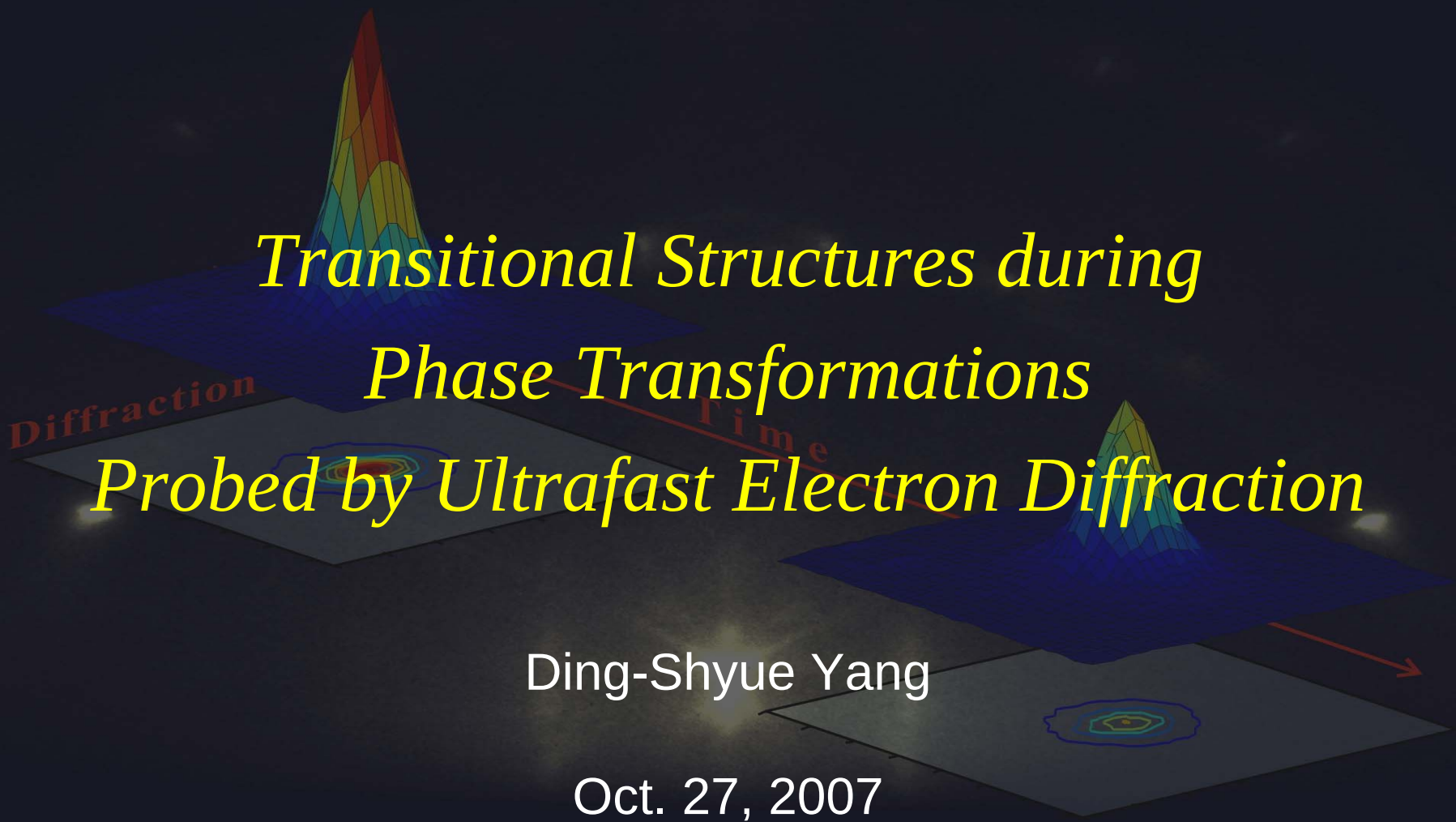


Transitional Structures during Phase Transformations Probed by Ultrafast Electron Diffraction

Ding-Shyue Yang

Oct. 27, 2007

UST
LMS

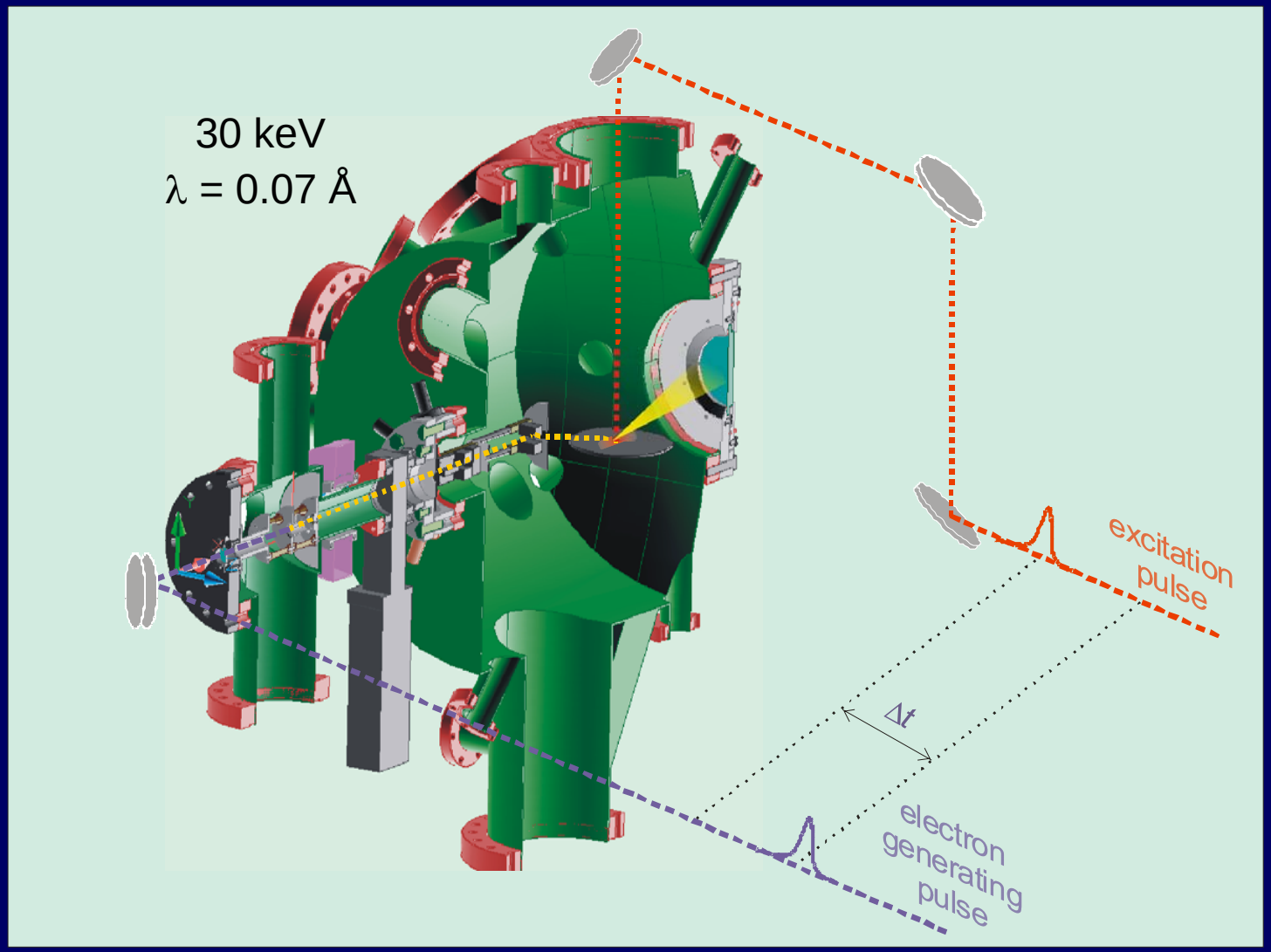
GORDON AND BETTY MOORE FOUNDATION

NSF

Advantages of Electron Diffraction

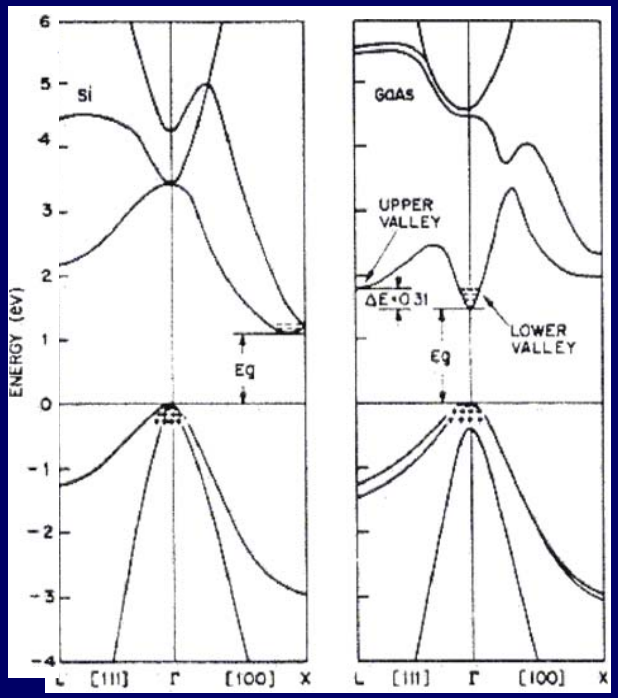
- Cross section of electron scattering
- Short penetration depth → surface sensitive
- Less damaging per useful scattering event
- Unprecedented sensitivity in detecting changes
- Tabletop apparatus

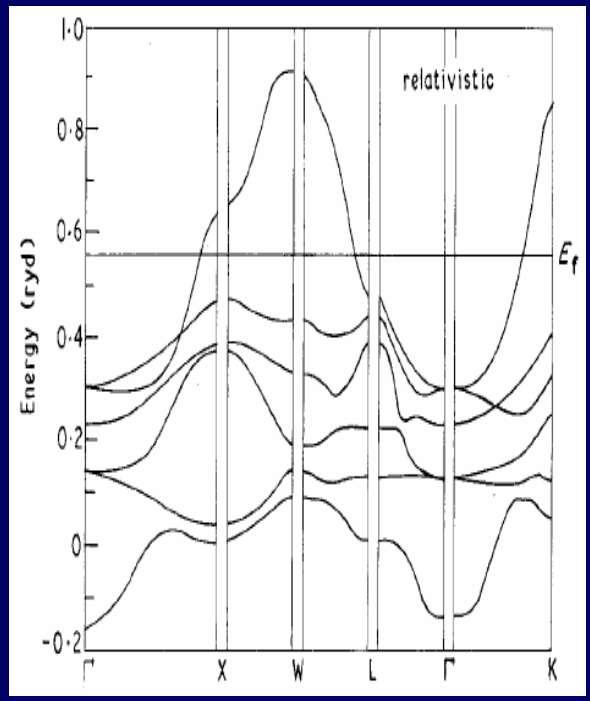
Ultrafast Electron Crystallography (UEC)



UEC Studies in Last Three Years

- Semiconducting and metallic substrates
  silicon, gallium arsenide, gold, etc.





Silicon: Ruan, Vigliotti, Lobastov, Chen, Zewail *PNAS* **101**, 1123 (2004)
GaAs: Vigliotti, Chen, Ruan, Lobastov, Zewail *Angewandte Chemie* **43**, 2705 (2004)
Gold: Ruan, Yang, Zewail *JACS* **126**, 12797 (2004)

UEC Studies in Last Three Years

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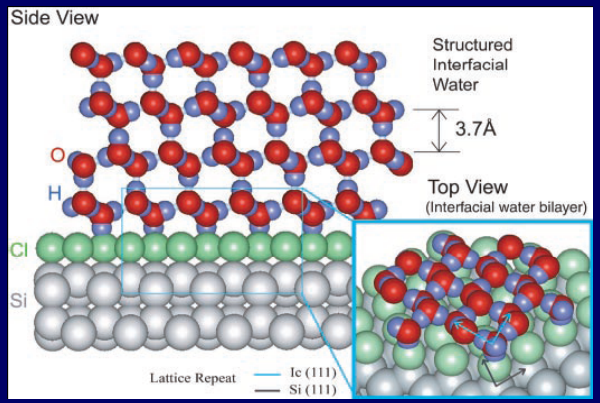
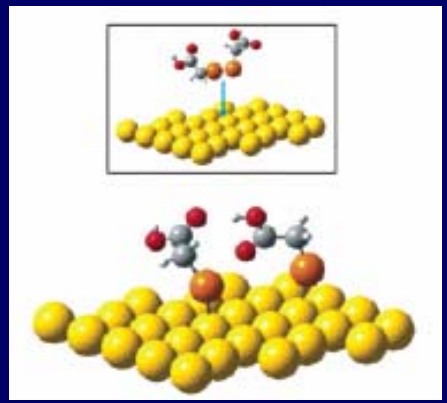
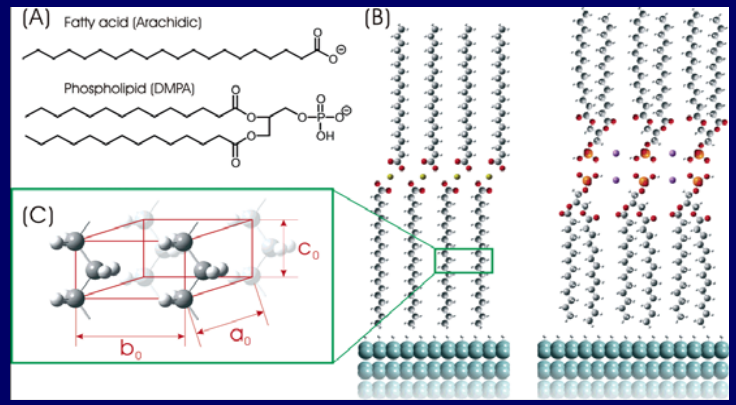
  silicon, gallium arsenide, gold, etc.
- Self-assembled and Langmuir-Blodgett adsorbates
  water, alkanethiols, fatty acids, phospholipids



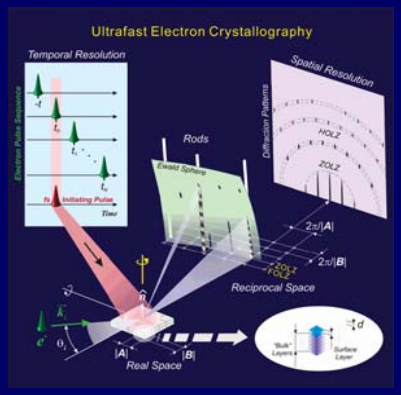


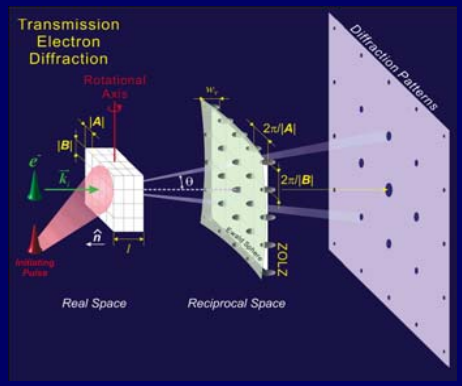


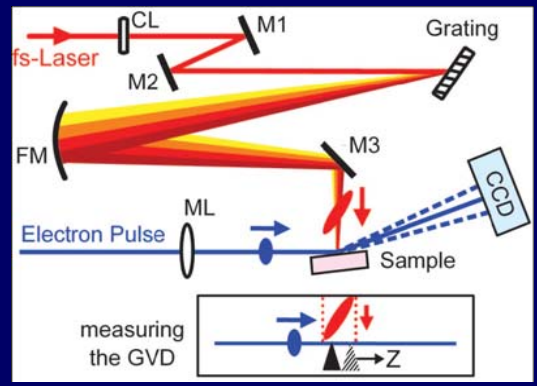
Interfacial ice: Ruan, Lobastov, Vigliotti, Chen, Zewail *Science* **304**, 80 (2004)
Alkanethiols: Ruan, Yang, Zewail *JACS* **126**, 12797 (2004)
Fatty acids: Chen, Seidel, Zewail *PNAS* **102**, 8854 (2005)
Phospholipids: Chen, Seidel, Zewail *Angewandte Chemie* **45**, 5154 (2006)

UEC Studies in Last Three Years

- Semiconducting and metallic substrates
  silicon, gallium arsenide, gold, etc.
- Self-assembled and Langmuir-Blodgett adsorbates
  water, alkanethiols, fatty acids, phospholipids
- Reflection and transmission detection modes
  Pulse-tilting scheme







UEC: Yang, Gedik, Zewail *J. Phys. Chem. C* **111**, 4889 (2007)
Tilting: Baum, Zewail *PNAS* **103**, 16105 (2006)

UEC Studies in Last Three Years

- Semiconducting and metallic substrates
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- Self-assembled and Langmuir-Blodgett adsorbates
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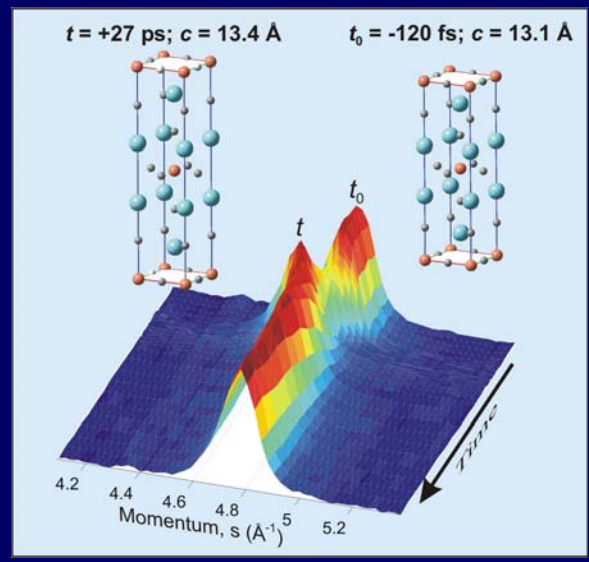
  Pulse-tilting scheme
- Superconducting materials
  nonequilibrium phase transition

Gedik, Yang, Zewail *Science* **316**, 425 (2007)

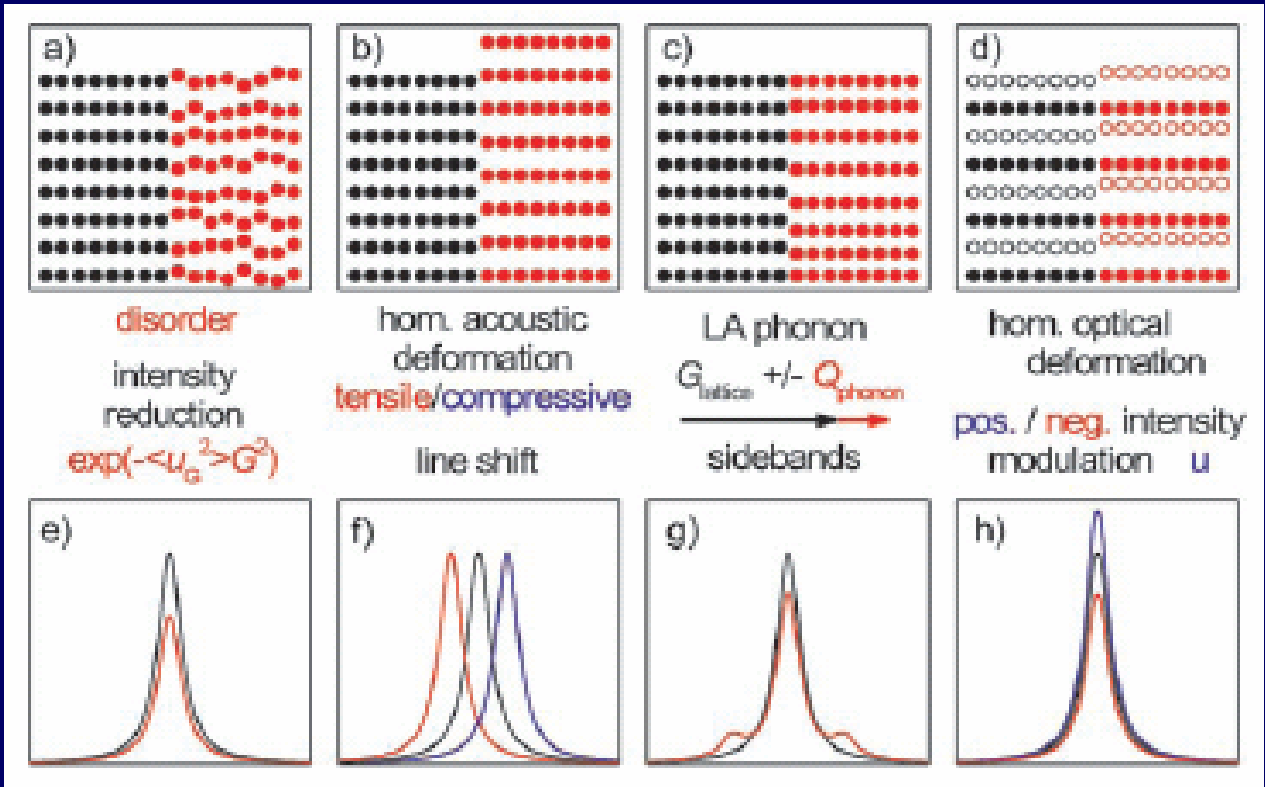


UEC Studies in Last Three Years

- Semiconducting and metallic substrates
  silicon, gallium arsenide, gold, etc.
- Self-assembled and Langmuir-Blodgett adsorbates
  water, alkanethiols, fatty acids, phospholipids
- Reflection and transmission detection modes
  Pulse-tilting scheme
- Superconducting materials
  nonequilibrium phase transition
- Phase transitions between thermodynamically stable phases

Baum, Yang, Zewail *Science* **318** (2007, in press)

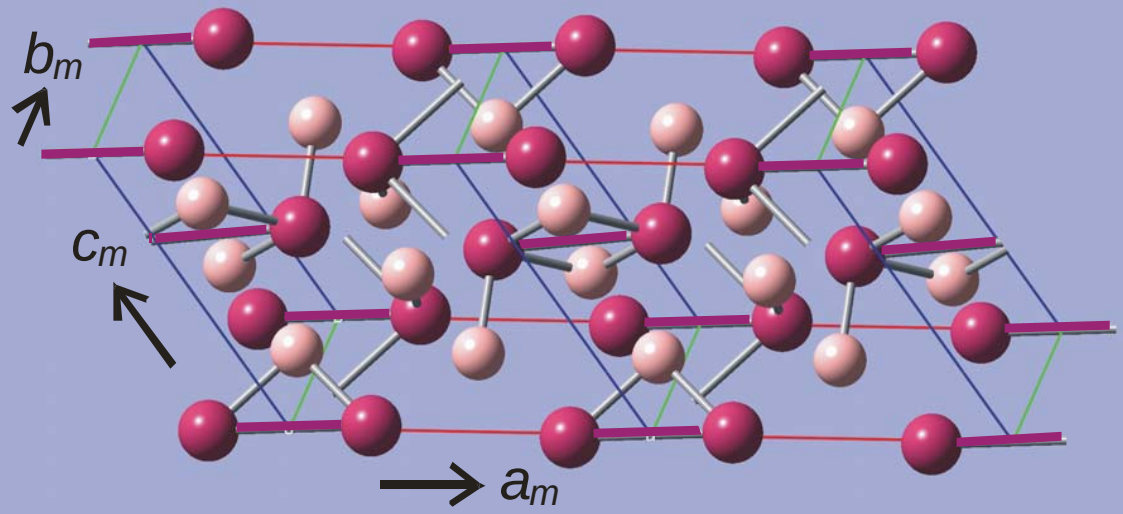
Important Features in a Diffraction Pattern

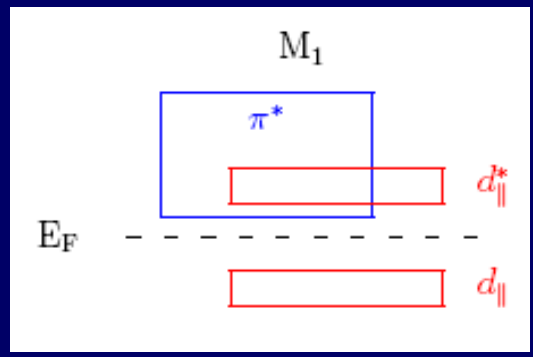


- **Intensity**
  incoherent thermal motion
  coherent lattice vibrations
  phase transitions
- **Position**
  lattice expansion
  or contraction
- **Width & line shape**
  dynamical inhomogeneity
  crystallite size

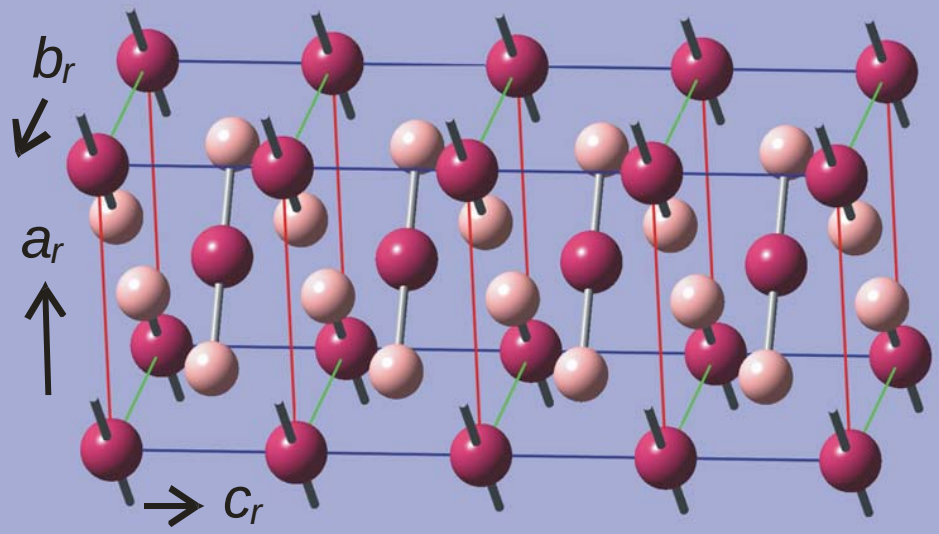
X-ray: Bargheer, Zhavoronkov, Woerner, Elsaesser *ChemPhysChem* **7**, 783 (2006)
UEC: Yang, Gedik, Zewail *J. Phys. Chem. C* **111**, 4889 (2007)

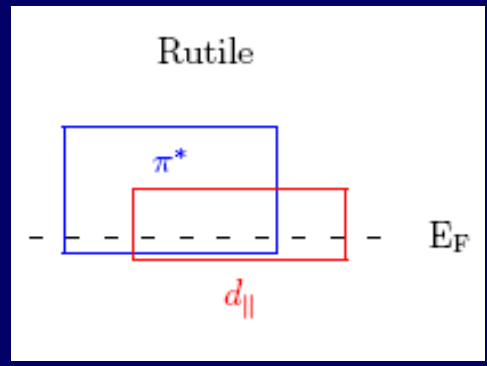
monoclinic phase

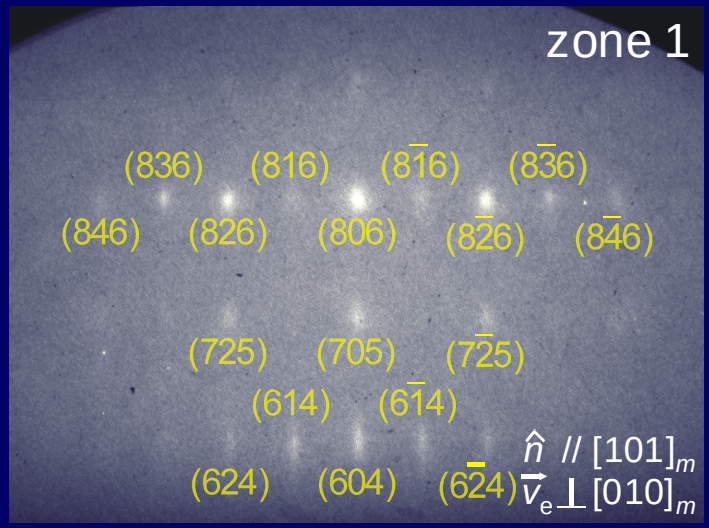


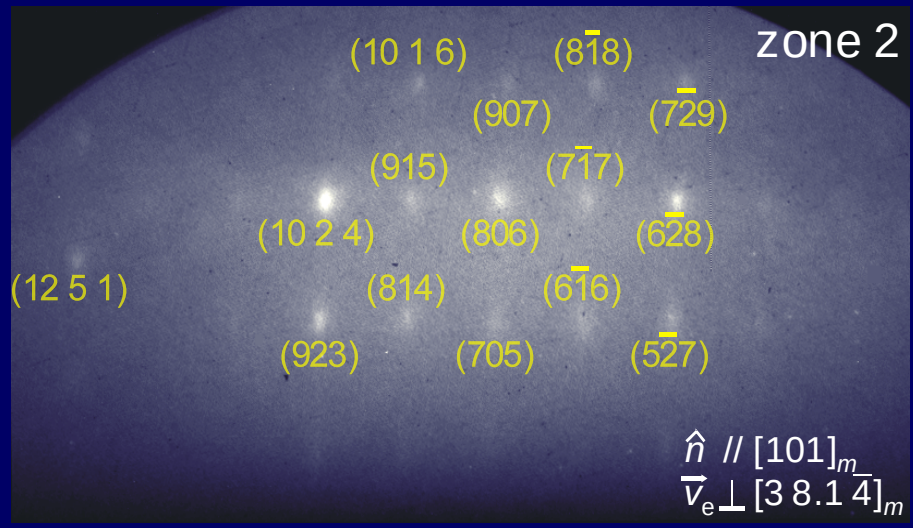


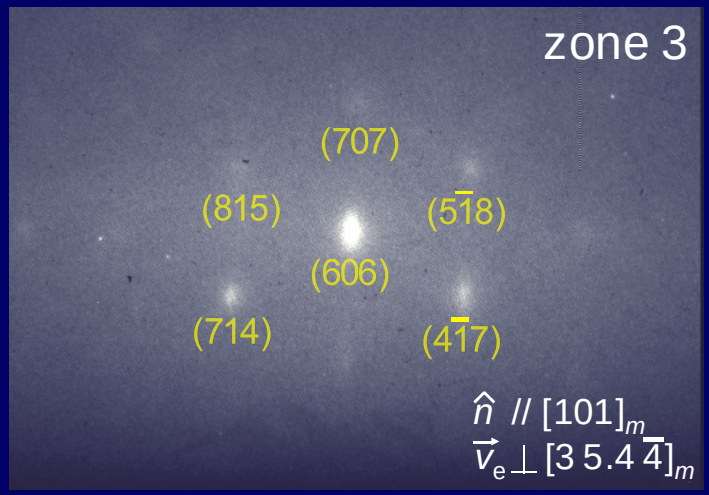
tetragonal (rutile) phase

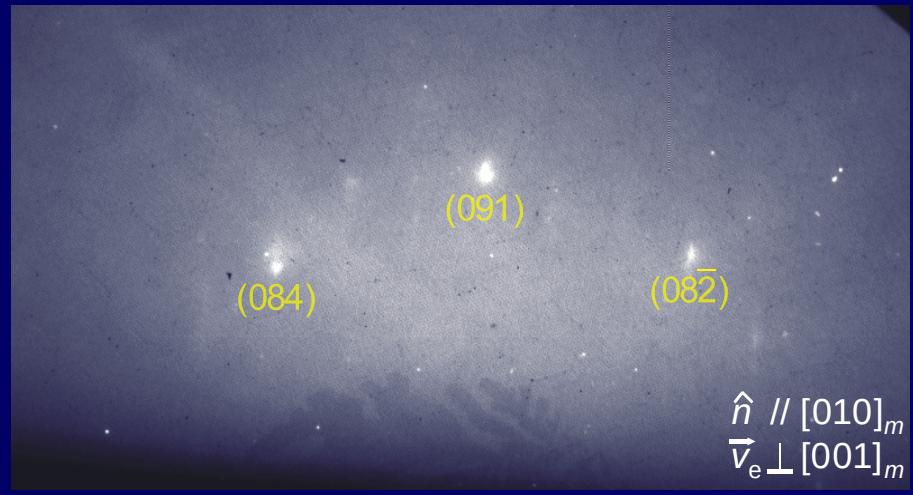




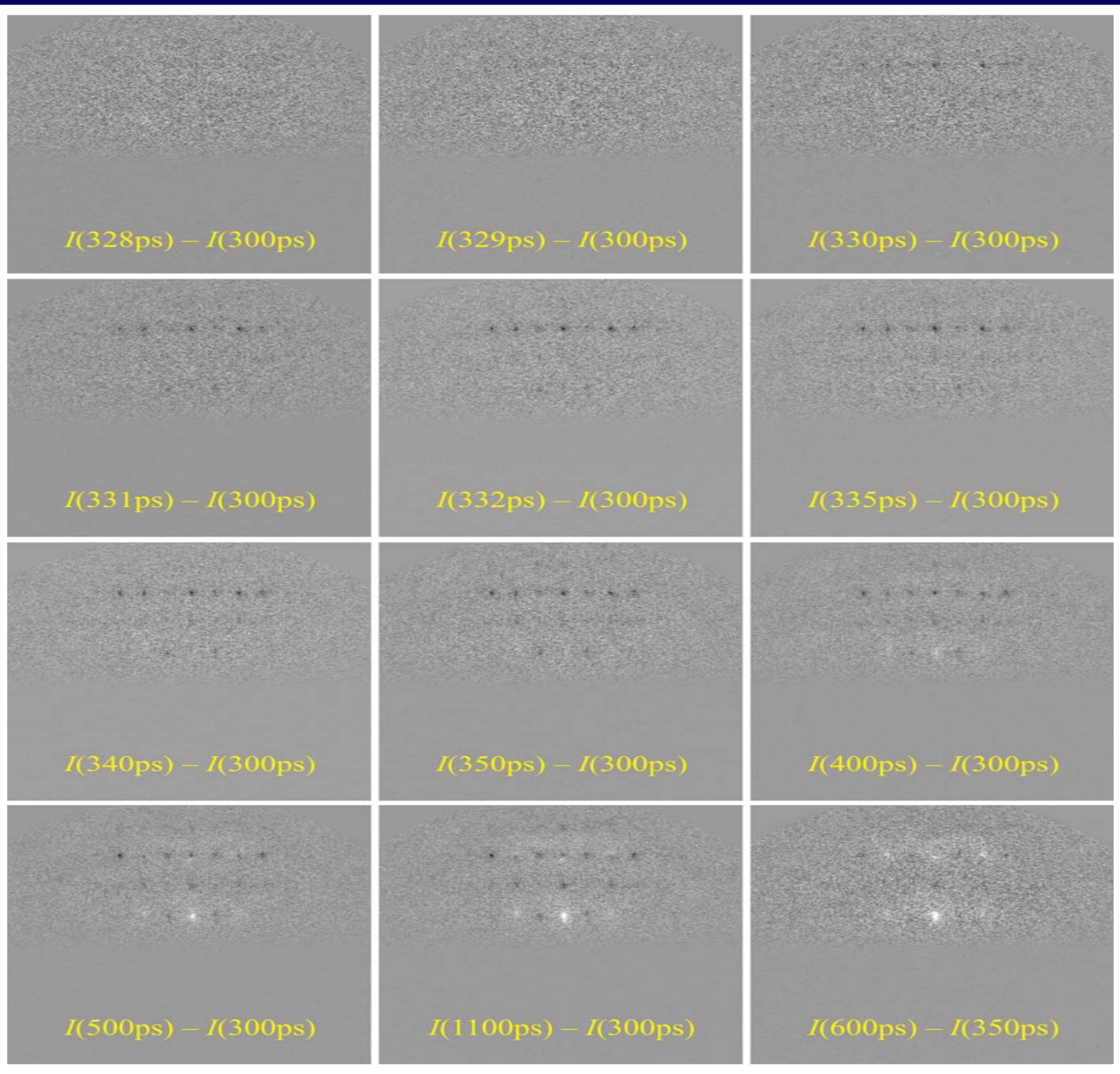

zone 1
(836) (816) (8$\bar{1}$6) (8$\bar{3}$6)
(846) (826) (806) (8$\bar{2}$6) (8$\bar{4}$6)
(725) (705) (7$\bar{2}$5)
(614) (6$\bar{1}$4)
(624) (604) (6$\bar{2}$4)
$\hat{n}$ // [101]$_m$
$\vec{v}_e \perp$ [010]$_m$


zone 2
(10 1 6) (8$\bar{1}$8)
(907) (7$\bar{2}$9)
(915) (7$\bar{1}$7)
(10 2 4) (806) (6$\bar{2}$8)
(12 5 1) (8$\bar{1}$4) (6$\bar{1}$6)
(923) (705) (5$\bar{2}$7)
$\hat{n}$ // [101]$_m$
$\vec{v}_e \perp$ [3 8.1 $\bar{4}$]$_m$

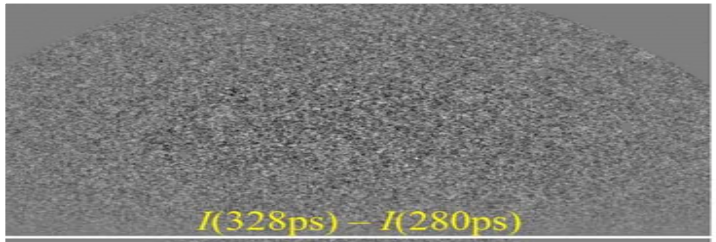

zone 3
(707)
(815) (5$\bar{1}$8)
(606)
(714) (4$\bar{1}$7)
$\hat{n}$ // [101]$_m$
$\vec{v}_e \perp$ [3 5.4 $\bar{4}$]$_m$

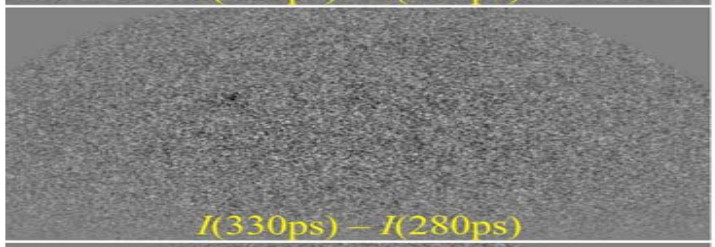

(091)
(084) (08$\bar{2}$)
$\hat{n}$ // [010]$_m$
$\vec{v}_e \perp$ [001]$_m$

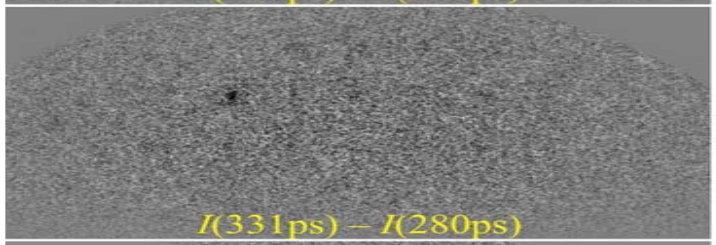
Zone axis 1

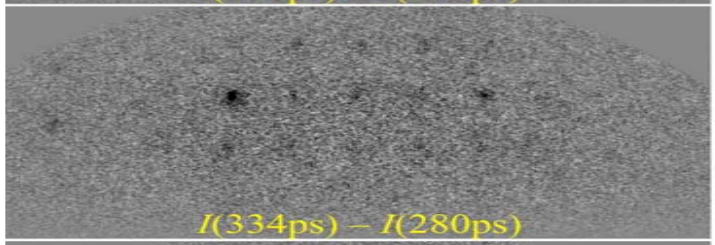

I(328ps) – I(300ps)
I(329ps) – I(300ps)
I(330ps) – I(300ps)
I(331ps) – I(300ps)
I(332ps) – I(300ps)
I(335ps) – I(300ps)
I(340ps) – I(300ps)
I(350ps) – I(300ps)
I(400ps) – I(300ps)
I(500ps) – I(300ps)
I(1100ps) – I(300ps)
I(600ps) – I(350ps)

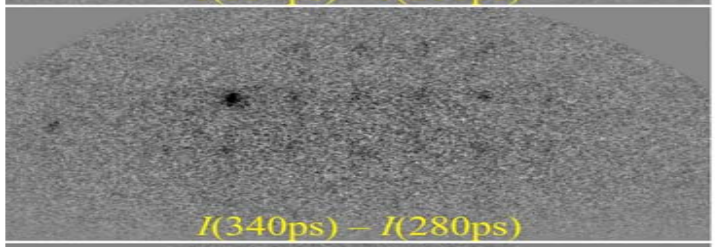
Zone axis 2

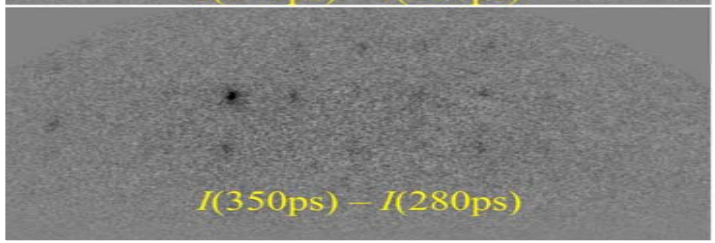

I(328ps) – I(280ps)

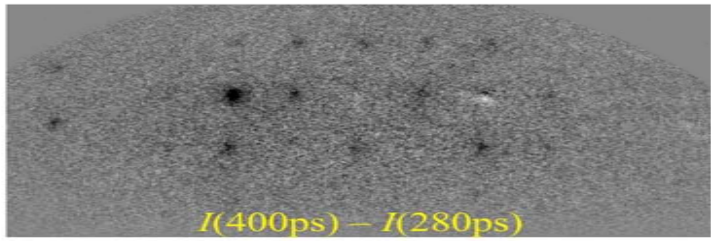

I(330ps) – I(280ps)

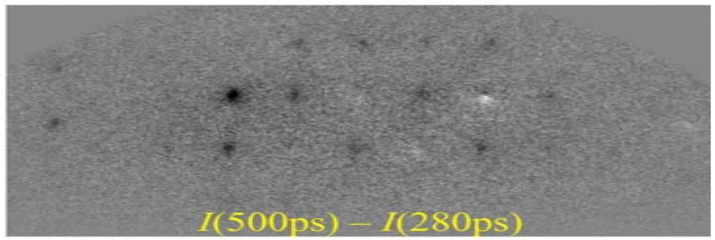

I(331ps) – I(280ps)

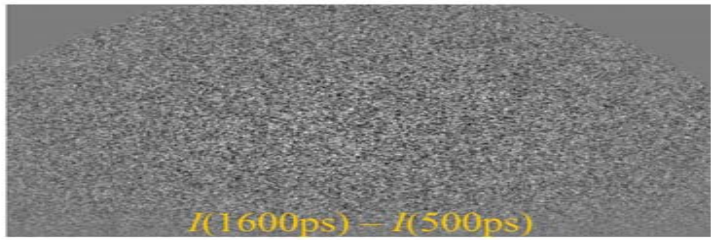

I(334ps) – I(280ps)

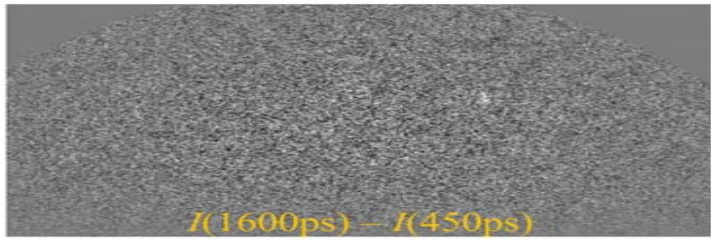

I(340ps) – I(280ps)

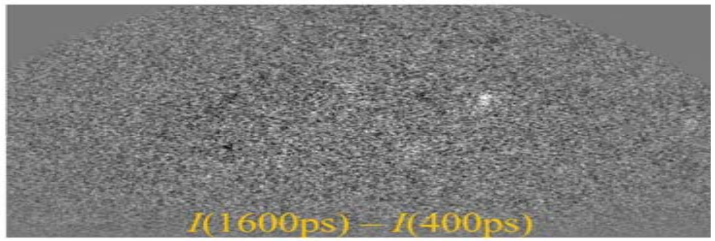

I(350ps) – I(280ps)


I(400ps) – I(280ps)


I(500ps) – I(280ps)

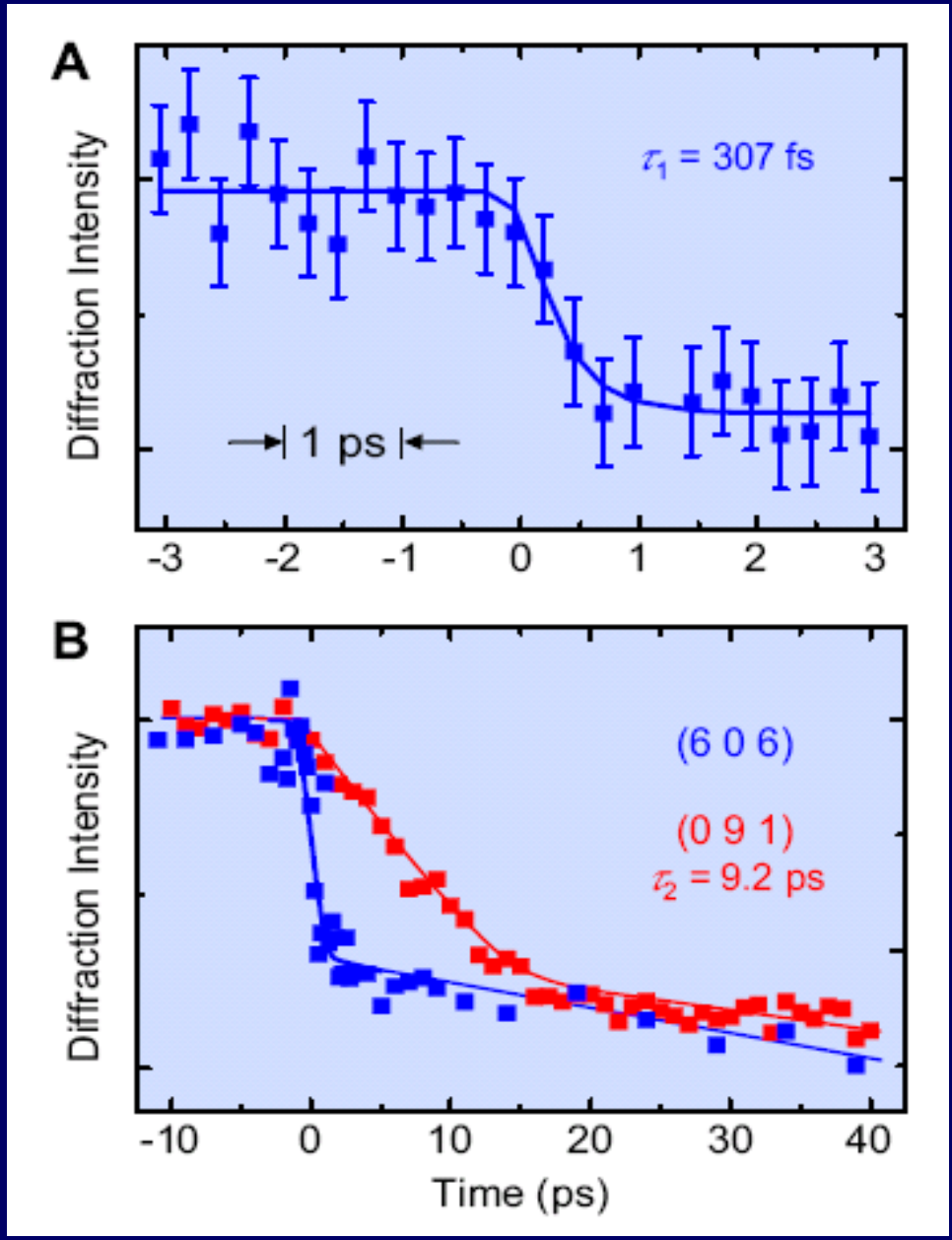

I(1600ps) – I(500ps)


I(1600ps) – I(450ps)

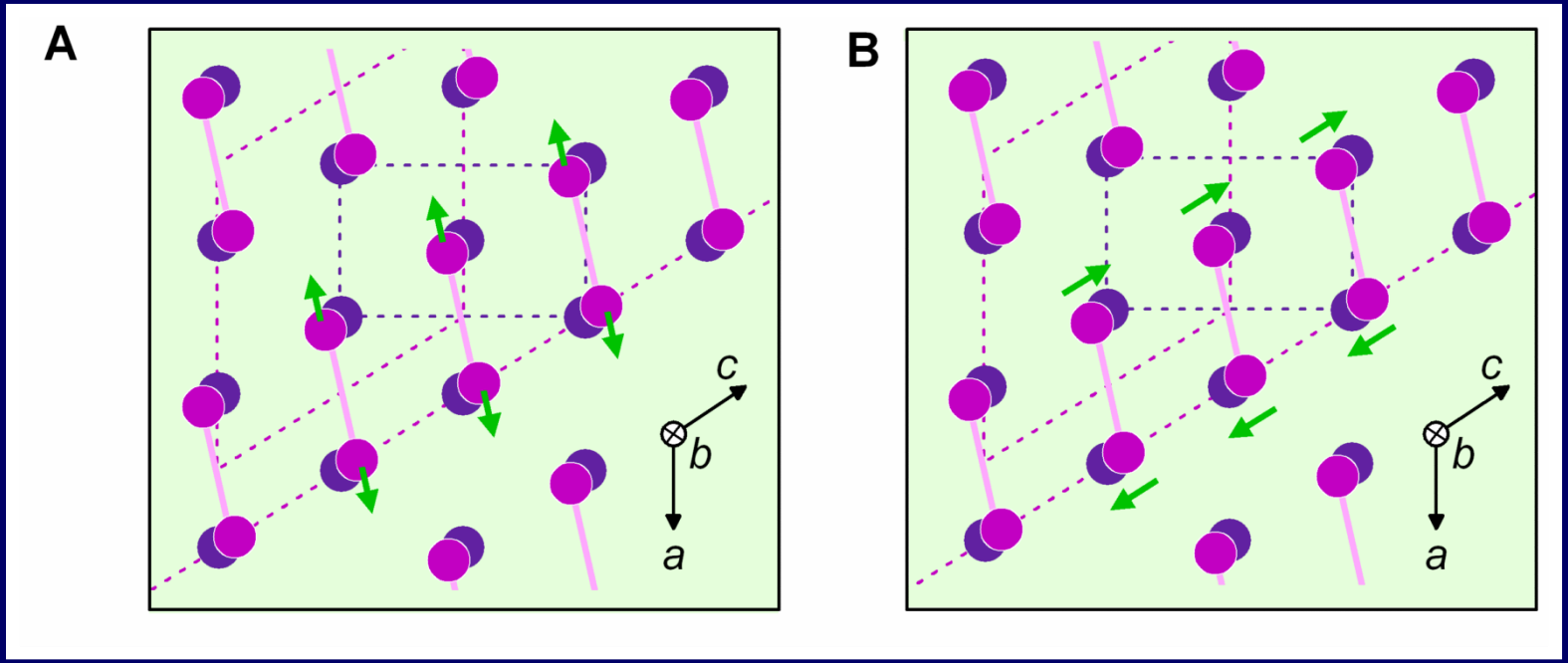

I(1600ps) – I(400ps)

Initial dynamics

fs dynamics	ps dynamics
(6 0 6) (8 0 6) (8 2 6) (8 -2 6) (8 4 6) (8 -4 6) (7 1 4) (4 -1 7) (10 2 4) (6 -2 8)	(0 9 1) (0 8 4) (0 8 -2)



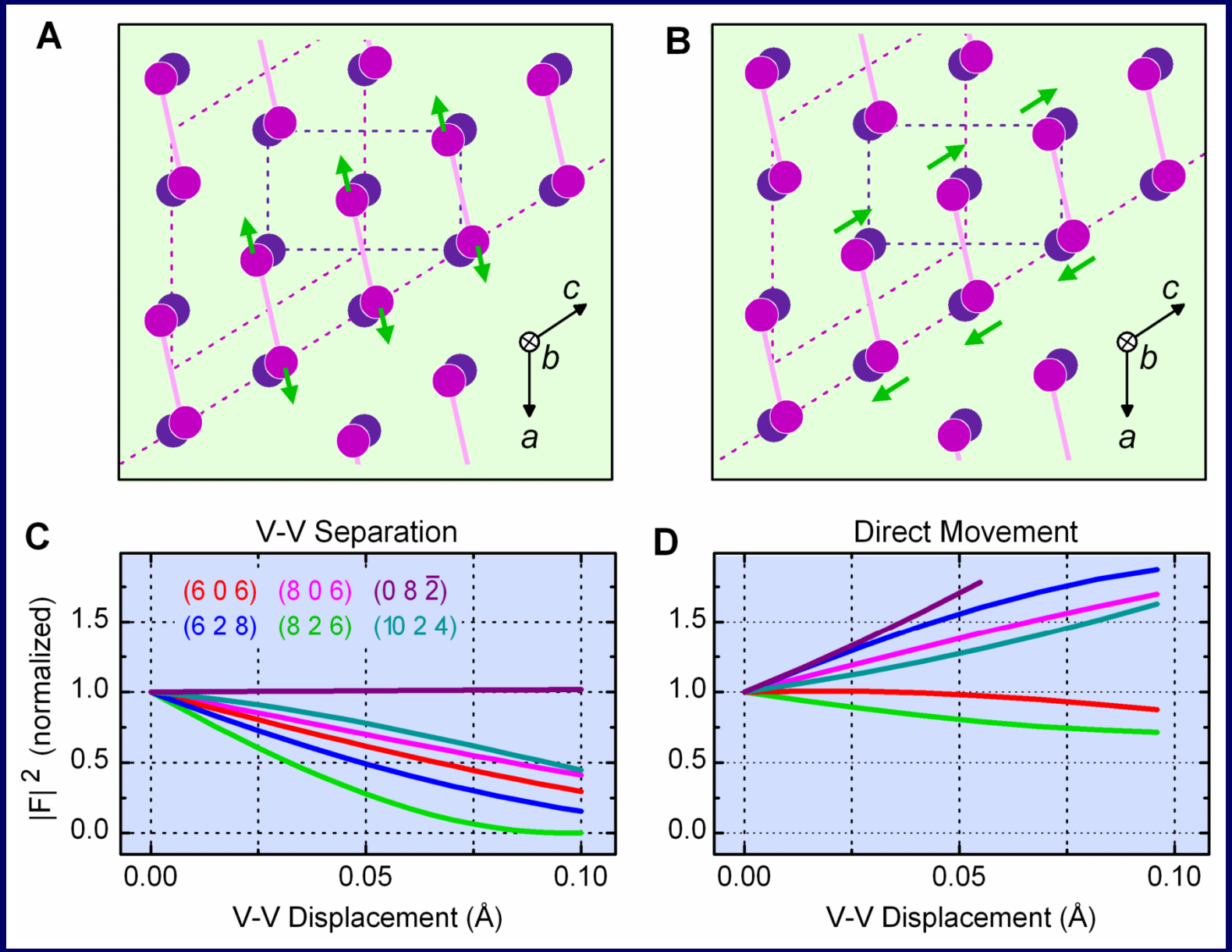
Pathways for Atomic Movements



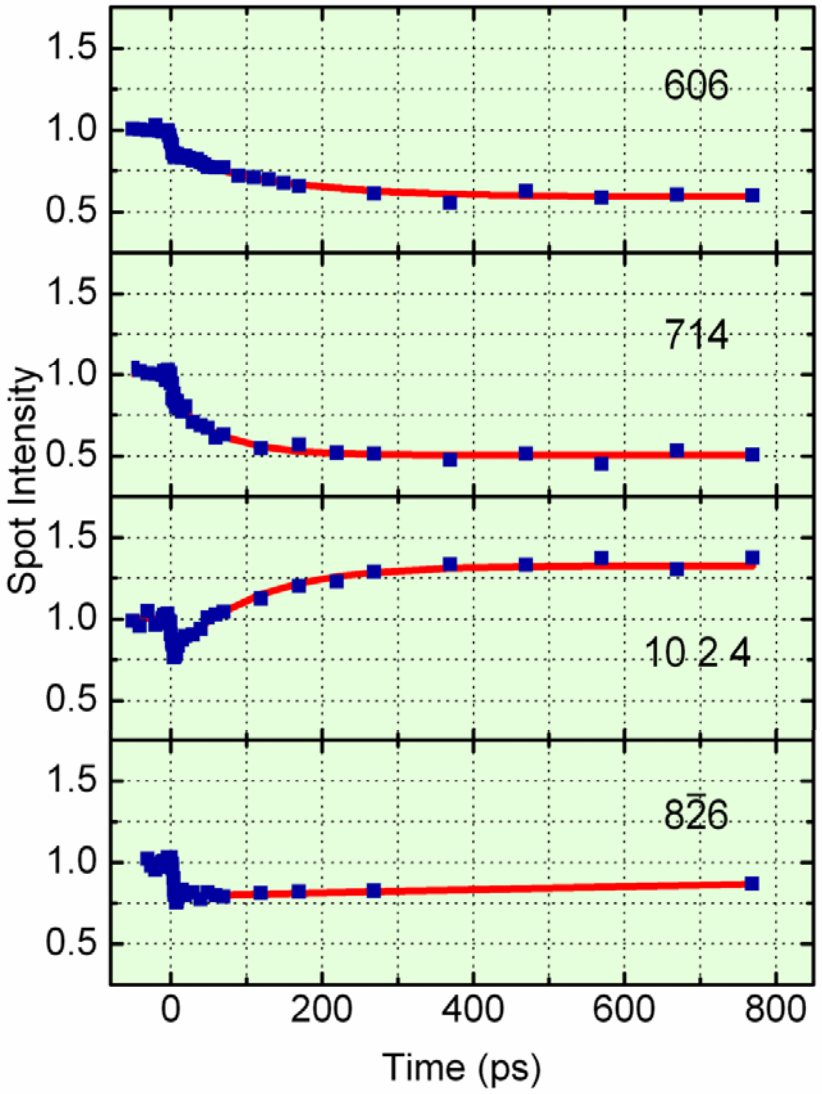
$$F(hkl) = \sum_j f_j \exp\left[-2\pi i\,(hkl)\cdot(xyz)_j\right]$$

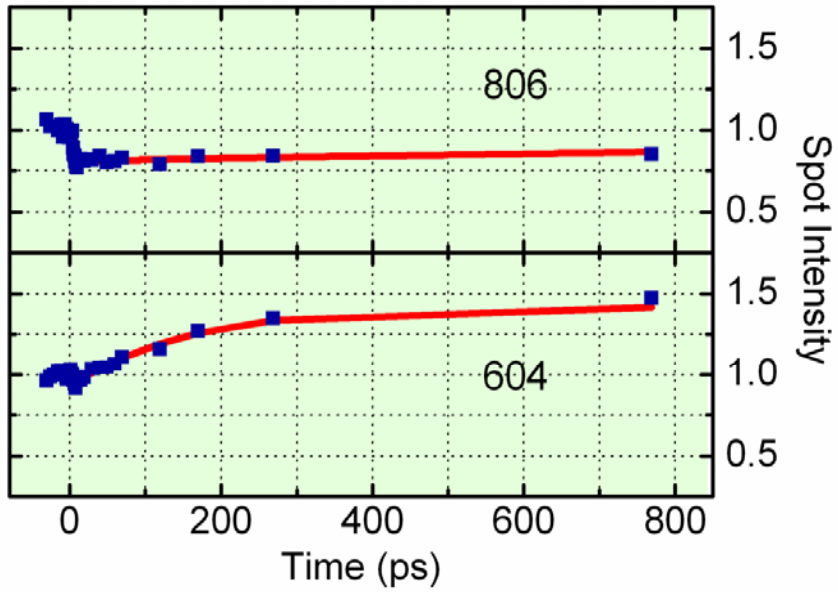
$$I(hkl) \propto \left|F(hkl)\right|^2$$

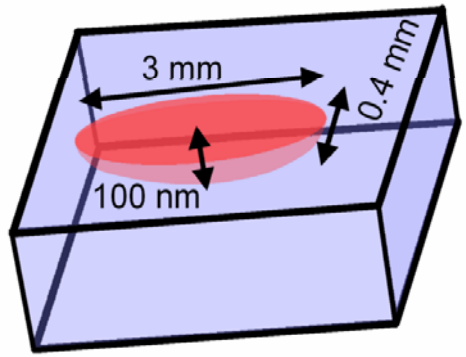
Pathways for Atomic Movements

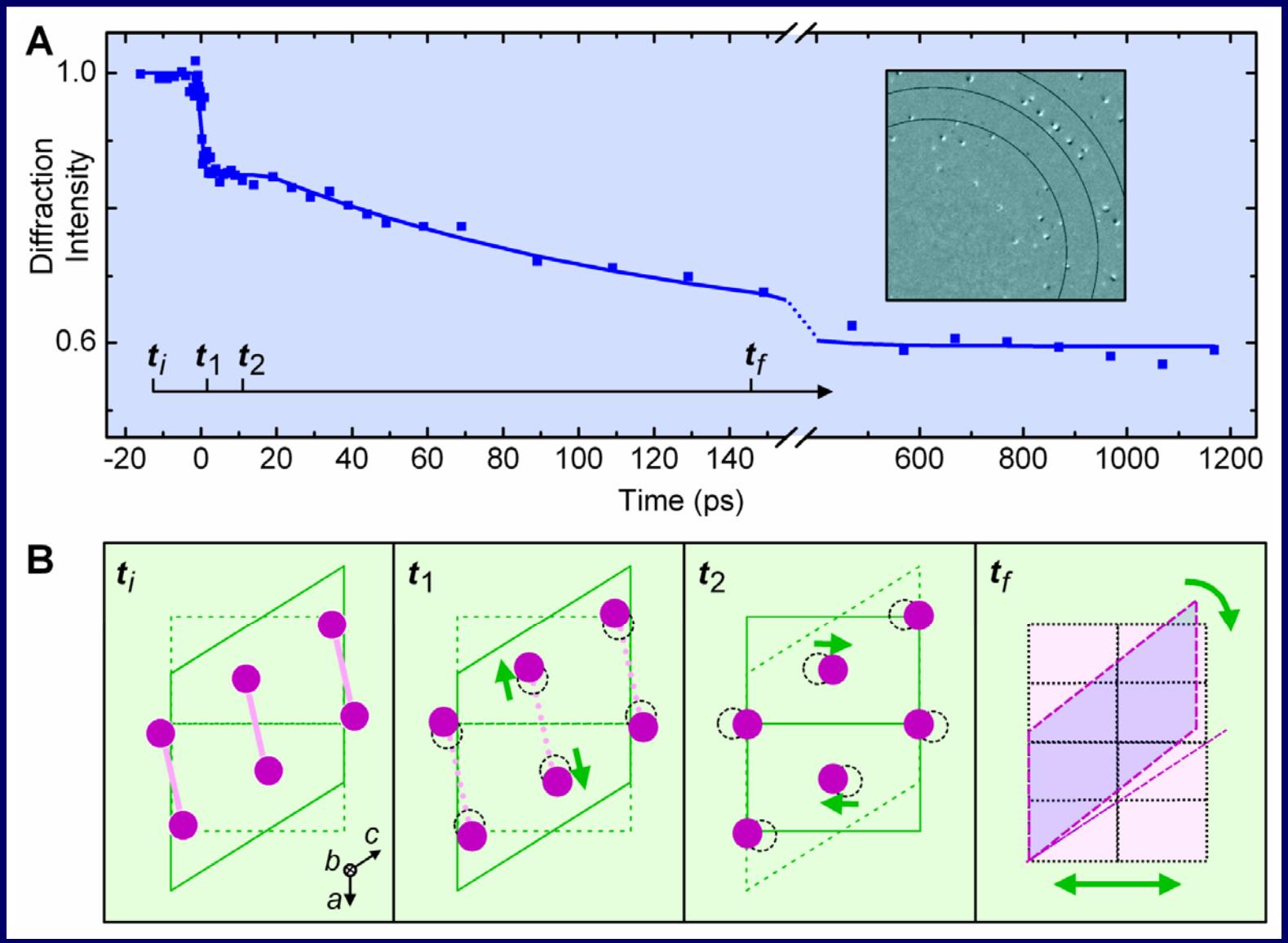


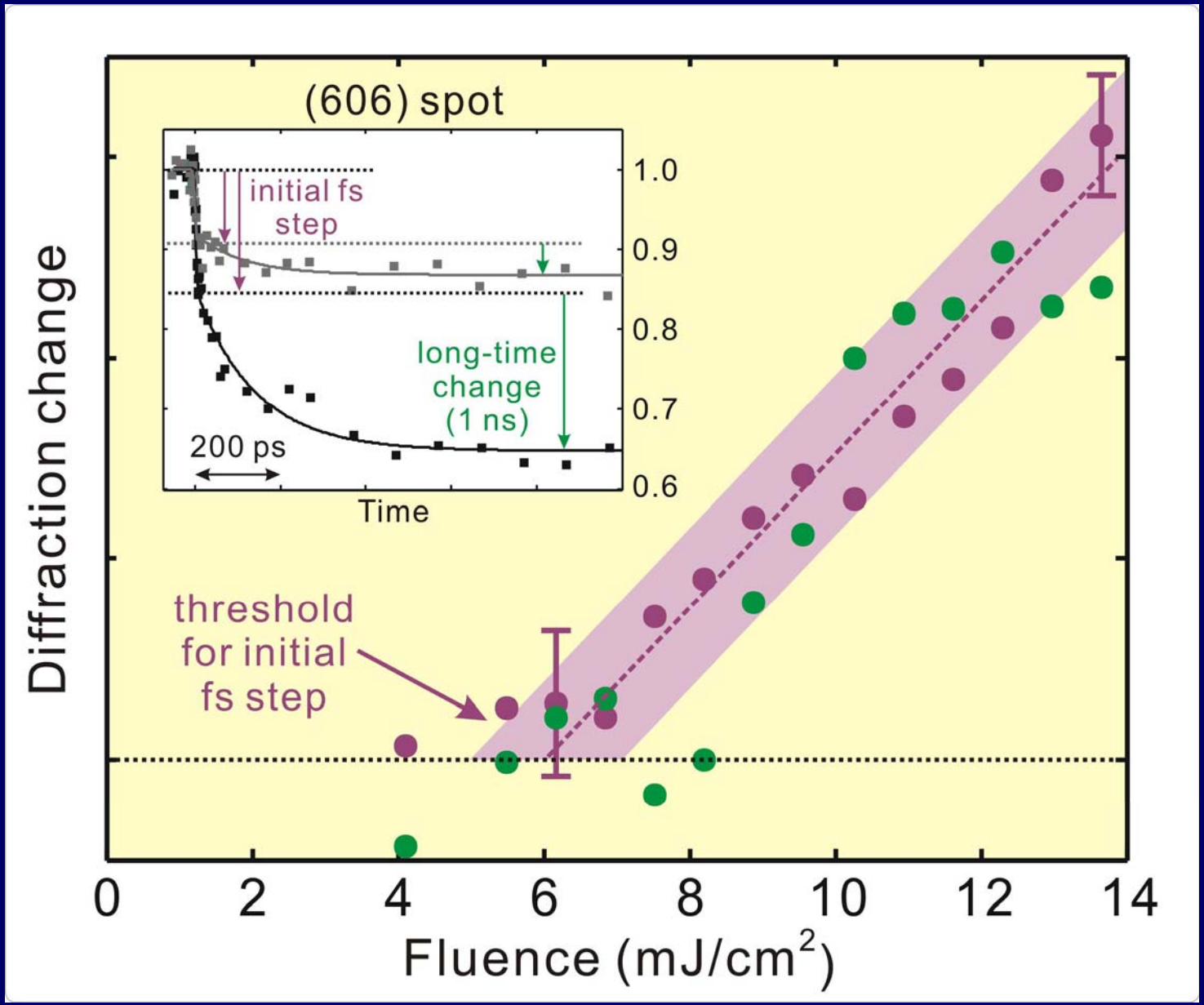
Long-time Behavior of Different Bragg Spots





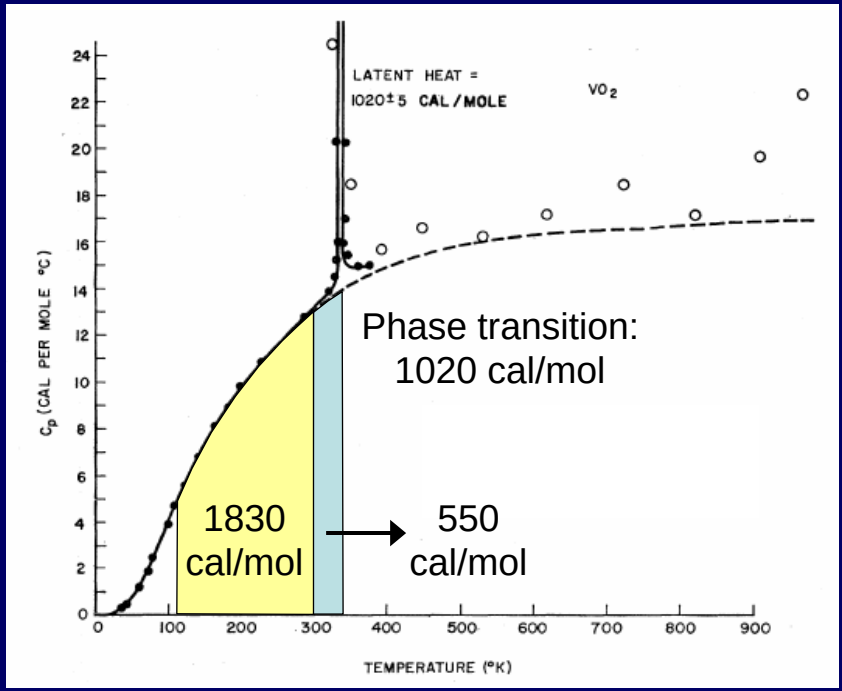



A
1.0
0.6
Diffraction Intensity
t_i t_1 t_2
t_f
-20 0 20 40 60 80 100 120 140 600 800 1000 1200
Time (ps)
B
t_i
t_1
t_2
t_f
c
b
a



Energy density threshold = 0.4 ± 0.1 J/mm^3

Temperature Dependence of Threshold



Thermodynamics

energy required for
the phase transition

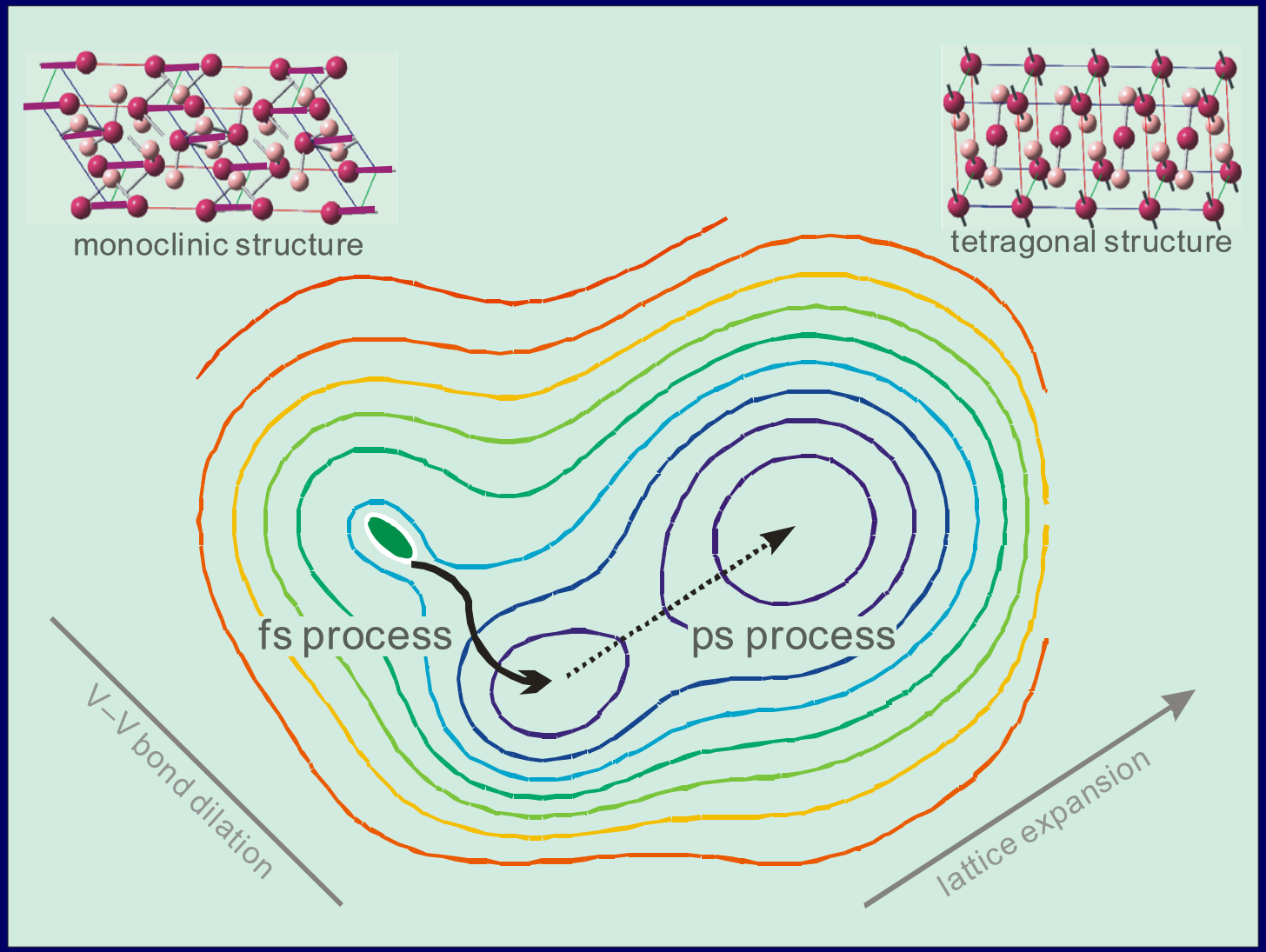
0.38 J/mm^3 @ 300 K
0.80 J/mm^3 @ 110 K

Dynamics studies

same intensity decrease
(~30% drop)

@ 12.3 mJ/cm^2, 300 K
@ 18.4 mJ/cm^2, 110 K

Stepwise Pathway during Phase Transition



Conclusions

- UEC is capable of resolving the pathway in a phase transformation and capturing transition-state or intermediate structure(s).

- Stages in the photoinduced structural phase transformation in VO_2
  (1) the (intra-cell) breakage of the V-V bond on the fs time scale
  (2) the (intra-cell) atomic movements on the time scale of ~10 ps
  (3) the (inter-cell) lattice organization on the time scale of ~100 ps

- The threshold of laser fluence to initiate the transformation and its temperature dependence coincide well with the thermal energy required for the phase transition → the transformation pathways in thermodynamics and dynamics study to be similar.