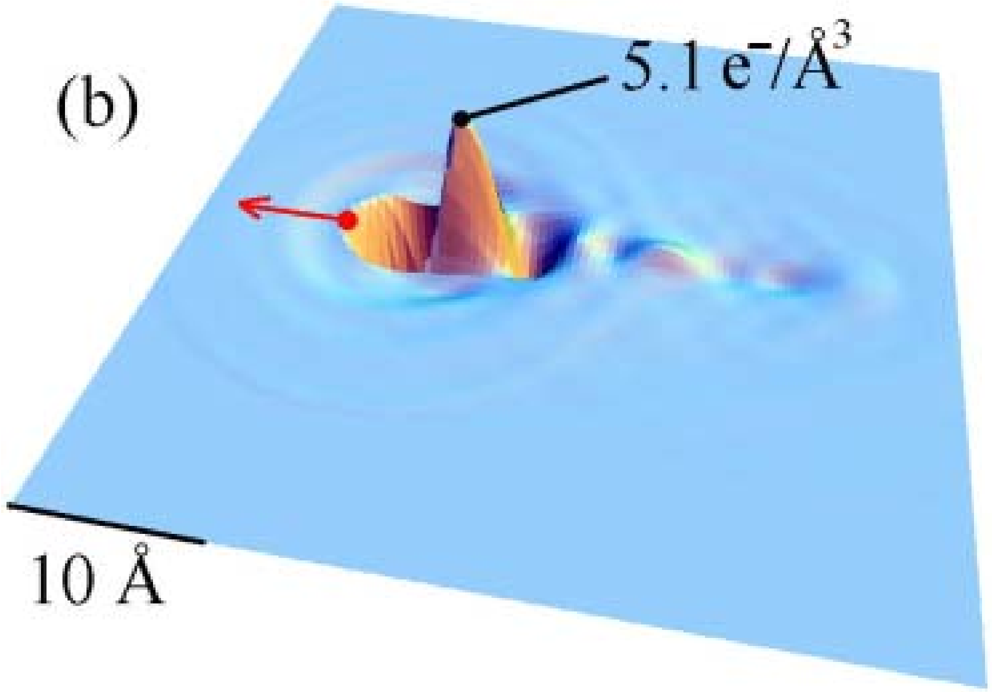
Compound sources – oscillating dipole

$$n_{free}(\mathbf{x},t) = \left[\delta^3(x - 0.5\text{Å}) - \delta^3(x + 0.5\text{Å})\right]\cos(\omega_0 t)$$



Compound sources – wake from 9 MeV Au ion

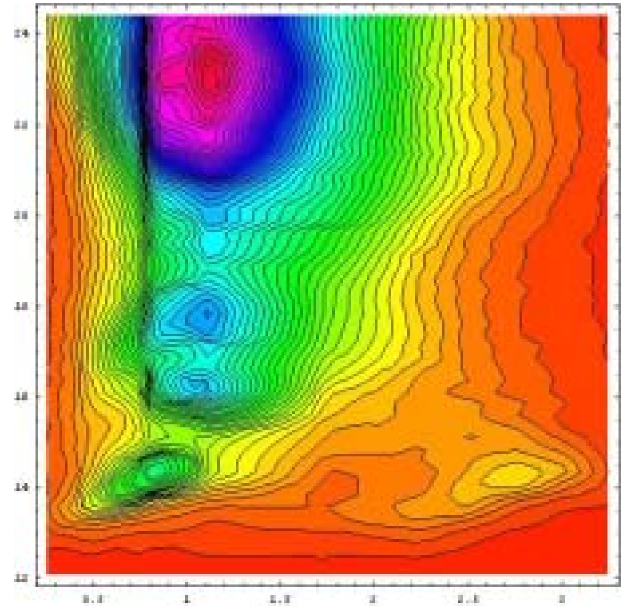
$$n_{free}(\mathbf{x},t) = Z\,\delta^3(\mathbf{x}-\mathbf{v}t)$$



- *Phys. Rev. Focus*, 14 June 2004
- *Chemical & Engineering News*, **82**, 5 (2004)

Attoscience experiment on LiF

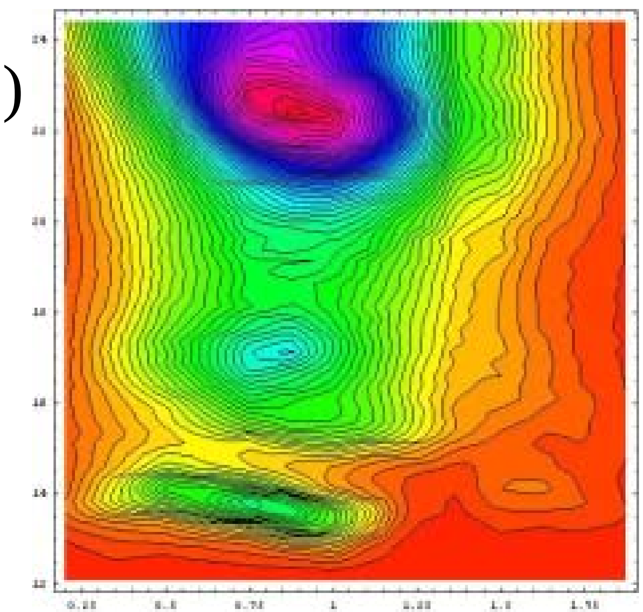
(100)



Fragmentation → *F center formation*

Wave packet evolution → *Exciton dynamics*

(110)



- Burst of excitons in attoseconds
- Dressed by optical phonons
- Decay into acoustic phonons (heat)

↓ *Entropy grows*

Summary

- Causality allows solution to "phase problem" for IXS $\Rightarrow$ view dynamics explicitly in space and time.

- Not as flexible as pump-probe, but can have any time resolution you want (zeptoseconds).

- Is there information in this which cannot be read off the raw spectra?!
1. Extrapolation   2. *Causality*

- Energy-loss data contains information about *extended sources*.

- *Fine print*: in all materials $\chi = \chi(\mathbf{k}_1,\mathbf{k}_2;\omega)$. χ must be considered an ensemble average.