Science and Engineering of Laser Interactions with Matter

The University of Virginia

NSU NORFOLK STATE UNIVERSITY

Jefferson Lab

Laser/Surface Dynamics

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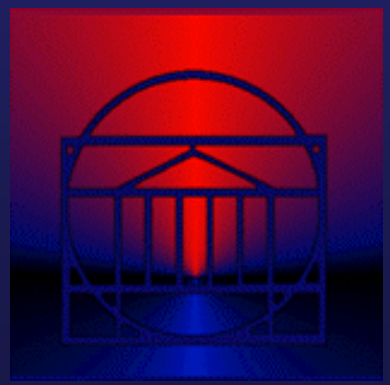
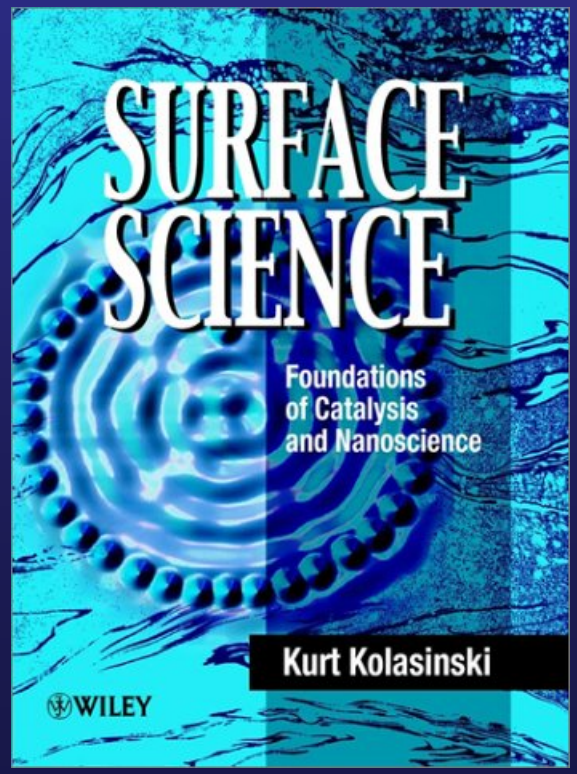
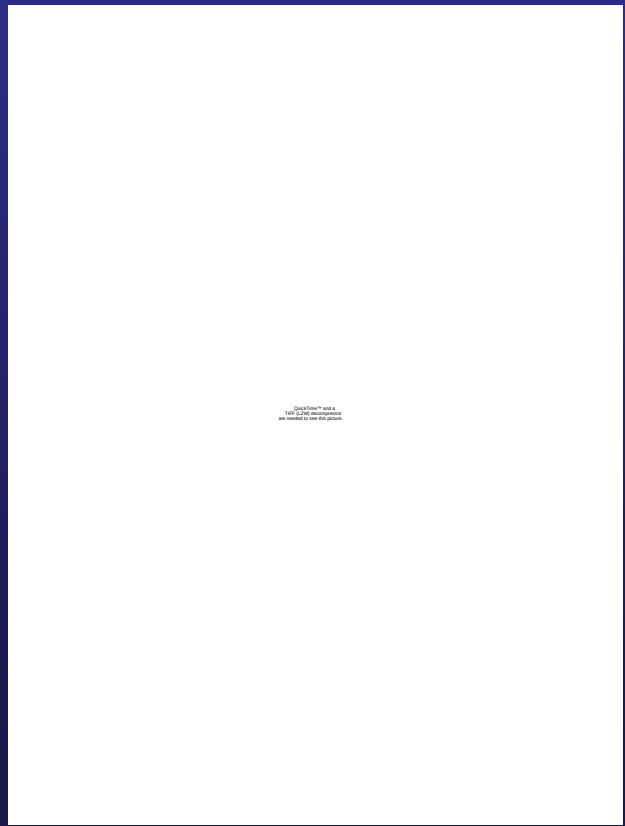




CAMOS

Center for Atomic, Molecular, and Optical Science

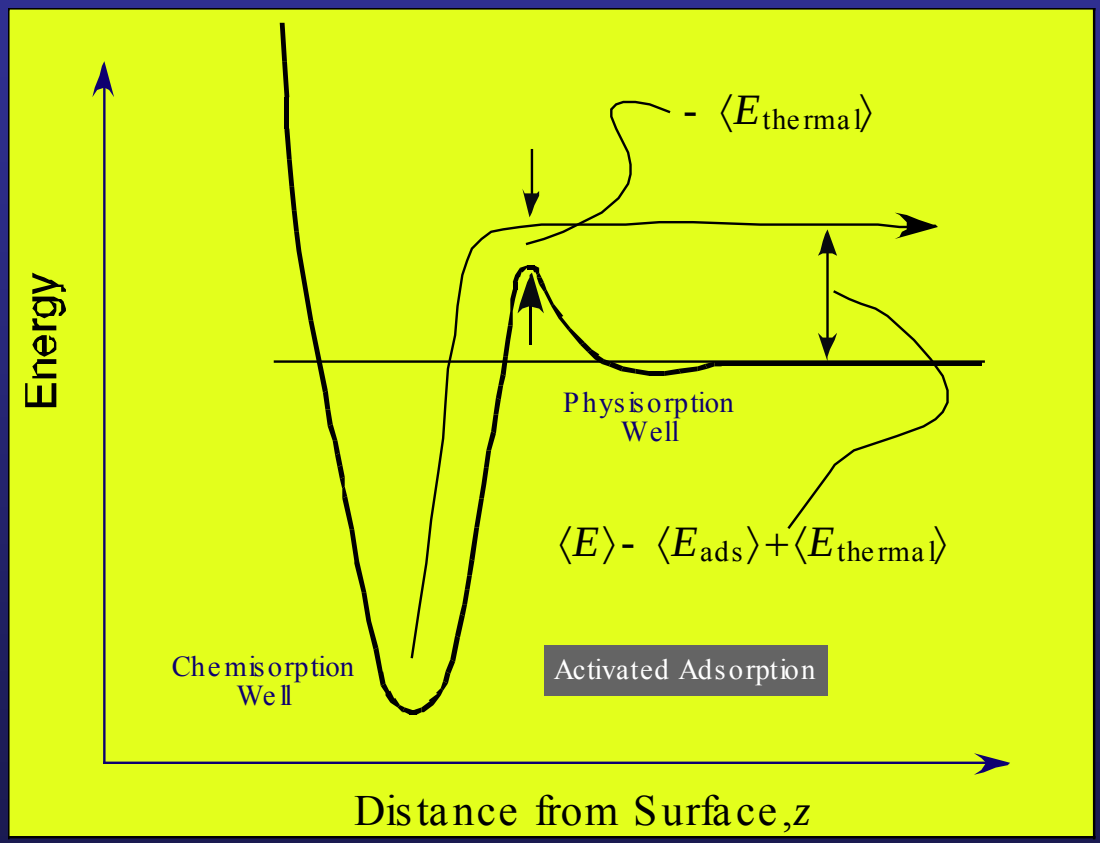
- Ultrafast Laser Facility
- Ian Harrison, UVa Chemistry
  Kristy De Witt, Leticia Valadez, Heather Abbott
- Bob Jones, UVa Physics
- Brooks Pate, UVa Chemistry
  Pam Crum



Lasers to Study Thermal & Stimulated Surface Chemistry

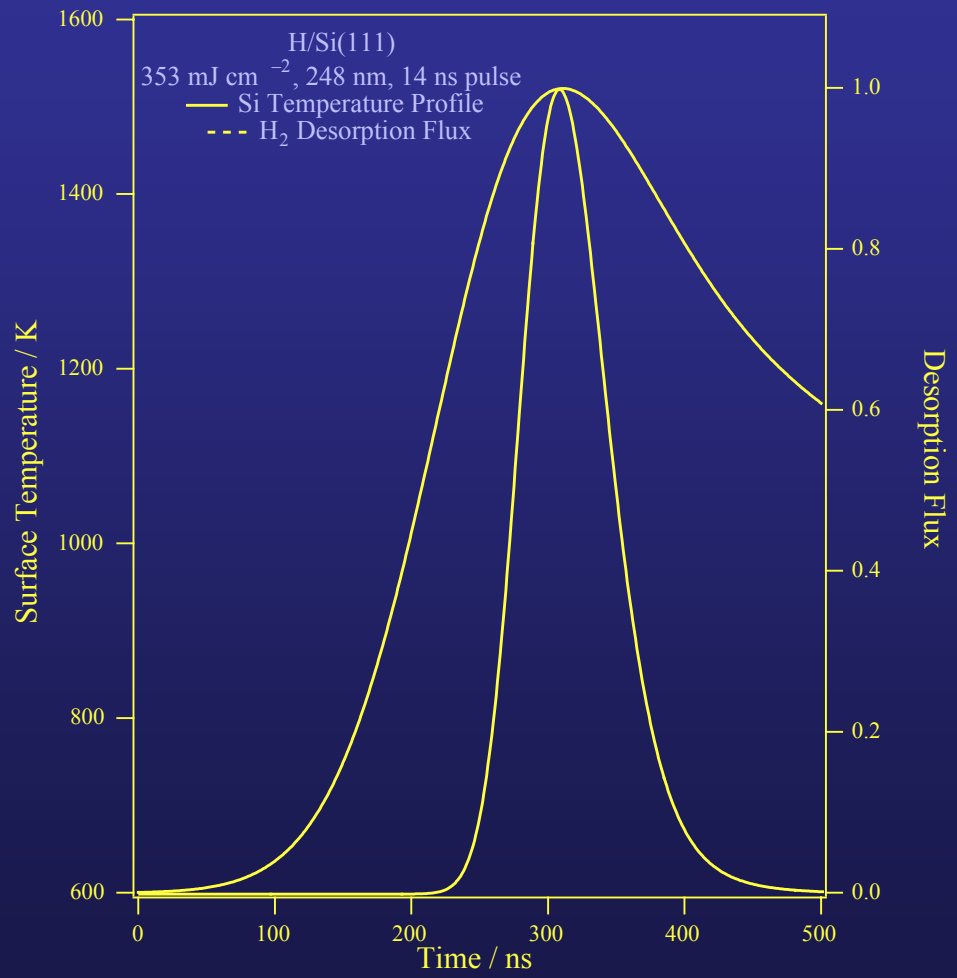
- Laser induced thermal desorption
- Desorption induced by electronic transitions
- Desorption induced by multiple electronic transitions
- Probing the role of vibrational relaxation dynamics at surfaces
- High harmonic generation
- Sum frequency generation
- Resonant laser induced desorption

Thermal Desorption



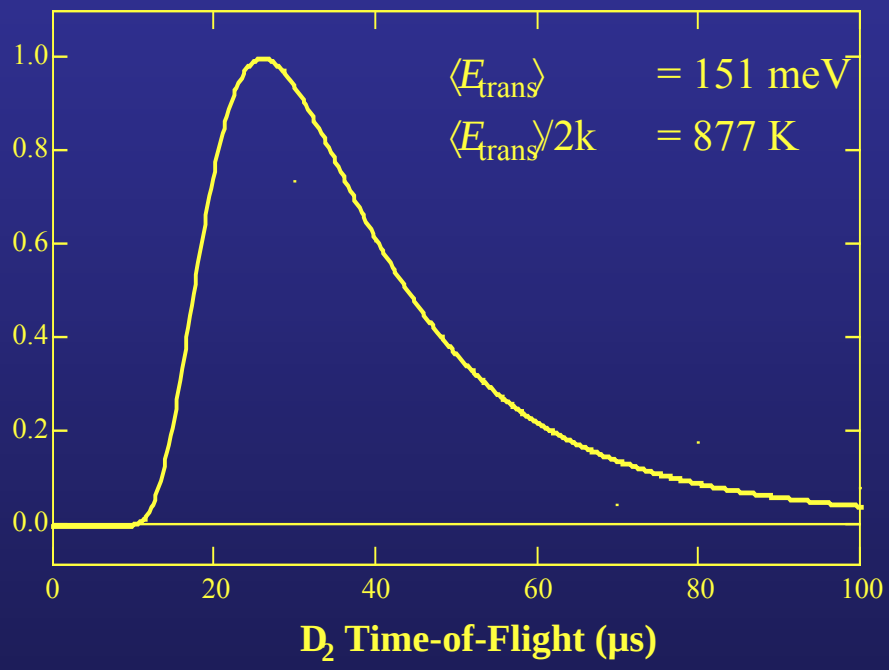
- A Markovian walk up the adsorption well
- Many collisions between molecule and surface

Laser Induced Thermal Desorption (LITD)



- 14 ns, 248 nm pulses lead to a rapid temperature rise
- Well-defined t_0 makes time-of-flight measurements of kinetic energy possible

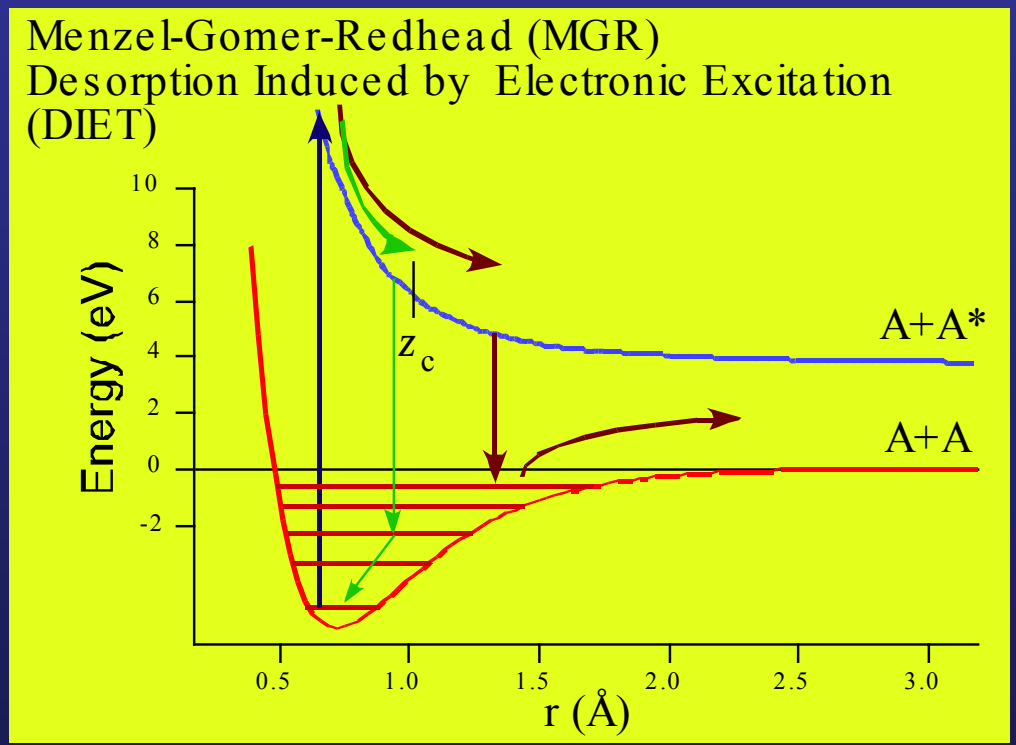
LITD TOF Spectrum D_2/Si(100)



- E_K only slightly above thermal expectation
- Contrasts with small sticking coefficient and large adsorption barrier
- Indicates unusually important role for surface excitations and configuration

Kolasinski, Nessler, de Meijere & Hasselbrink, Phys. Rev. Lett., 1994, **72**, 1356.

Desorption Induced by Electronic Transitions (DIET)

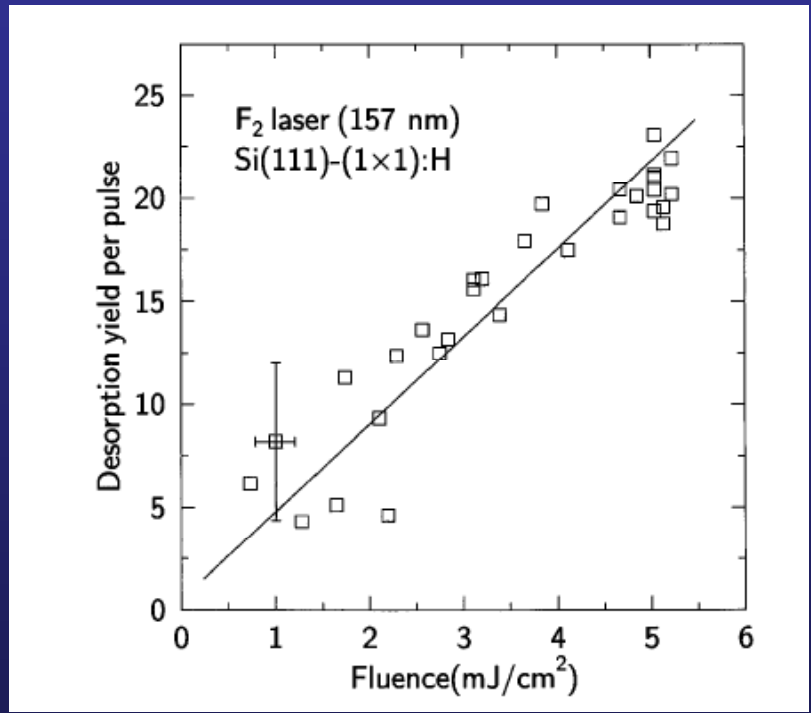


- A single Franck-Condon transition to excited state
- Efficient quenching
- Vibrational relaxation faster than excitation rate
- Excitation from v=0

Menzel & Gomer, J. Chem. Phys., 1964, **41**, 3311.
Redhead, Can. J. Phys., 1964, **42**, 886.

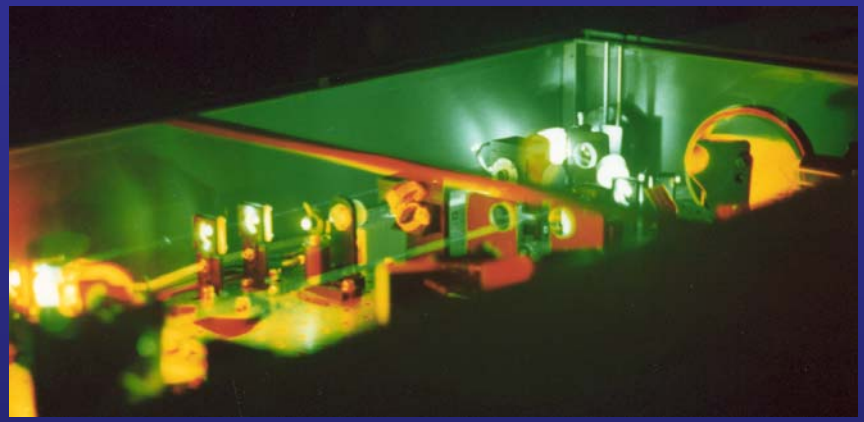
DIET of H/H_2 from Si

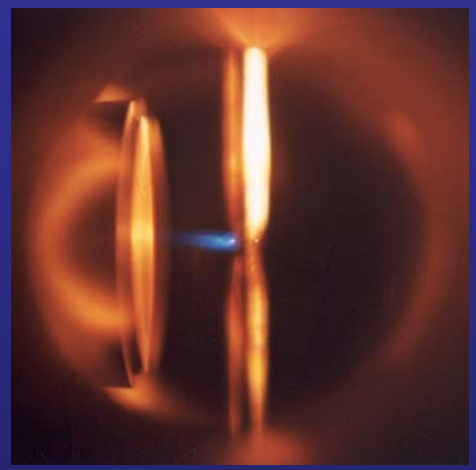
- Direct σ–σ^* excitation at 157 nm leads to H/H_2 desorption
- Linear relationship between number of incident photons and desorbed H/H_2
- Si core excitation at >23 eV leads to H^+ desorption



Pusel, Wetterauer & Hess, Phys. Rev. Lett., 1998, **81**, 645.

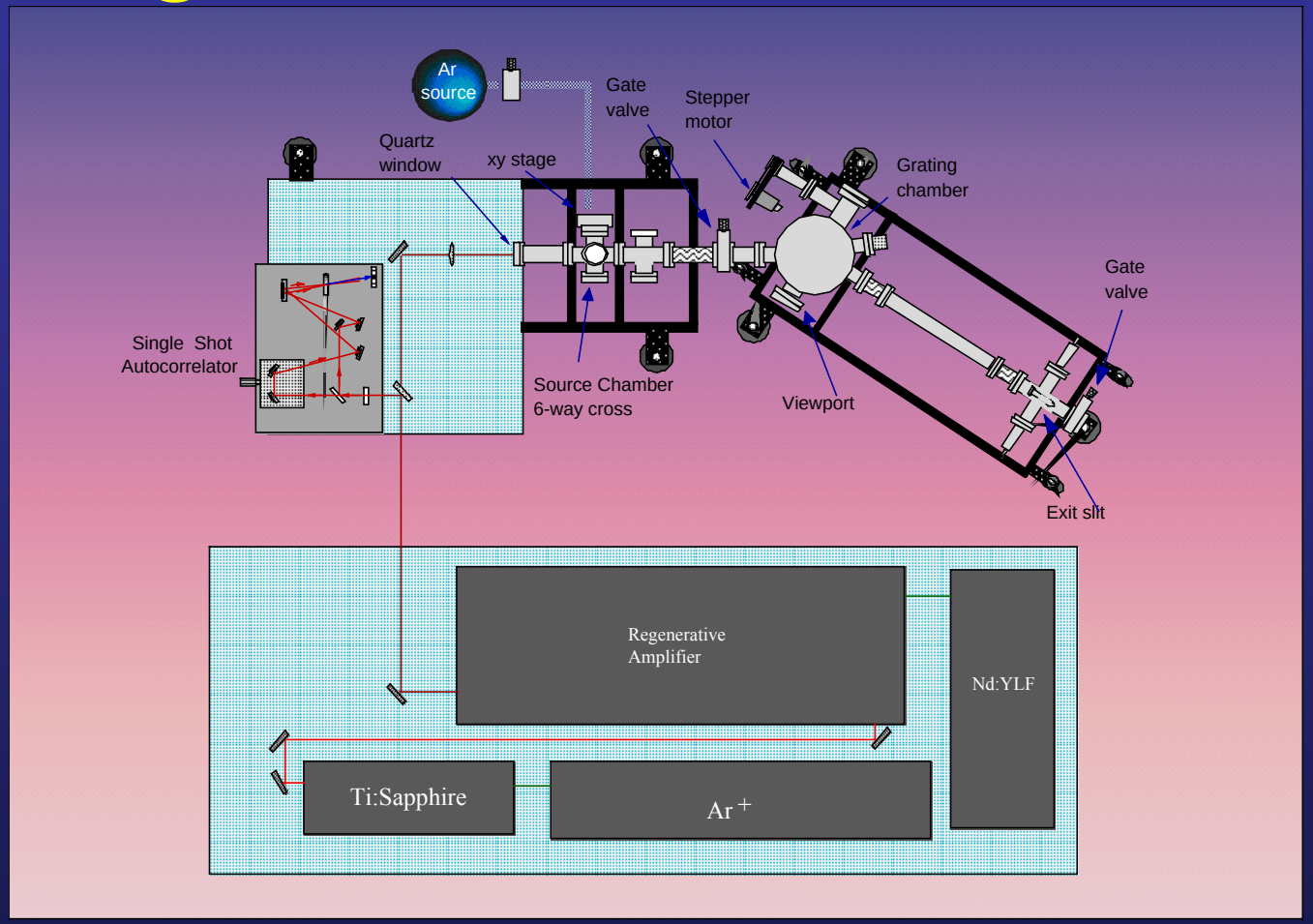
High Harmonic Generation





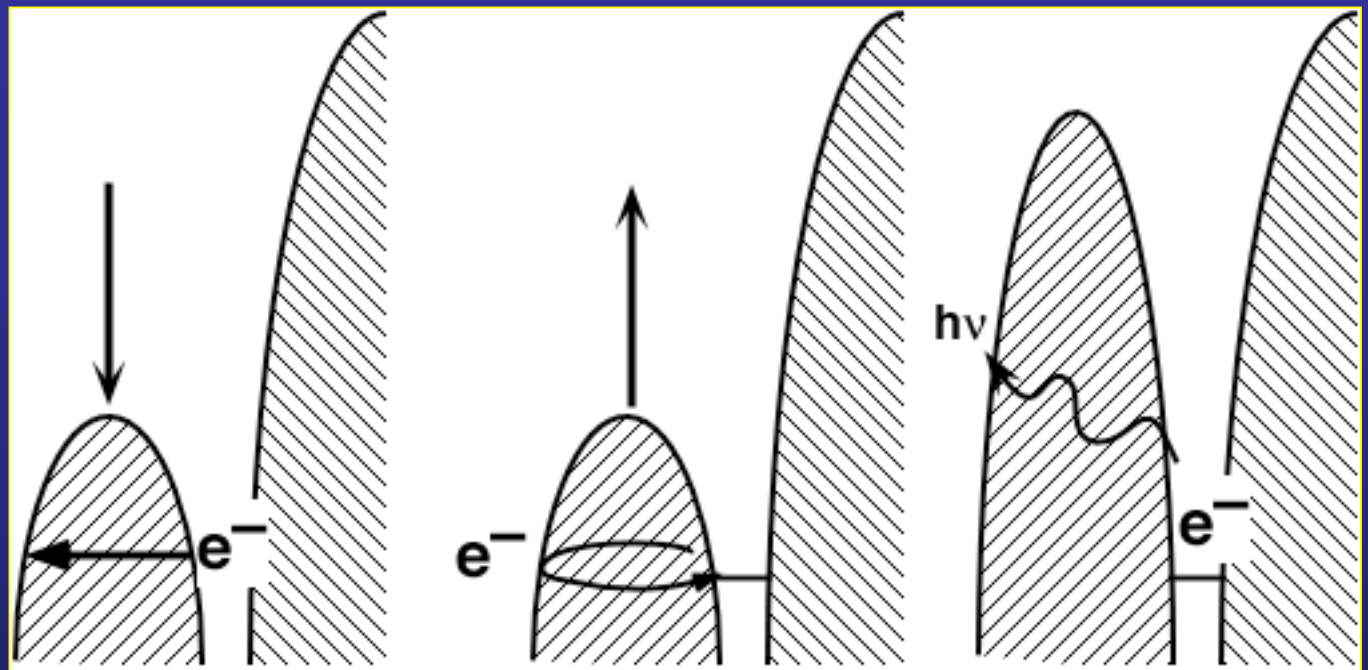
- University of Birmingham, UK
- First use of HHG for time-resolved PL
- First initiation of surface photochemistry with HHG

High Harmonic Generation



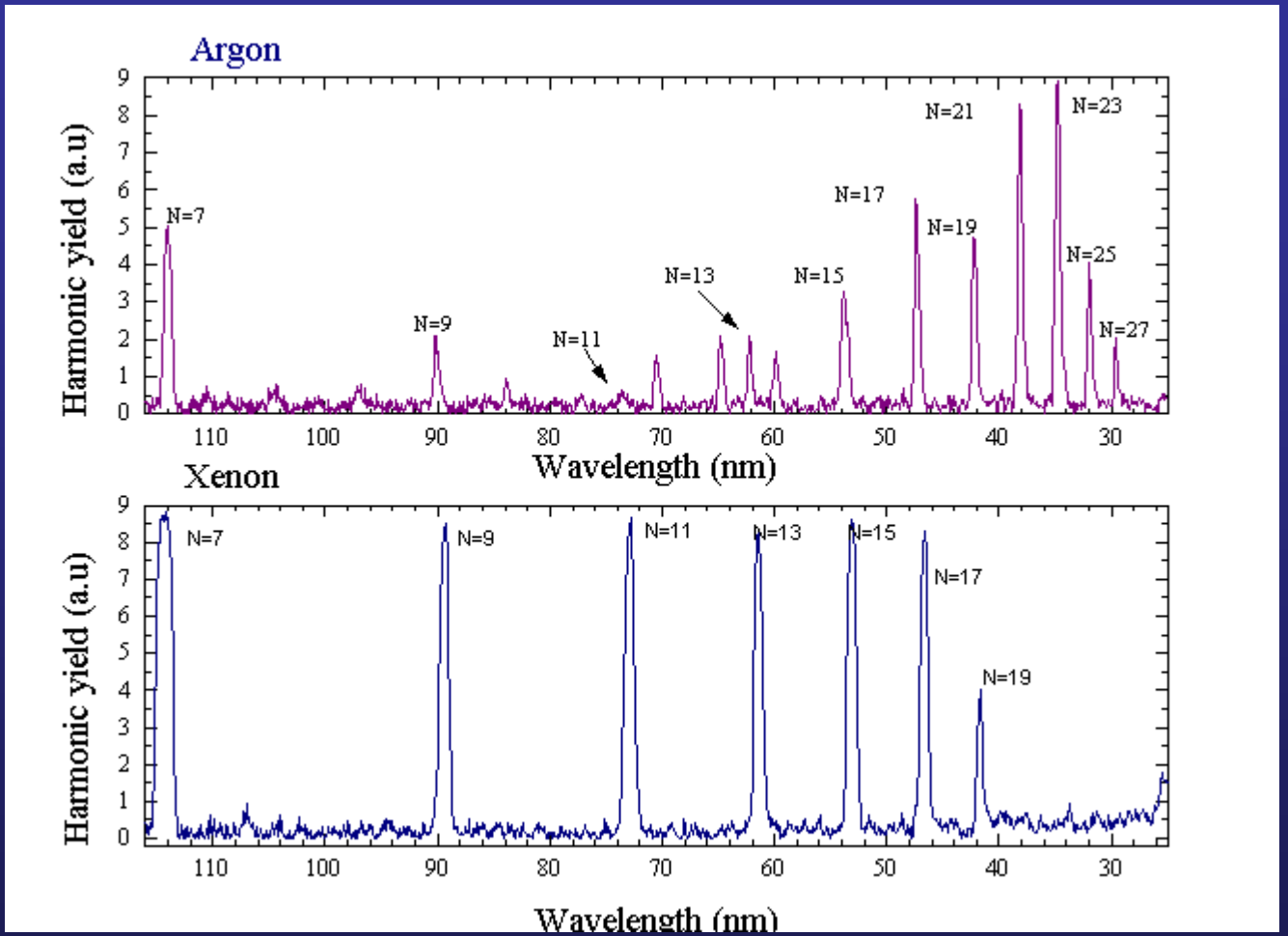
Riedel, Hernández-Pozos, Baggott, Kolasinski, Palmer, and Foord
Rev. Sci. Instrum. **72**, 1977 (2001).

High Harmonic Generation



- Electron tunnels out under the influence of the field
- After tunnelling the electron has zero kinetic energy
- Acceleration due to *quantized* EM field
- Energy released during recombination

HHG in Ar & Xe

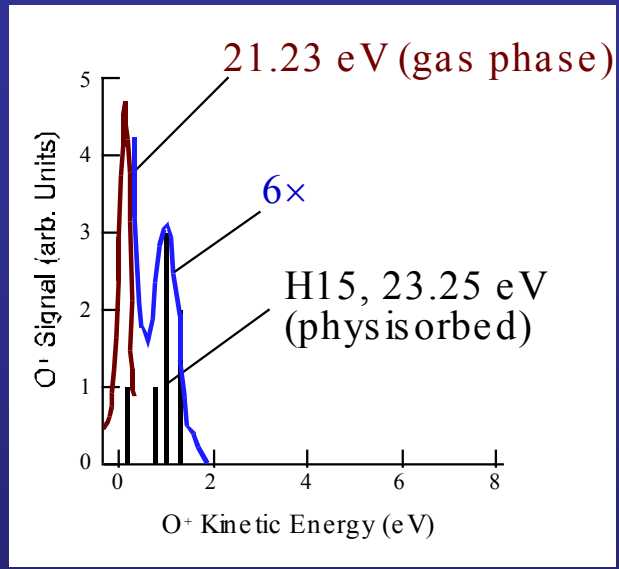


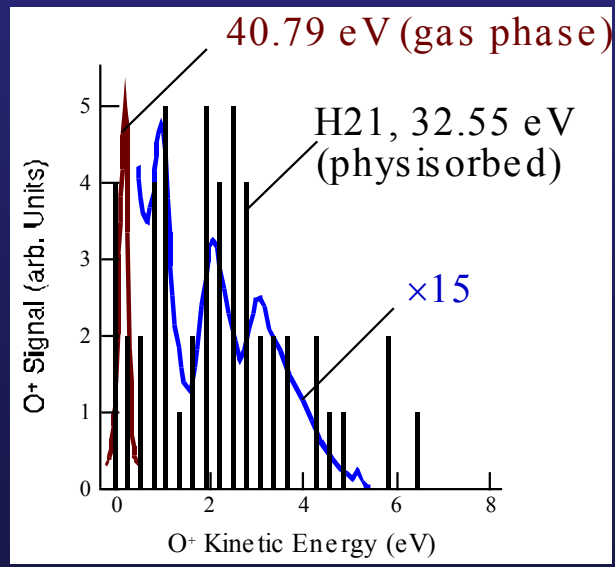
$\lambda = 800$ nm $E_P = 2.2$ mJ $\tau = 150$fs

40 mbar Ar 30 mbar Xe 1 kHz rep. rate

Kinetic Energy Dist of O^+

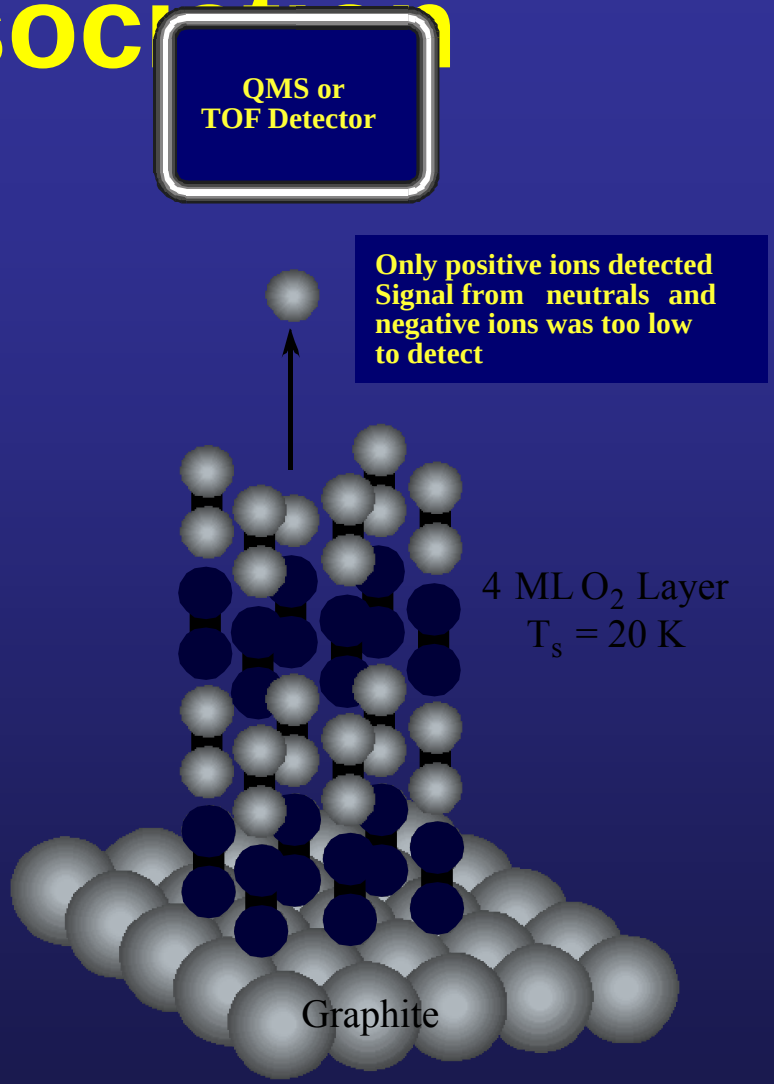
- Excitation at 23.3 and 32.6 eV both lead to slow O^+ centered at ~1 eV
- Only excitation at 32.6 eV leads to fast O^+ centered at ~2.5 eV
- High kinetic energy channel opens above ~30 eV and coincides with increased desorption cross section
- Zero-kinetic energy peak greatly suppressed compared to gas phase





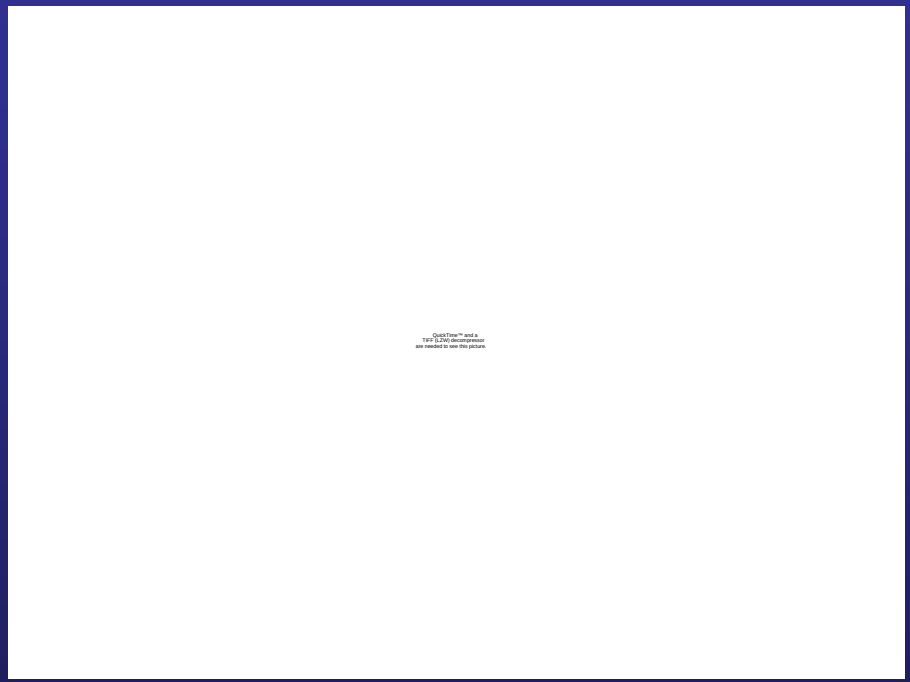
O_2/Graphite Photodissociation

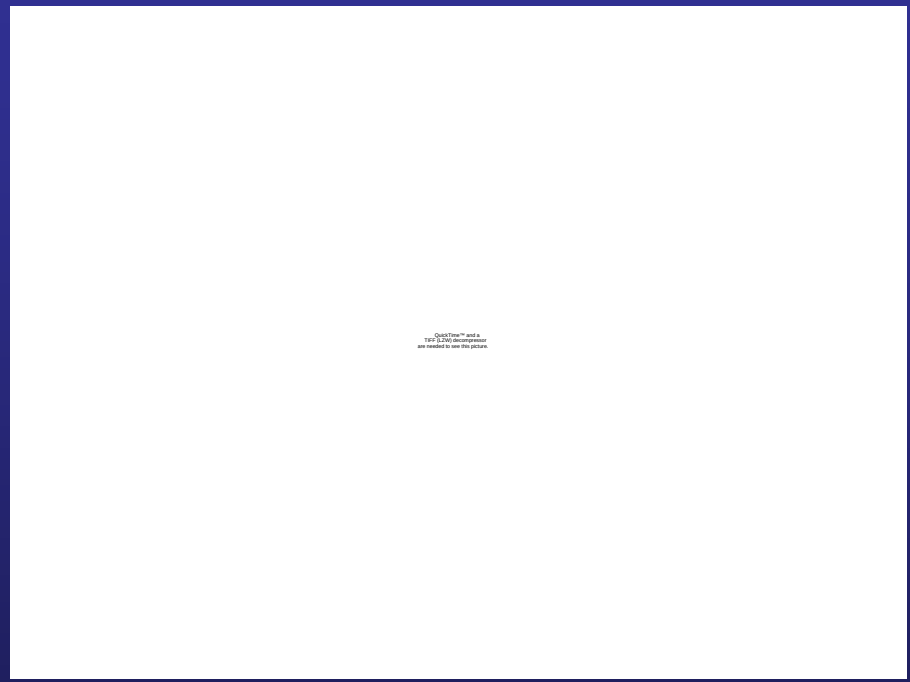
- Direct dissociative ionization
- Physisorption changes dissociative ionization dynamics little
- Recapture of low energy fragments via image potential



Riedel, Perdigão, Hernández-Pozos, Guo, Palmer, Foord, and Kolasinski
Phys. Rev. B **66**, 233405 (2002)

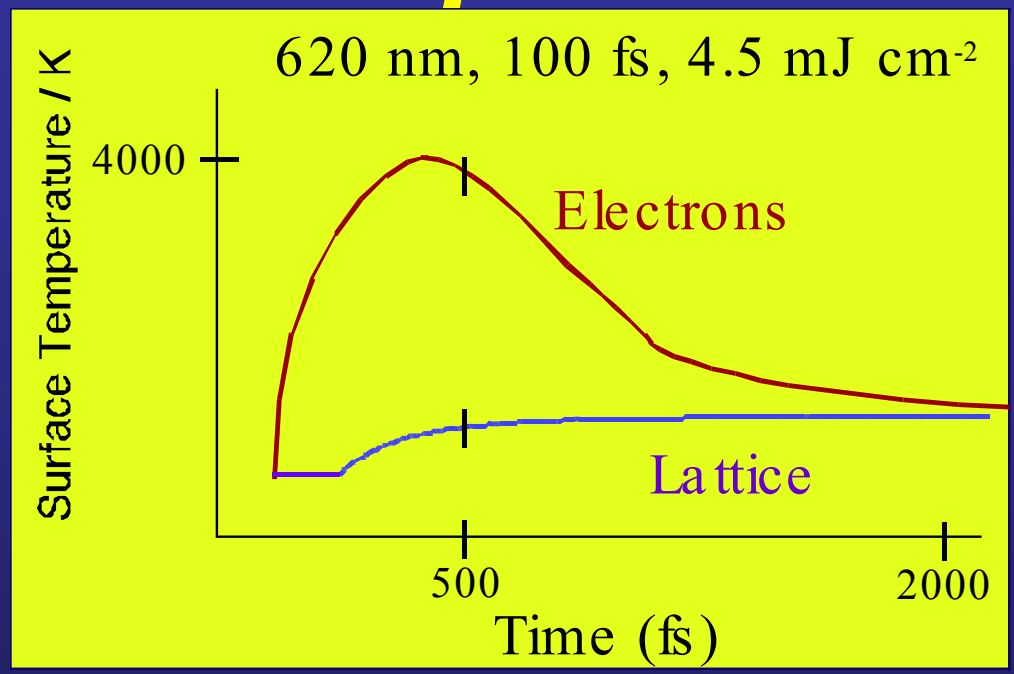
HHG at UVa





- Jones: High Harmonic Generation in a fiber
- <30 fs Regen, 1.2 mJ, 1 kHz

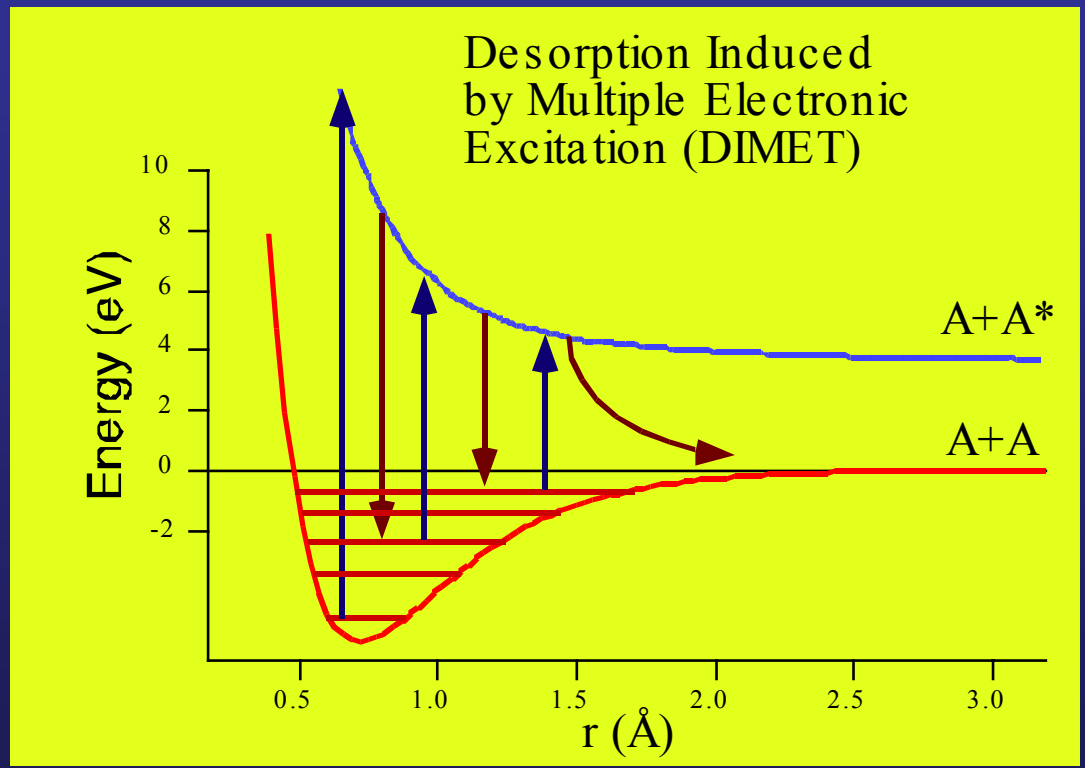
fs Excitation separates T_e from T



- Timescale for laser desorption
- 350 fs, CO/Cu(111), Prybyla, Tom & Aumiller, PRL 1992, **68**, 503.
- 500 fs, NO/Pd(111), Budde, Heinz, Loy, Misewich, de Rougemont & Zacharias, PRL 1991, **66**, 3024–3027.

Desorption Induced by Multiple Electronic Transitions

- Franck-Condon transitions up and down
- Population of vibrationally excited states
- Excitation rate > relaxation rate
- Can also be driven by inelastic scattering from hot electrons



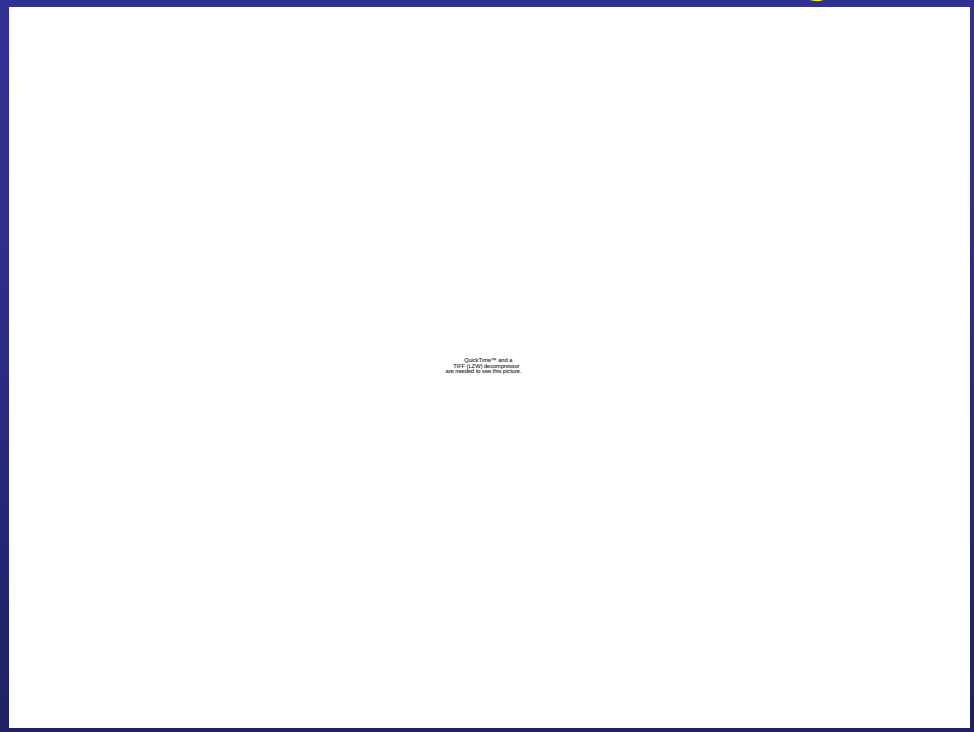
•Misewich, Heinz & Newns, PRL 1992, **68**, 3737.

•Brandbyge, Hedegård, Heinz, Misewich & Newns, PRB, 1995, **52**, 6042.

DIMET of H/H_2 from Si

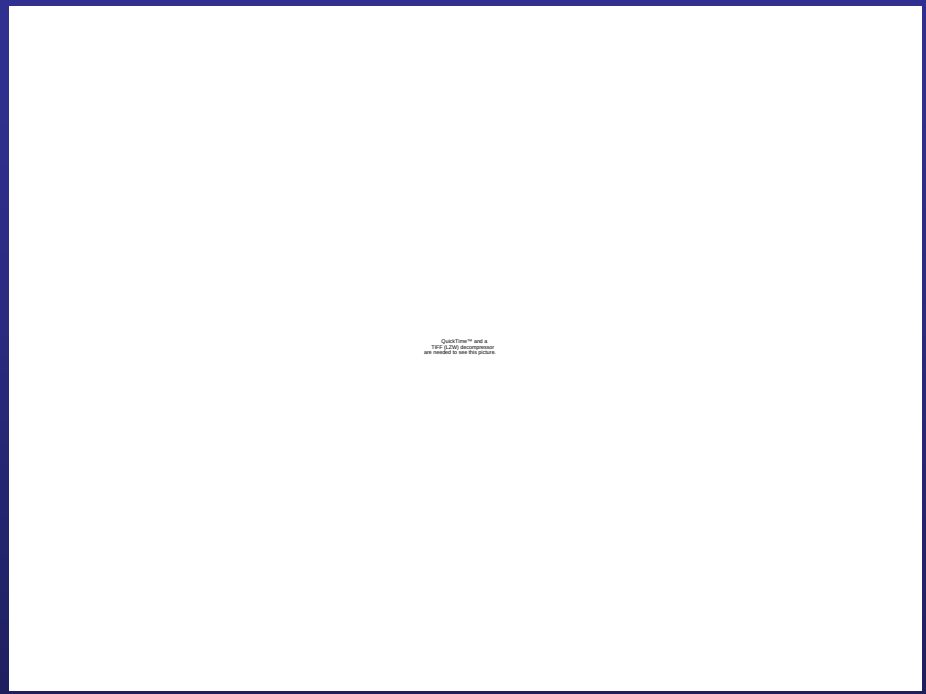
- Not yet investigated for Si
- Vibrational excitation intrinsic to DIMET but never observed directly
- Si–H vibrational lifetime unusually long, 1–10 ns
- Particularly attractive system to study by SFG to detected vibrationally excited species and to measure their lifetimes
- Use HHG to make 8 & 23+ eV photons for electronic excitation and detect vibrationally excited Si–H

Surface Photochemistry & SFG



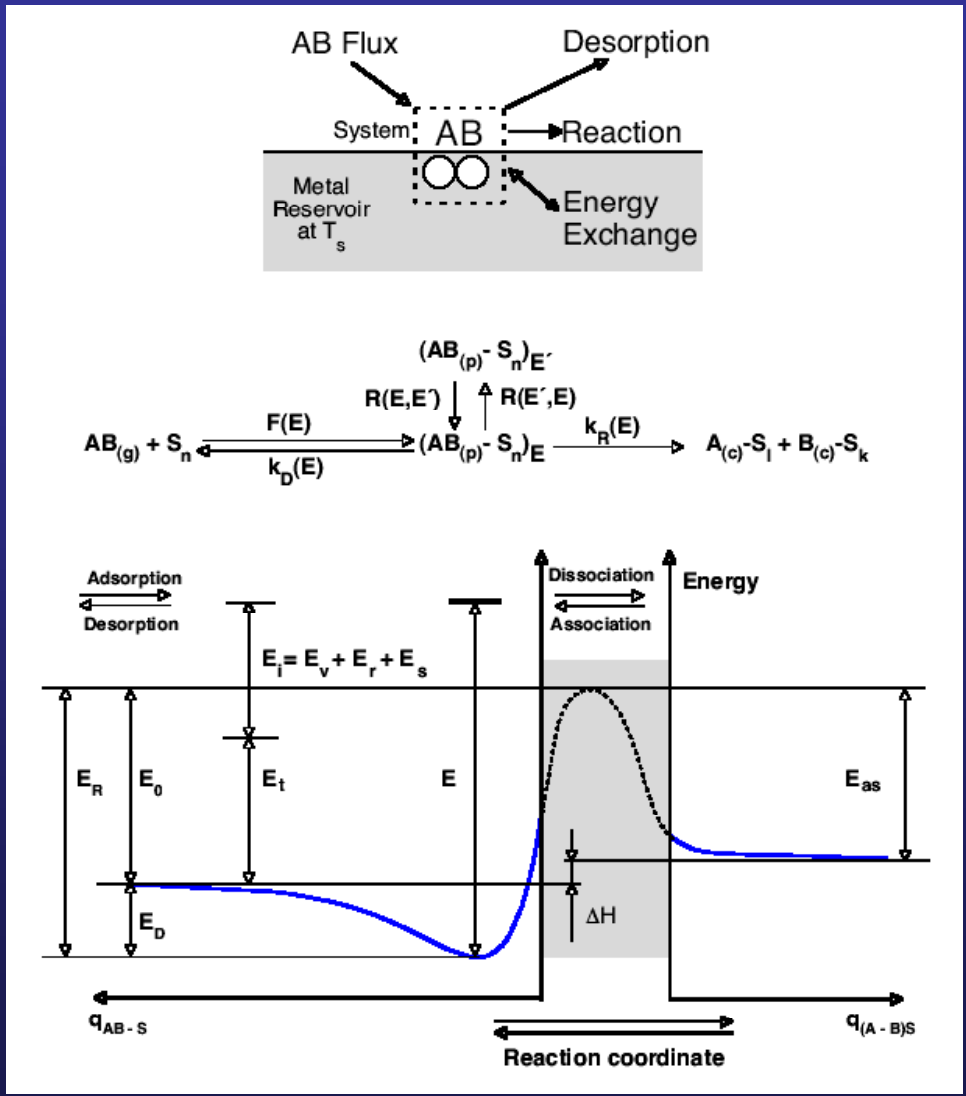
- Harrison: Dynamics of surface phenomena and laser/surface interactions

1-2 ps Ti:S synced to 100 fs Ti:S + 3 OPAs



- Pate: Dynamics of vibrational relaxation in C–H bonds
- 2, 3, 4 color experiments possible
- States ≥ 2, gas phase, in solution

PC-MURT & IVR

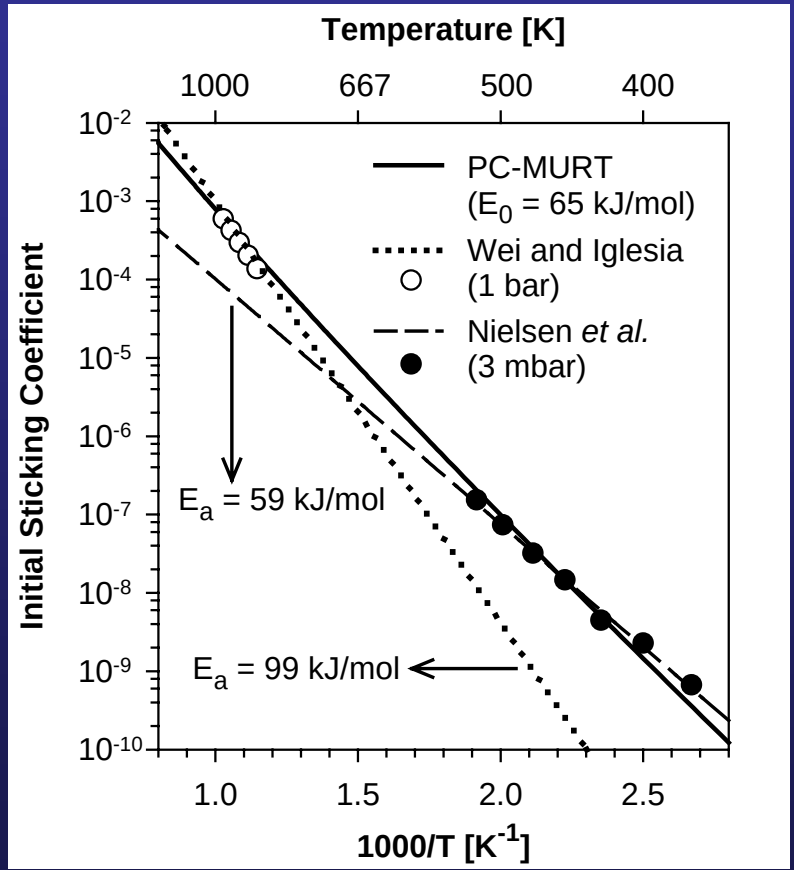


- Harrison: Physisorbed complex - microcononical unimolecular rate theory
- Intramolecular vibrational relaxation scrambles energy in the PC

H.L. Abbott, A. Bukoski and I. Harrison, J. Chem. Phys., 2004, **121**, 3792.

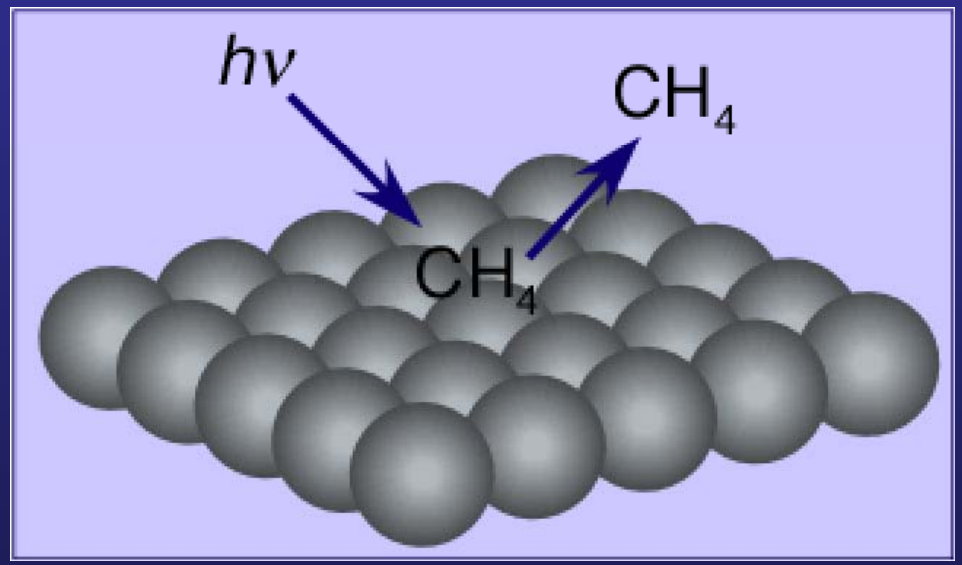
From Molecular Beam to Catalysis

- Molecular beam scattering data is used to optimize three model parameters (E_0, s, ν)
- Can successfully model high pressure reactivity data over real catalysts



Resonant Laser Induced Desorption

- Incident photon resonant with vibrational overtone of CH_4
- Vibrational energy > desorption activation energy
- IVR leads to desorption if energy leakage to the bulk is comparatively slow



Conclusions

- Ultrafast and nonlinear optics at surfaces for dynamical studies
- Applications of high harmonic generation
- Vibrational relaxation across many phases
- Adsorption, desorption and reaction dynamics at surfaces to understand thermal and stimulated chemistry