# Controlling Matter with Light

Robert J. Gordon
University of Illinois at Chicago

ALFF Workshop

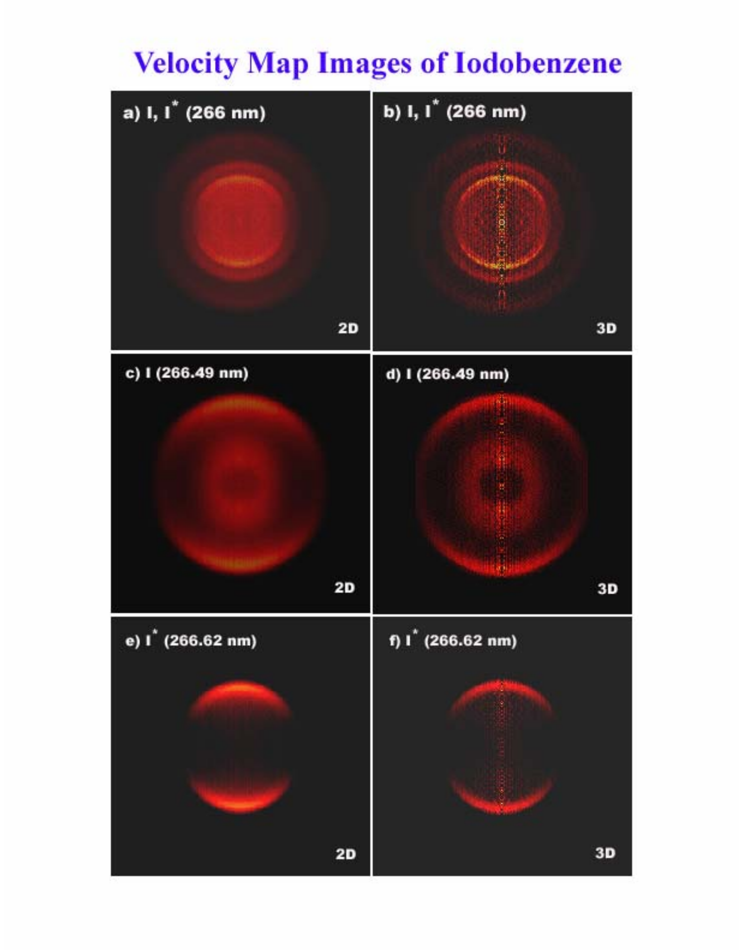
October 30, 2003

NSF, DOE, PRF, UIC/CRB, Motorola

# Outline

- Dissociative Ionization
- Molecular Optics
- Coherent Control
- Material Processing

# Photodissociation of $C_6H_5I$ at 266 nm



# Mechanism at 266 nm

## Outer Feature

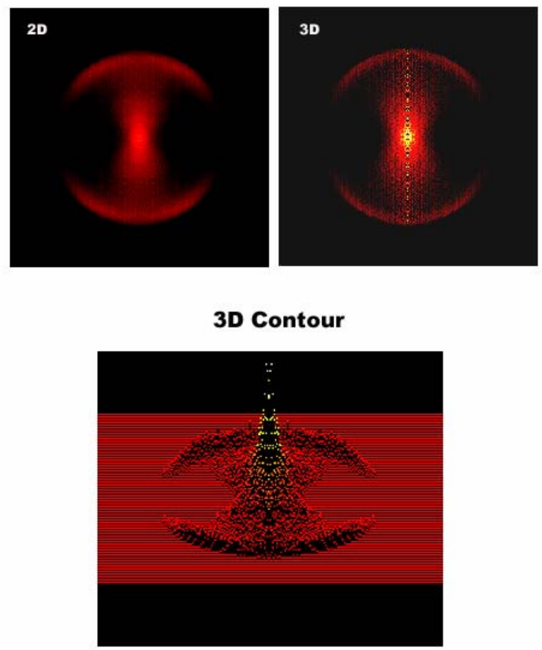
$$n^2 + h\nu \rightarrow {}^3Q_0(n,\sigma^*) \rightarrow C_6H_5 + I({}^2P_{1/2,3/2})$$

## Inner Feature

$$n^2 + h\nu \rightarrow S_1(\pi,\pi^*) \sim {}^1Q_1(n,\sigma^*) \rightarrow C_6H_5 + I({}^2P_{3/2})$$

# Photodissociation of $C_6H_5I$ at 532 nm

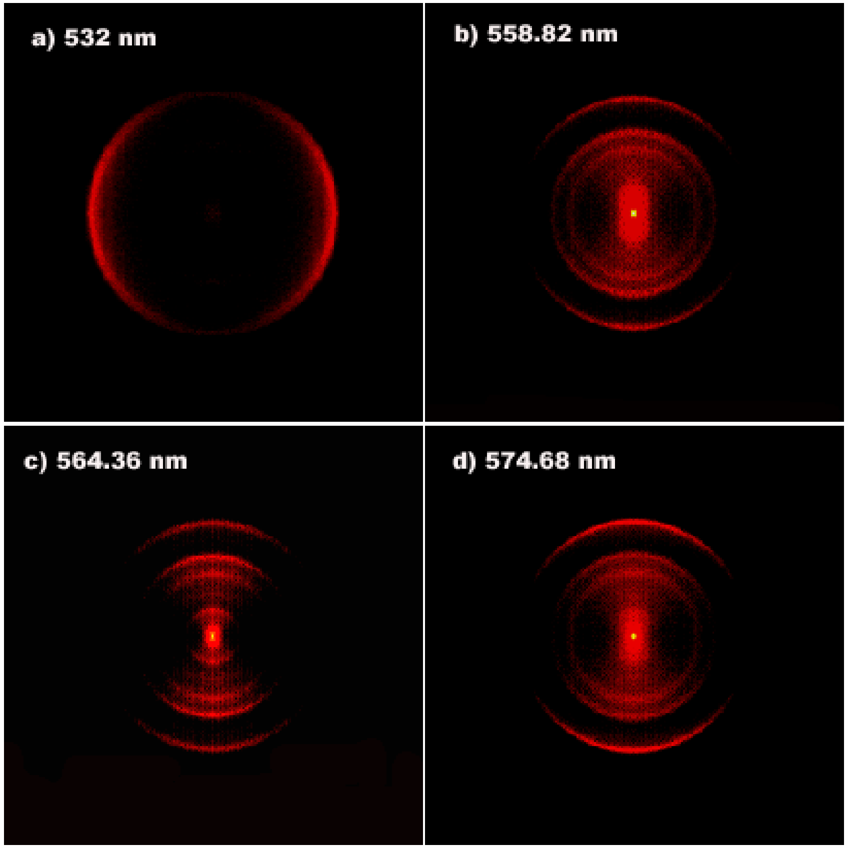
Velocity Map Images of Iodobenzene at 532 nm



# Photodissociation of $I_2$

532 nm

559 nm



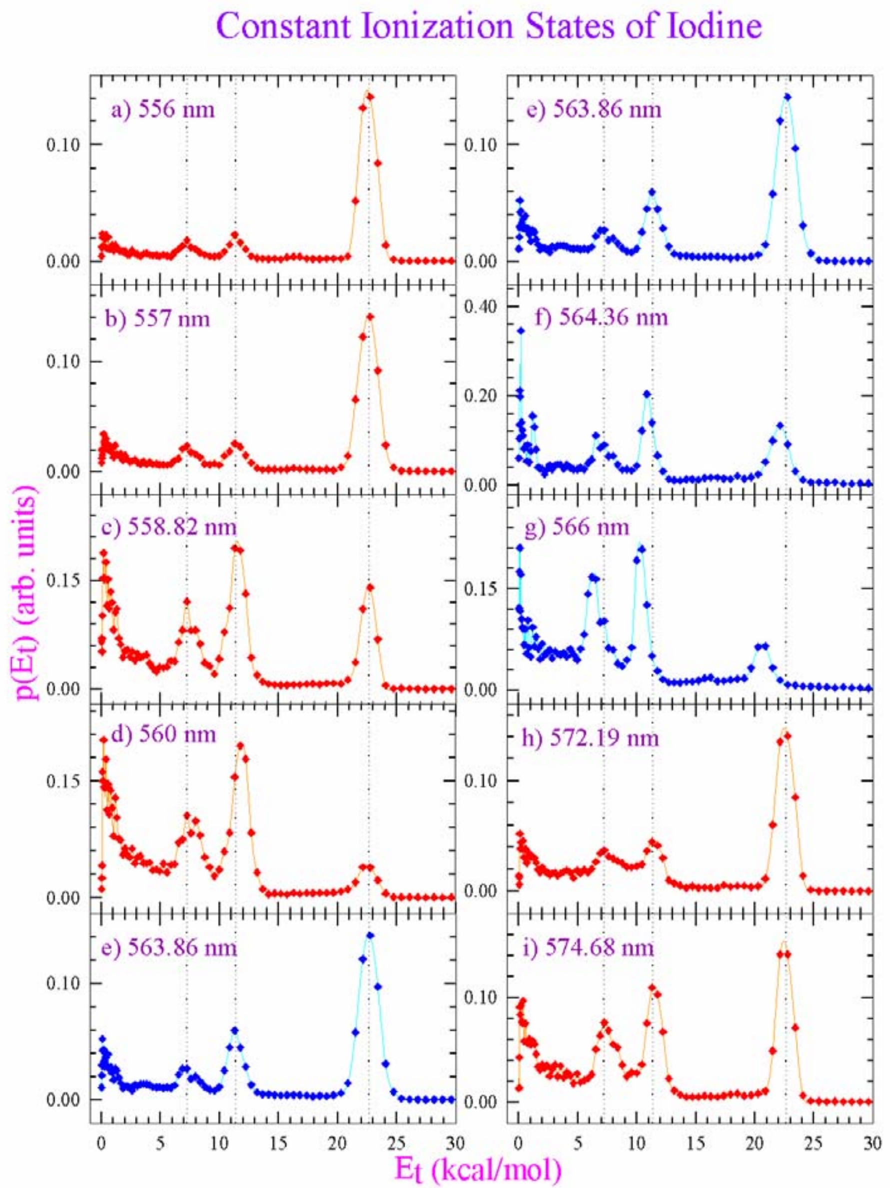

564 nm

575 nm

S. Unny, Y. Du, L. Zhu, R.J. Gordon, A. Sugita, M. Kawasaki, Y. Matsumi, T. Seideman, PRL **86**, 2245 (2001). 

# Kinetic Energy of Iodine

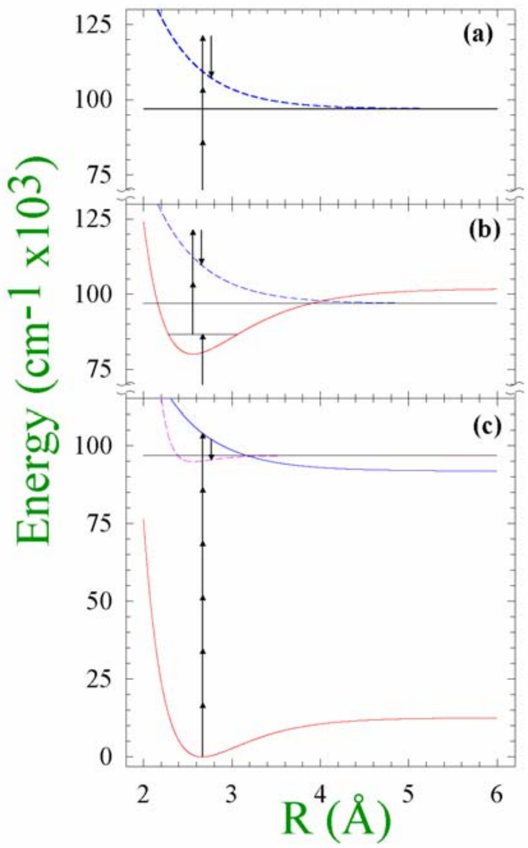
556.0 nm




574.7 nm

S. Unny, Y. Du, L. Zhu, R.J. Gordon, A. Sugita, M. Kawasaki, Y. Matsumi, T. Seideman, PRL **86**, 2245 (2001).

# Dissociative Ionization



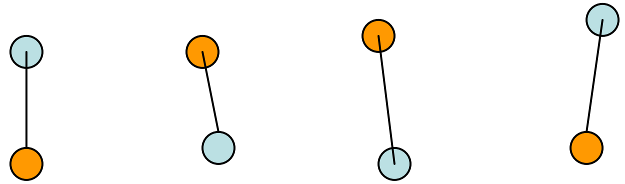

S. Unny, Y. Du, L. Zhu, R.J. Gordon, A. Sugita, M. Kawasaki, Y. Matsumi, T. Seideman, PRL **86**, 2245 (2001). Copyright 2001 by the American Physical Society.

# Possible FEL Experiments

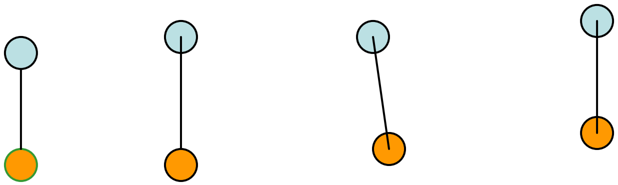
- 90 – 100 nm single photon excitation
- Pump-probe photoelectron-photoion coincidence
- Photoelectron angular distributions of aligned molecules

# Manipulating Molecules With Light

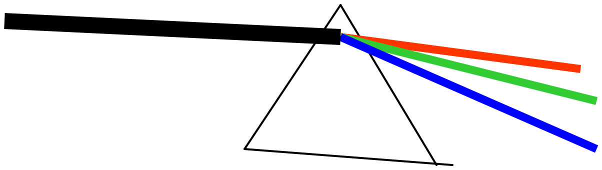
**Alignment**



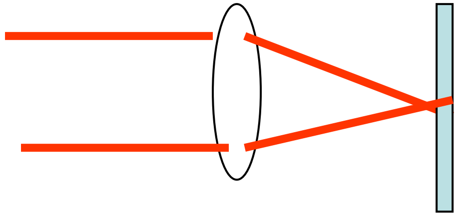
**Orientation**



**Deflection**



**Focusing**



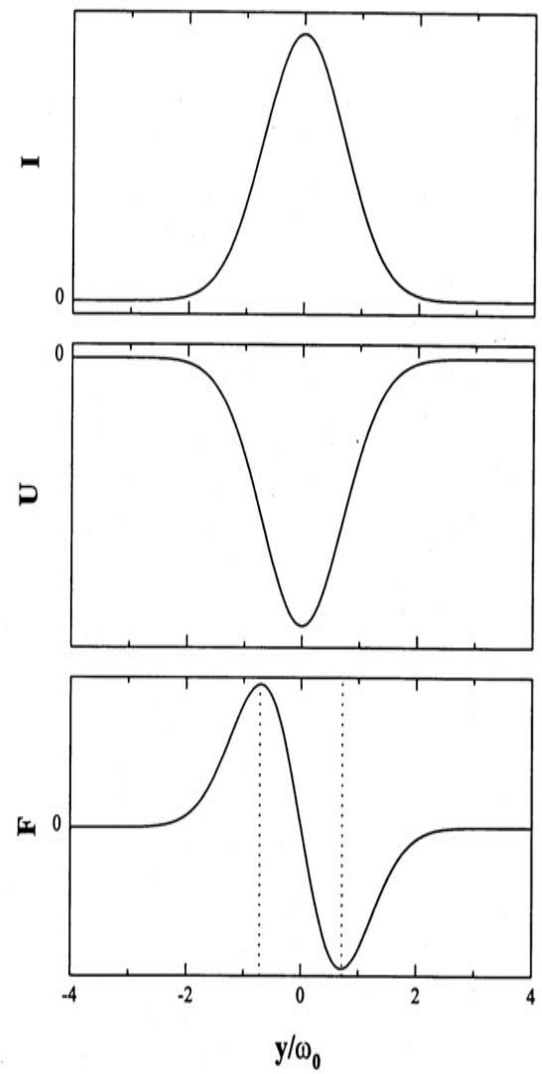
**Trapping**

# Interaction with a Focused Laser Beam

Intensity

Potential

Force



# Dipole Interaction

**Gaussian electric field**

$$E(r,t) = E_0 e^{-r^2/\omega^2} f(t)$$

**Dipole potential**

$$U(r,\theta) = -\mu E(r,t)\cos\theta - \frac{1}{2}E^2(r,t)\left(\alpha_{//}\cos^2\theta + \alpha_{\perp}\sin^2\theta\right)$$

**r → deflection & focusing**

**θ → alignment & orientation**

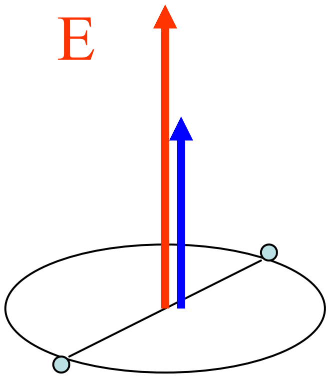
# Dipole Force

**Gaussian field** $$E = E_0 e^{-r^2/\omega^2}$$

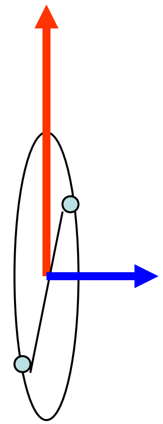
**Induced potential** $$U = -\frac{1}{4}\alpha_{//} E_0^2 e^{-2r^2/\omega^2}$$

**$U_0$(K) = 15 $\alpha_{//}$(Å$^3$) I(TW/cm$^2$)**

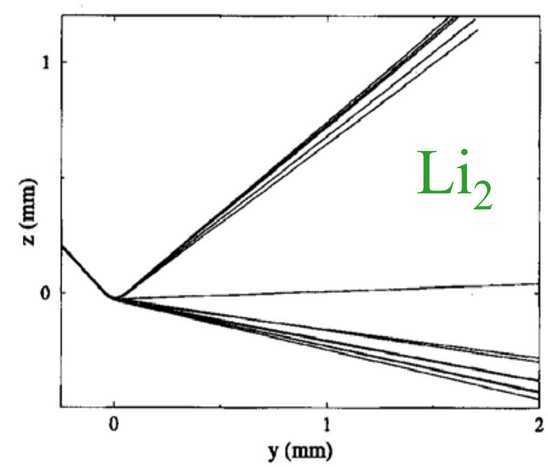
# Deflecting Molecules in Different $M_J$ States



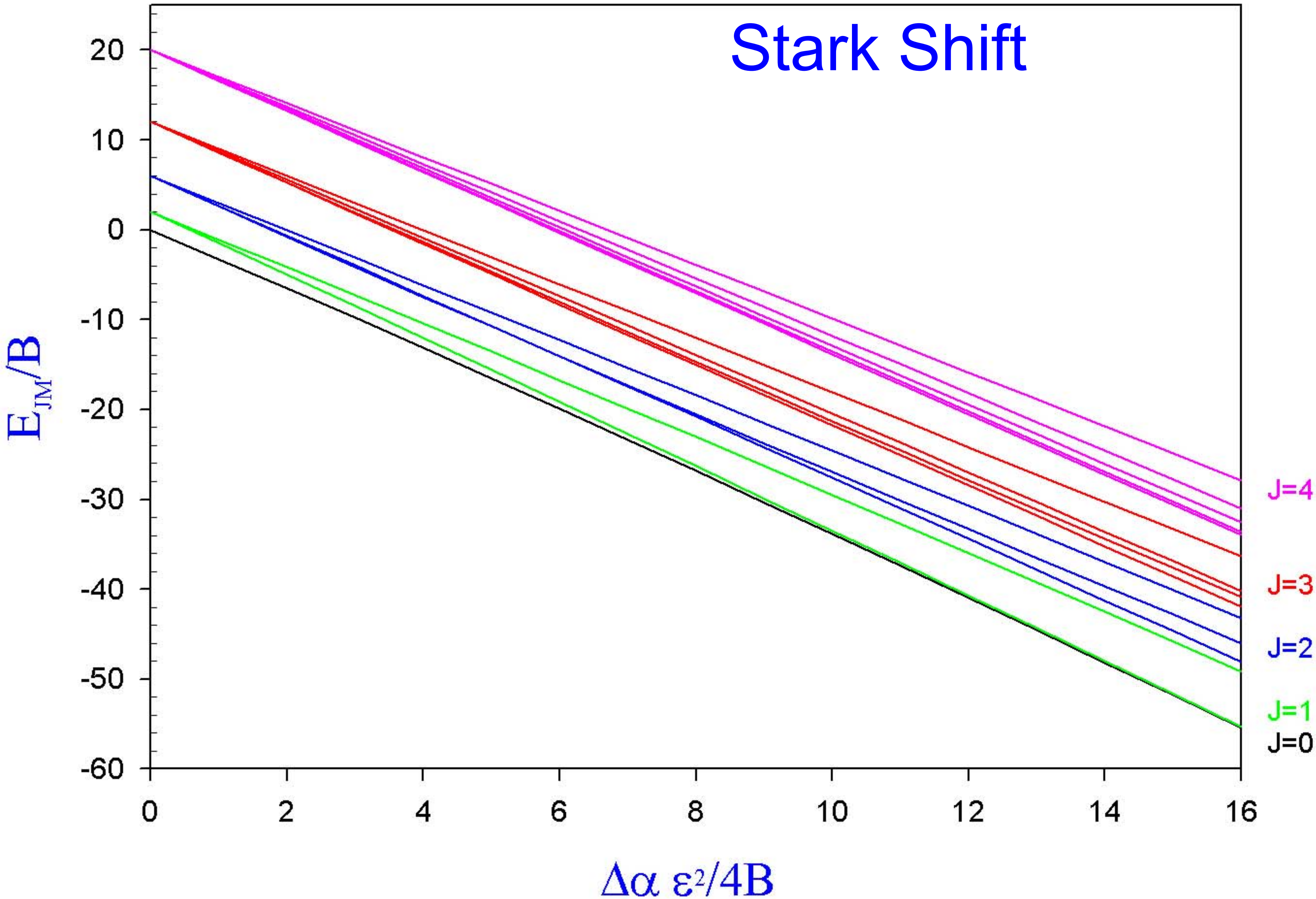

$|M| = J$



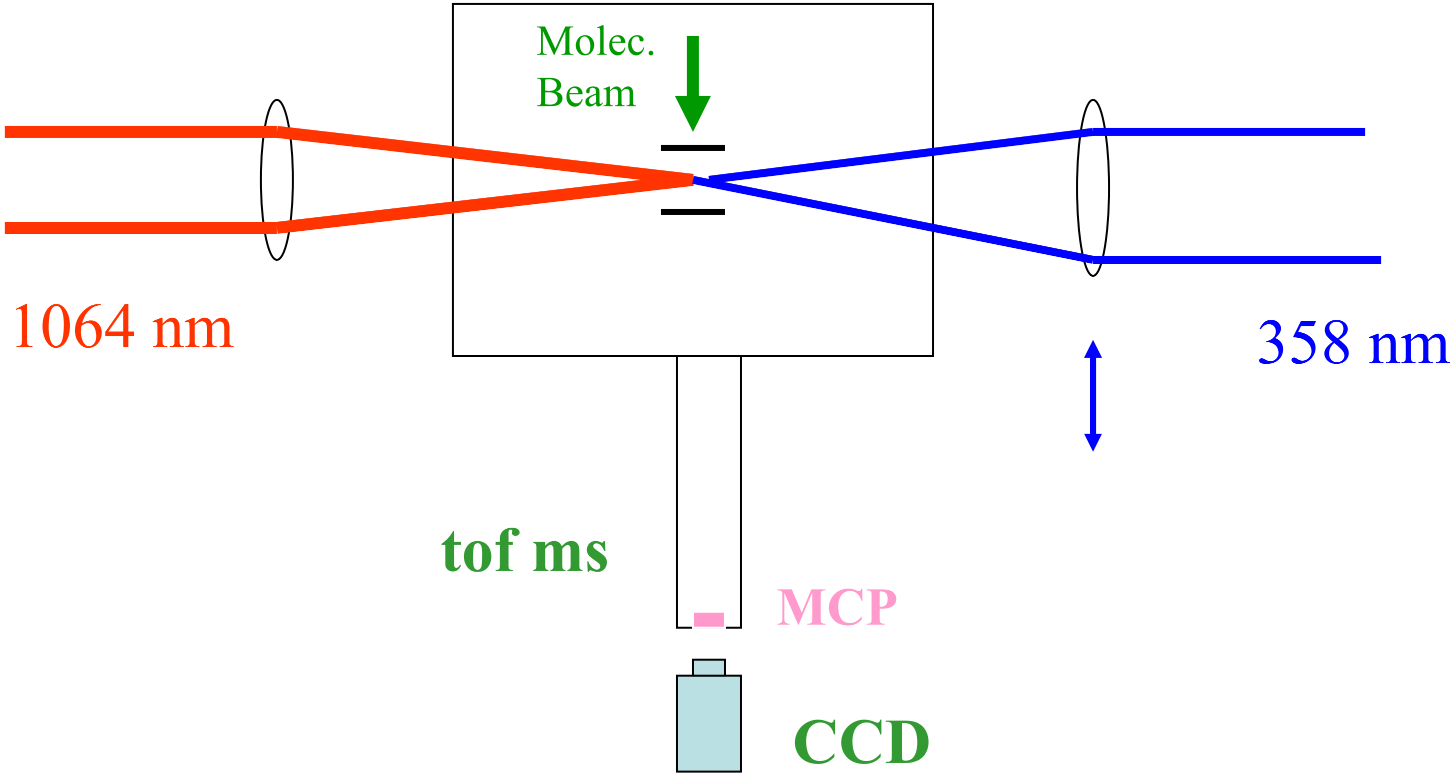
$M = 0$



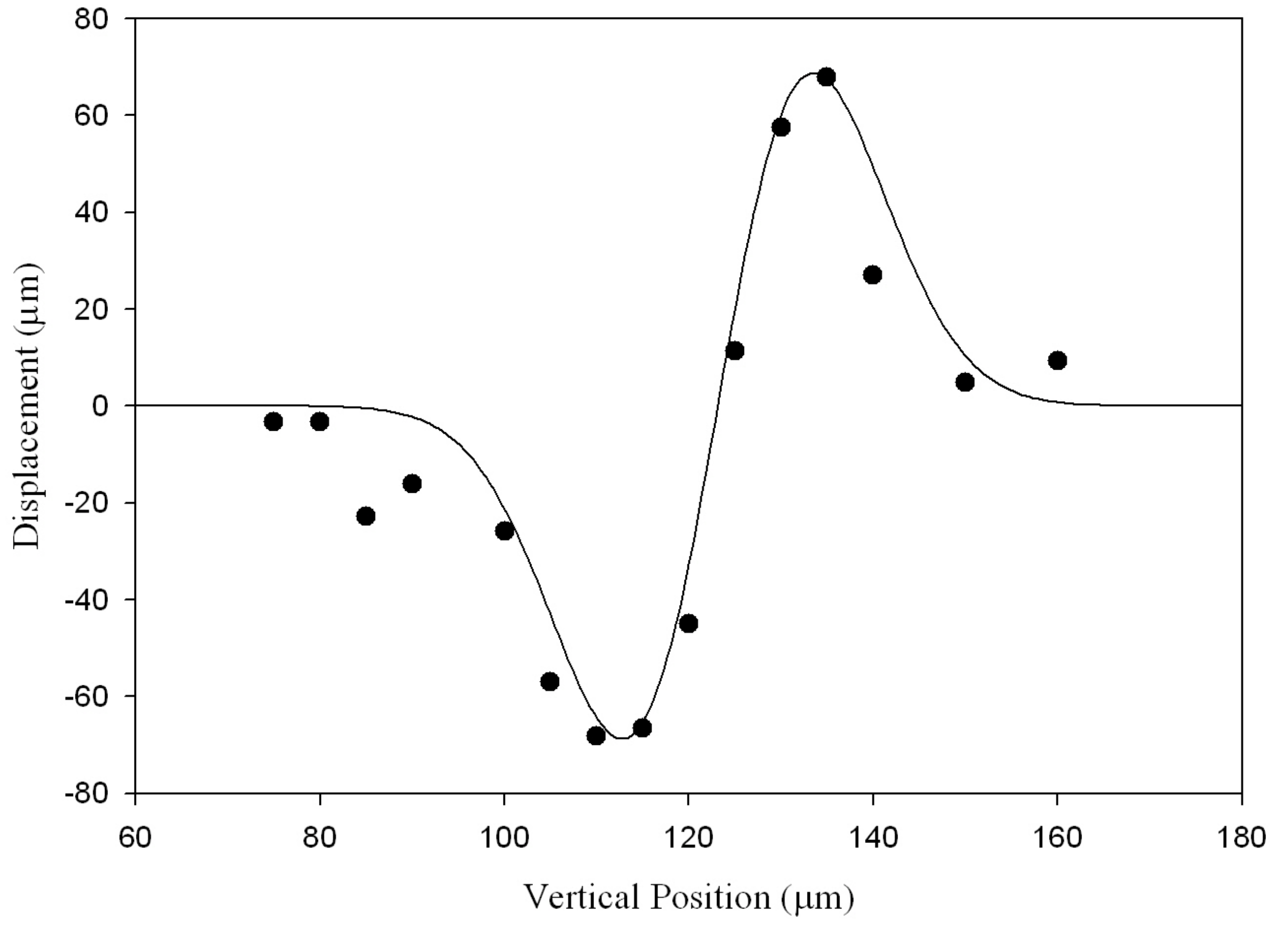
# HI Deflection Potential

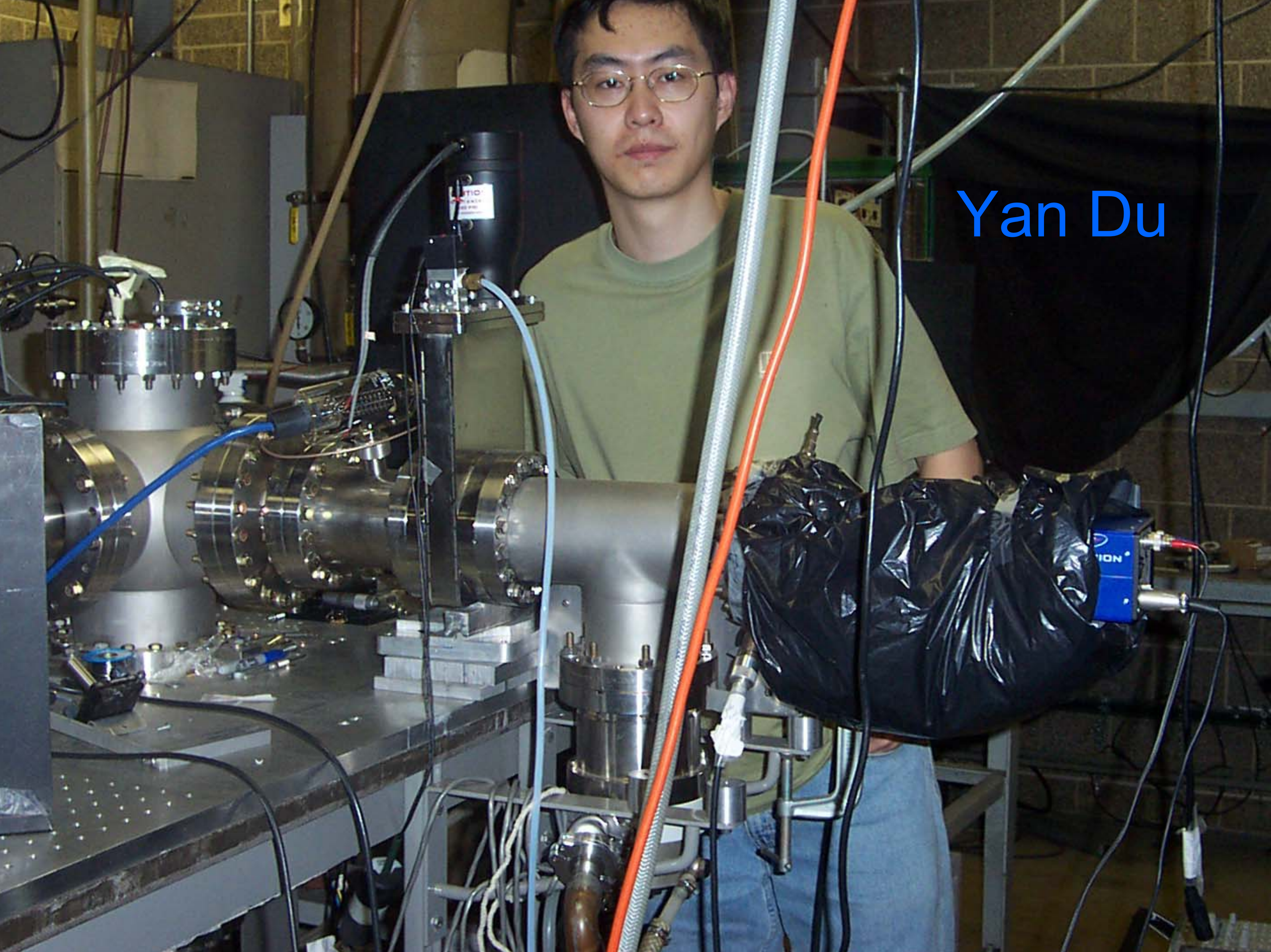


# Apparatus

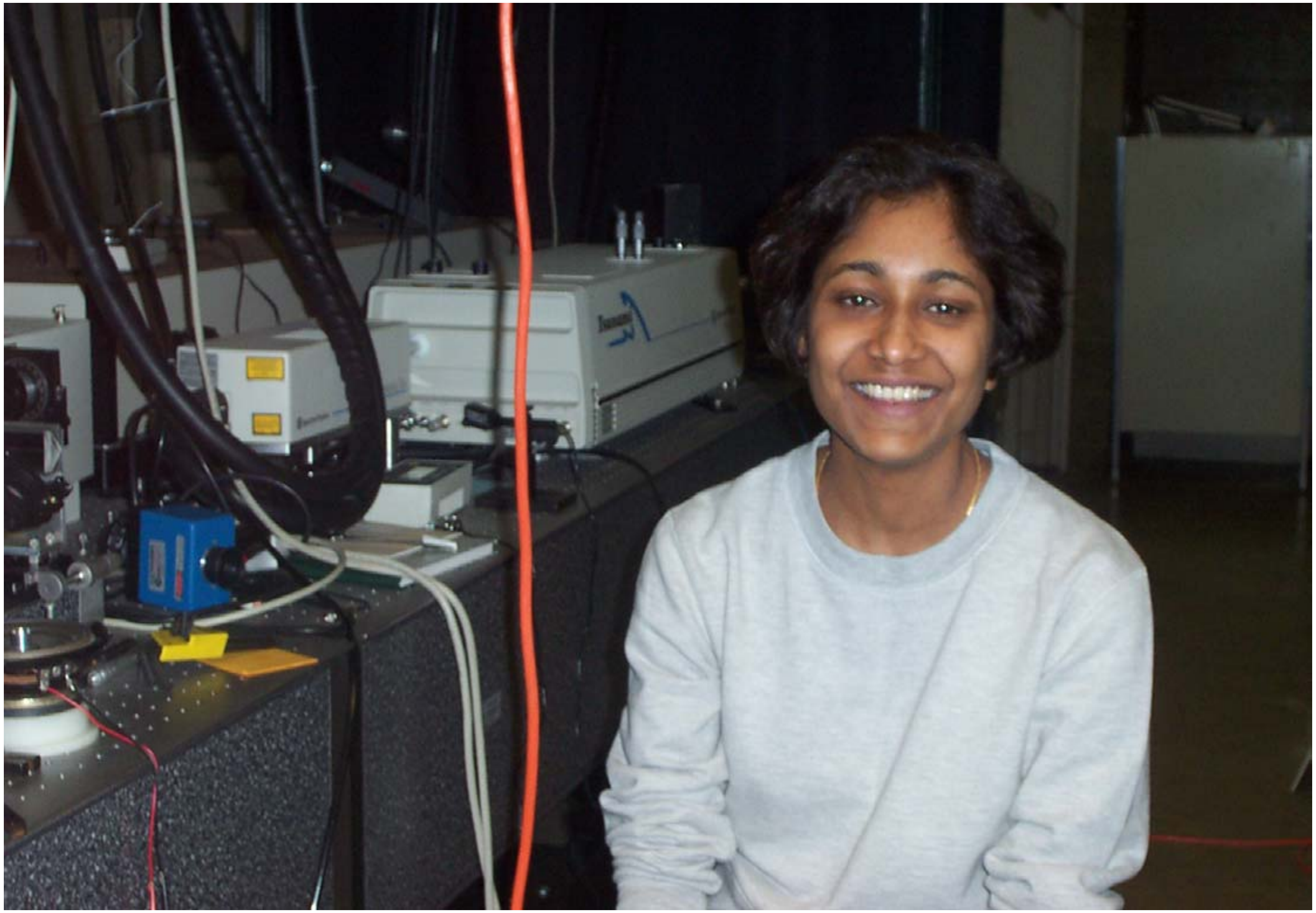


# $CS_2$ Deflection



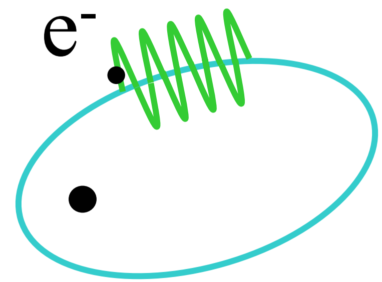

Yan Du

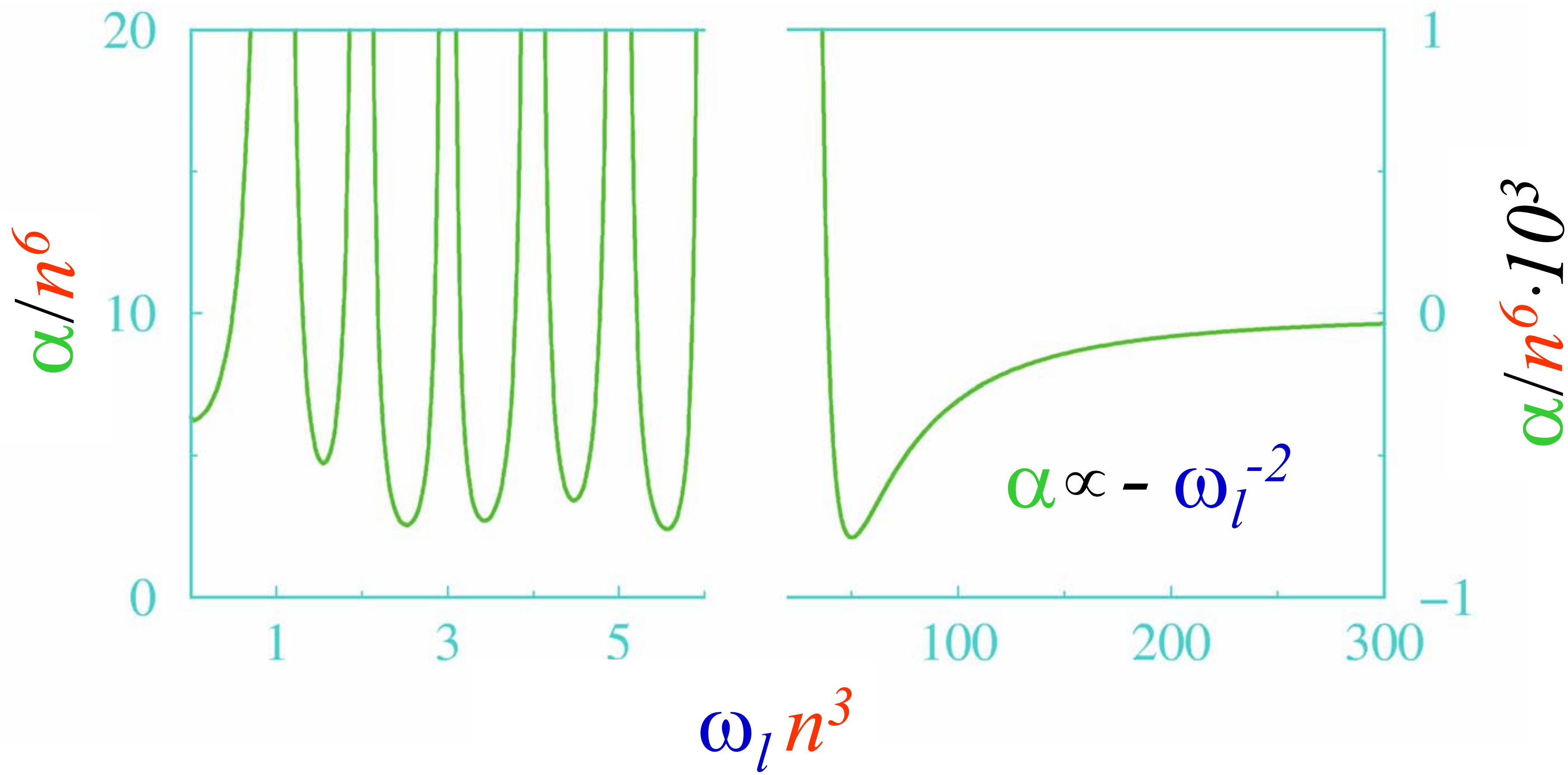

Joyce Willig



Sujatha Unny

# Dynamic Polarizability



# Molecular Mirror

**Classical forced oscillator:**

$$m\ddot{r} + kr = -eE_0 \cos \omega t$$

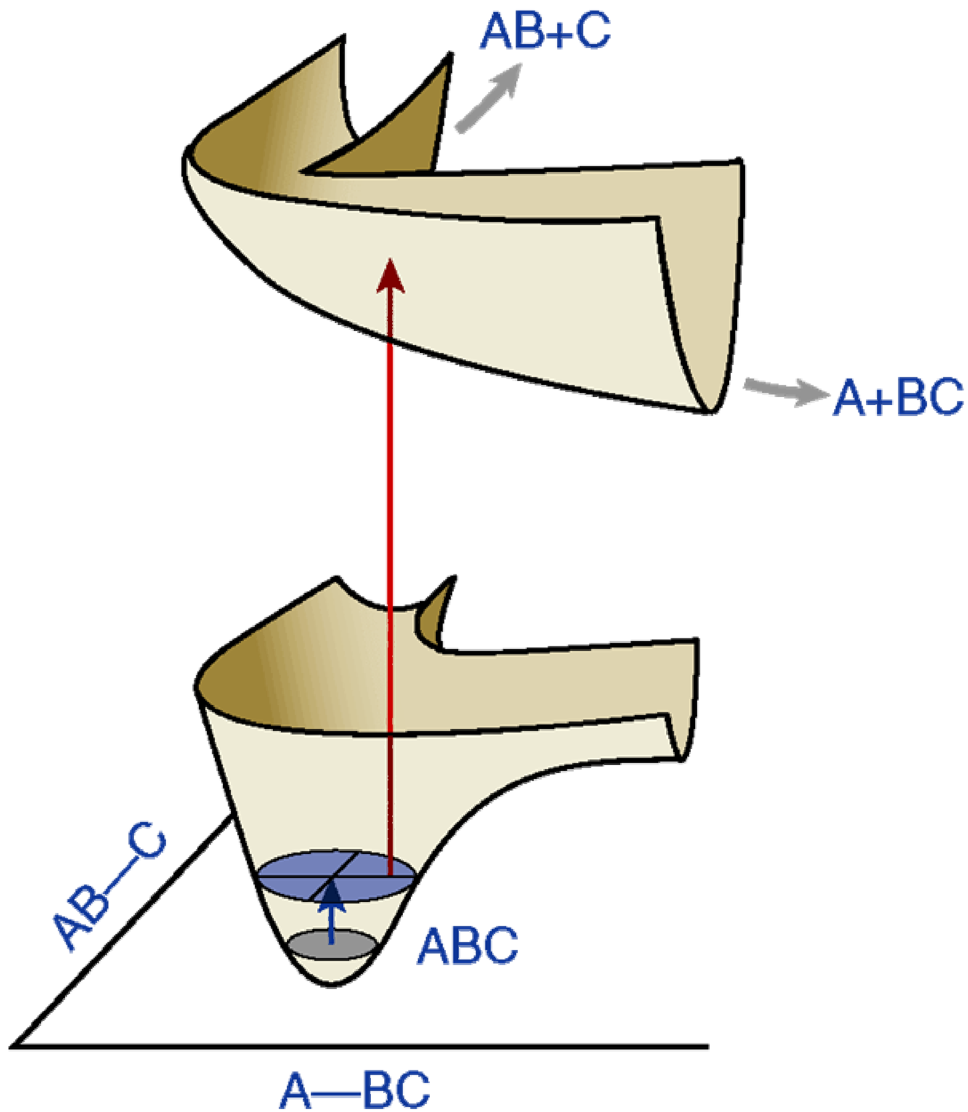
$$r = -\frac{\frac{e}{m} E_0 \cos \omega t}{\omega_0^2 - \omega^2}$$

**Sign reversal at high frequency**

# Possible FEL Experiments

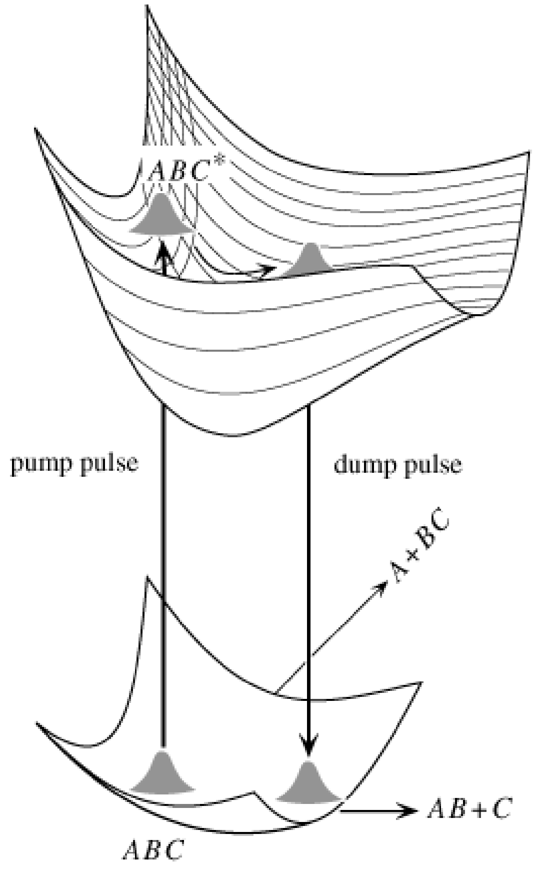
- Deflect molecules in high Rydberg states
- Use a near-resonant deflection field

# Passive Control of Chemical Reactions




Courtesy F. Crim.

# Active Control of Chemical Reactions



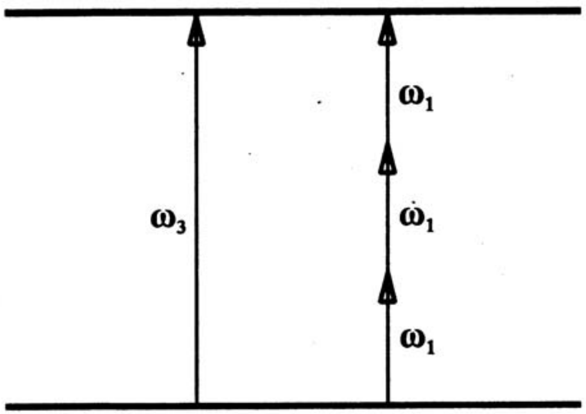
# Interference Between Competing Paths

$$P = P_1 + P_2 + P_{12}$$

$$P = |f_1 + f_2|^2$$

$$= |f_1|^2 + |f_2|^2 + f_1 f_2^* + f_1^* f_2$$

# Coherent Phase Control of Bound-Bound Transitions

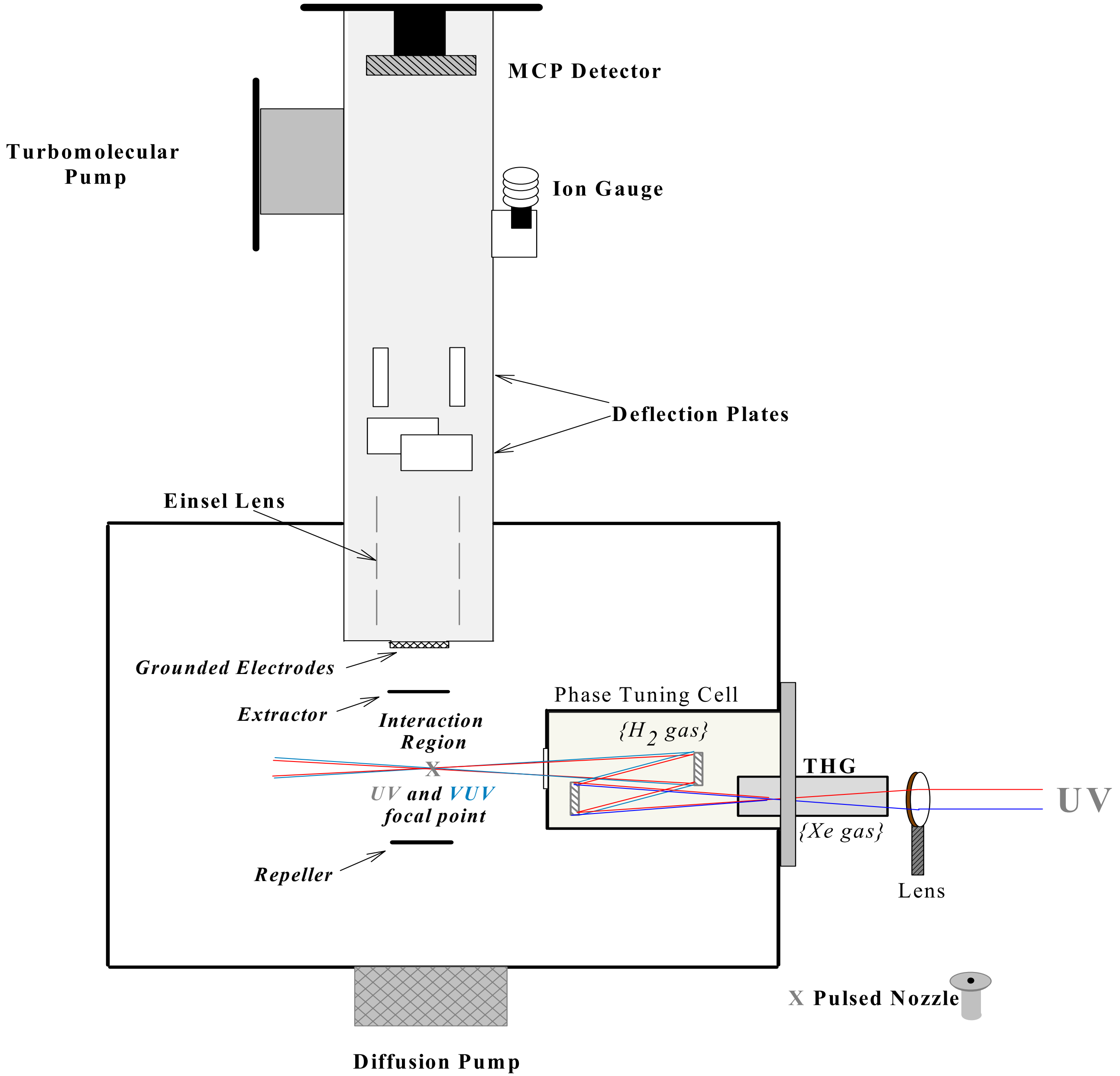



$$P = \left| f_1 + f_3 e^{i\phi} \right|^2$$

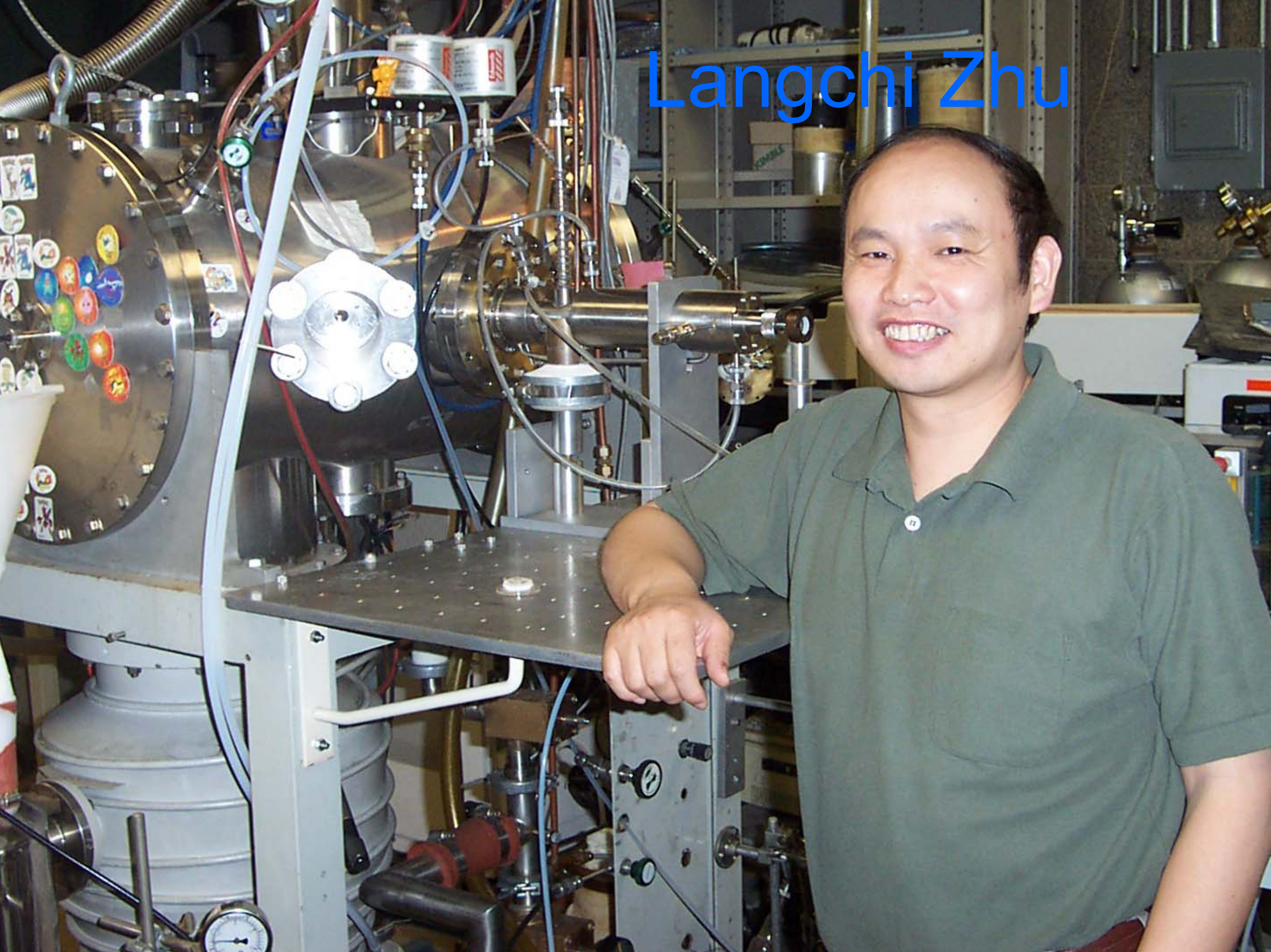
$$= P_1 + P_3 + 2\sqrt{P_1 P_3}\cos\phi$$

$$\phi = \phi_3 - 3\phi_1$$

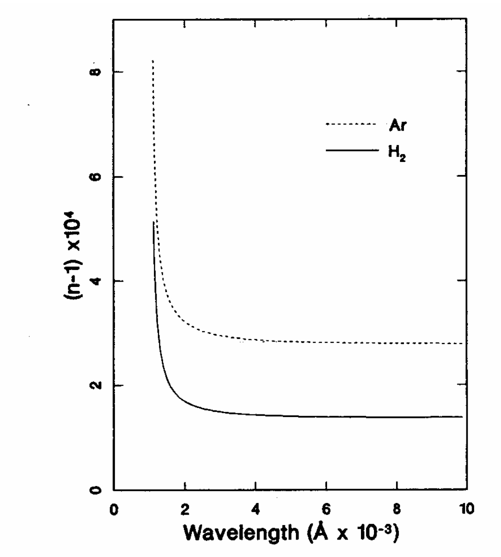
(See Shapiro, Hepburn, and Brumer, Chem. Phys. Lett. **149**, 451 (1988).)

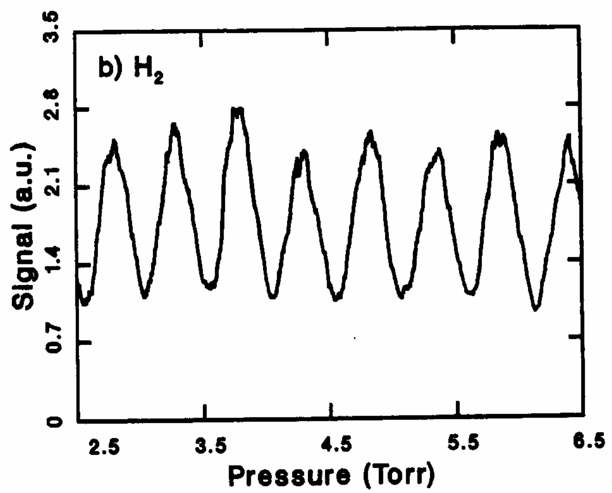


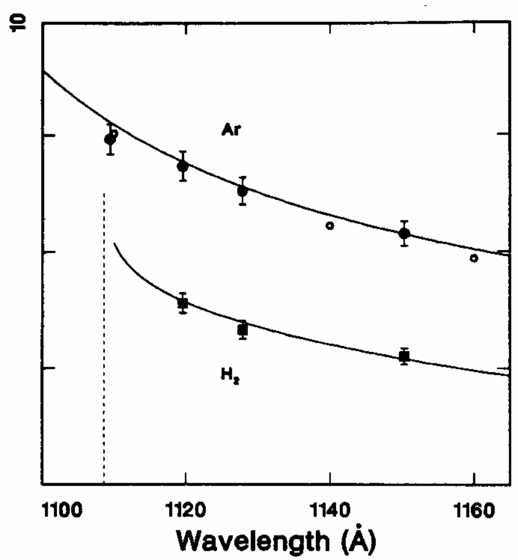
MCP Detector
Turbomolecular Pump
Ion Gauge
Deflection Plates
Einsel Lens
Grounded Electrodes
Extractor
Interaction Region
Phase Tuning Cell
{H 2 gas}
THG
UV
{Xe gas}
UV and VUV focal point
Repeller
Lens
X Pulsed Nozzle
Diffusion Pump


Langchi Zhu

# Phase Tuning



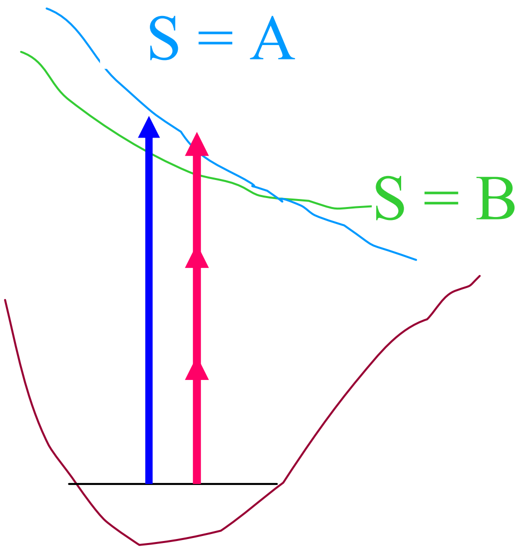




$$\phi = \phi_3 - 3\phi_1$$

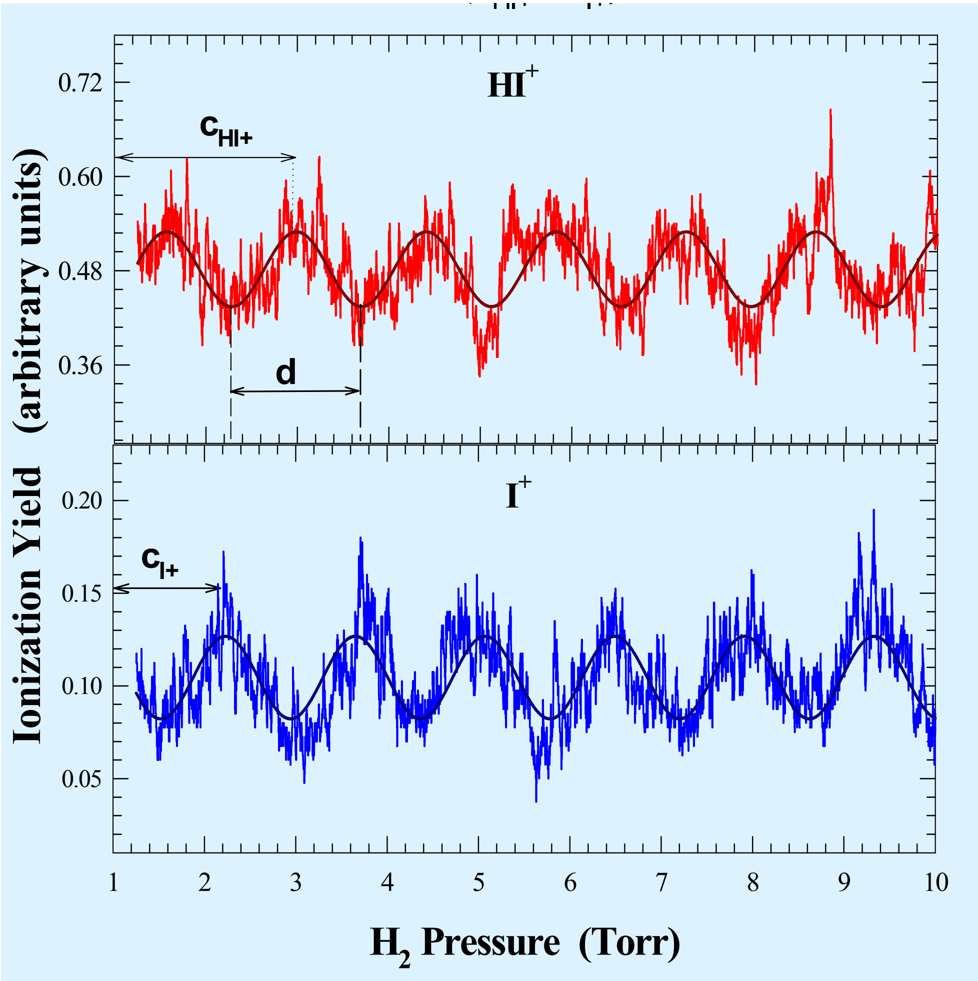
$$= l(\omega_3 / c)(n_3^0 - n_1^0)P / P^0$$

# Controlling Branching Ratios




$$P^S = P_1^S + P_3^S + 2P_{13}^S \cos\left(\phi + \delta_{13}^S\right)$$

# The Phase Lag




Reprinted with permission from L. Zhu, V. Kleiman, X. Li, S.P. Lu, K. Trentelman, R.J. Gordon, Science, **270**, 77 (1995). Copyright 1995 AAAS.

# The Channel Phase

$$\left|P_{13}^{S}\right| e^{i\left(\phi+\delta_{13}^{S}\right)} = \int \left\langle g \middle| D^{(1)} \middle| ES\hat{k} \right\rangle \left\langle ES\hat{k} \middle| D^{(3)} \middle| g \right\rangle d\hat{k}$$

# The Phase Lag

$$\Delta\delta(A,B) = \delta_{13}^{A} - \delta_{13}^{B}$$

# Molecular Phase

What are the sufficient conditions for a molecular phase to exist?

1. Coupled continua:

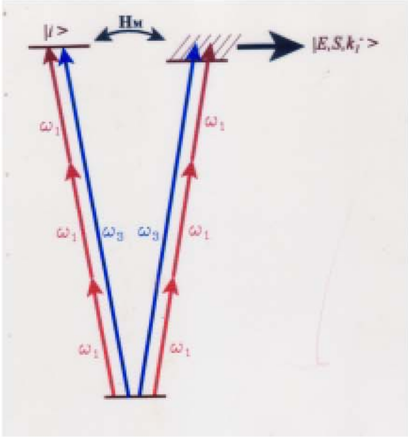
$$\left|ES\hat{k}\right\rangle = c_a\left|ES_a\hat{k}\right\rangle + c_b\left|ES_b\hat{k}\right\rangle$$

$$\delta_{13}^{S} = A + Be^{i(\delta_a-\delta_b)} + Ce^{-i(\delta_a-\delta_b)}$$

# Resonance Phase

What are the sufficient conditions for a molecular phase to exist?

2. Interference between direct and resonance-mediated transitions

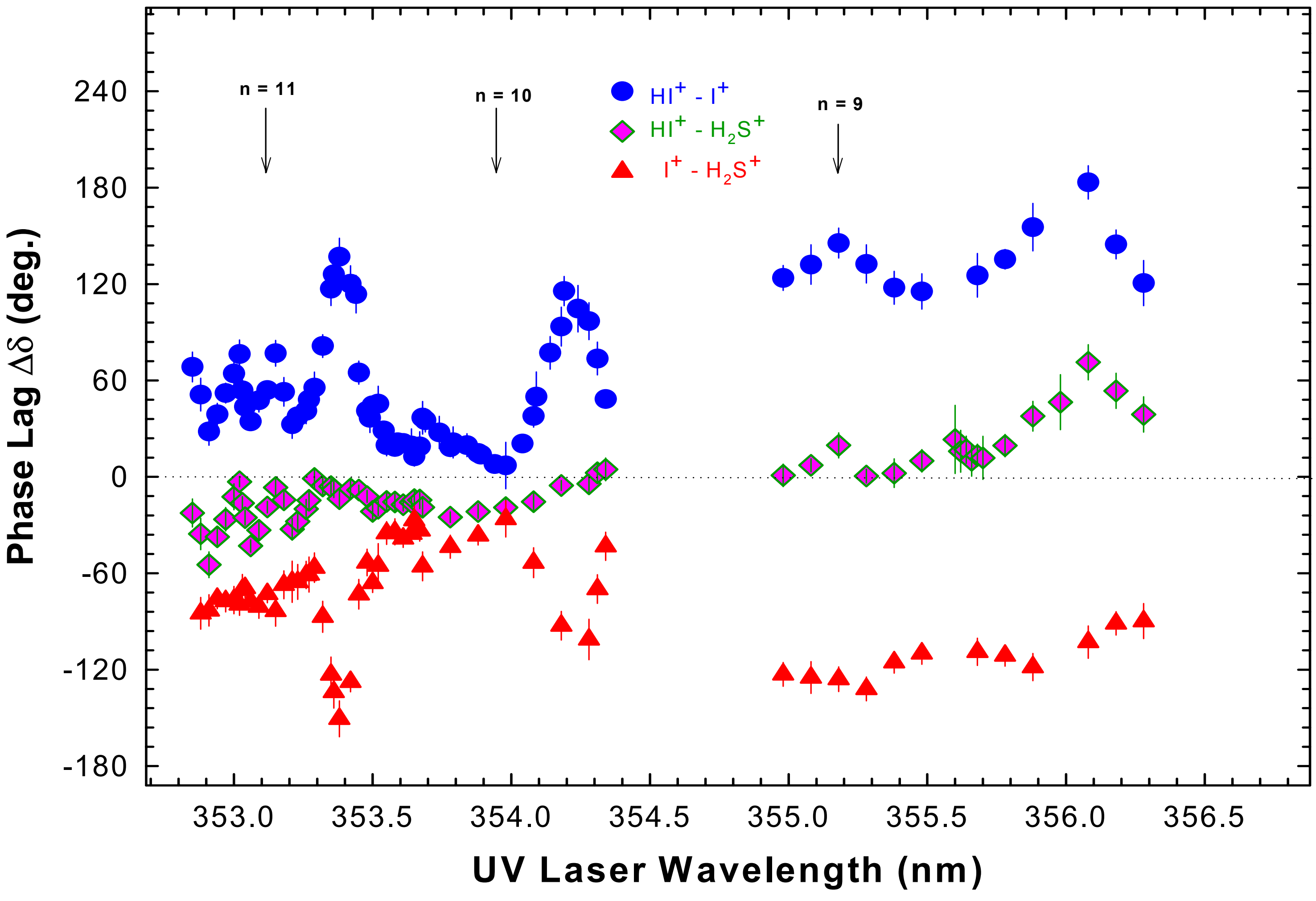



$$P = \iint \left| f^{1d} + f^{1r} + f^{3d} + f^{3r} \right|^2 d\hat{k}$$

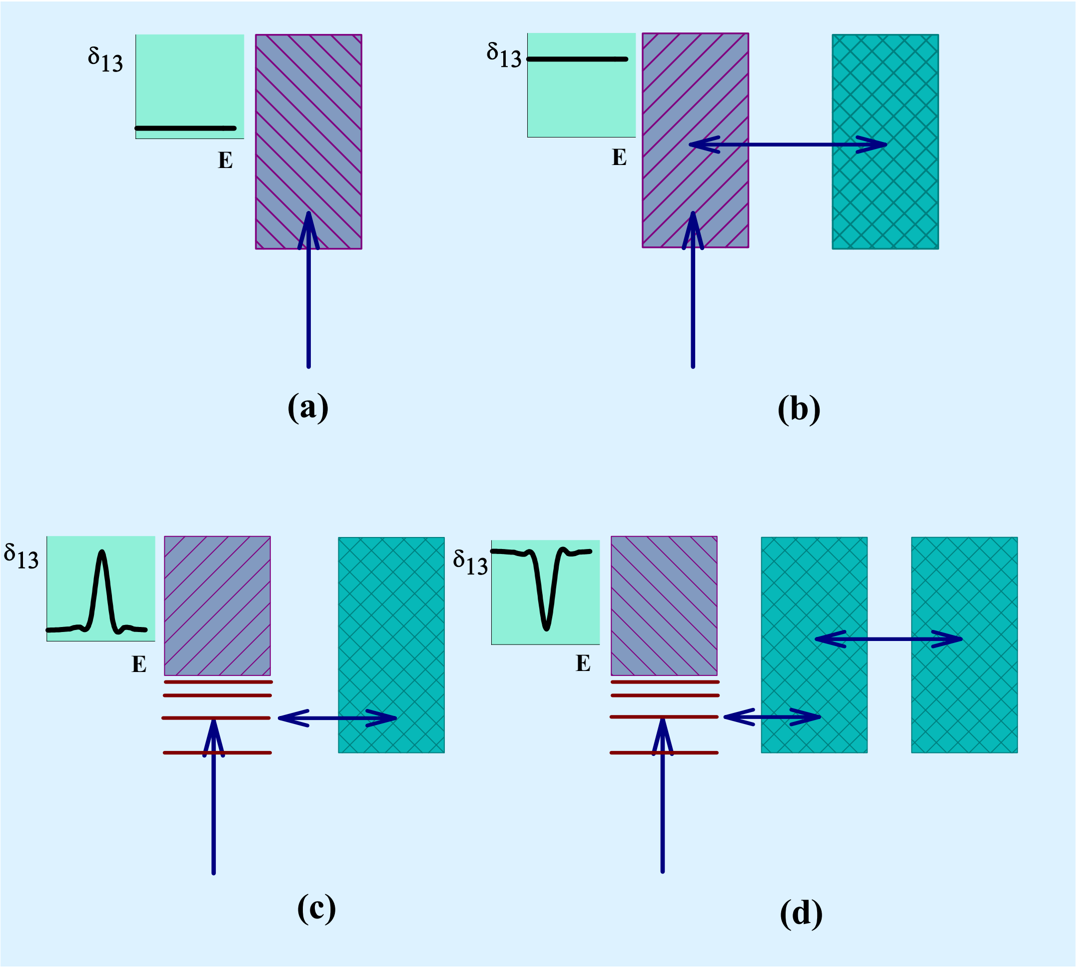
Example: Rotationally-selected resonance coupled to an elastic continuum:

$$\tan \delta_{13} = \frac{2(q^{(1)} - q^{(3)})}{\{\epsilon - \tfrac{1}{2}(q^{(1)} + q^{(3)})^2\} + \{4 - \tfrac{1}{4}(q^{(1)} - q^{(3)})^2\}}$$

# Phase Lag Spectrum of HI



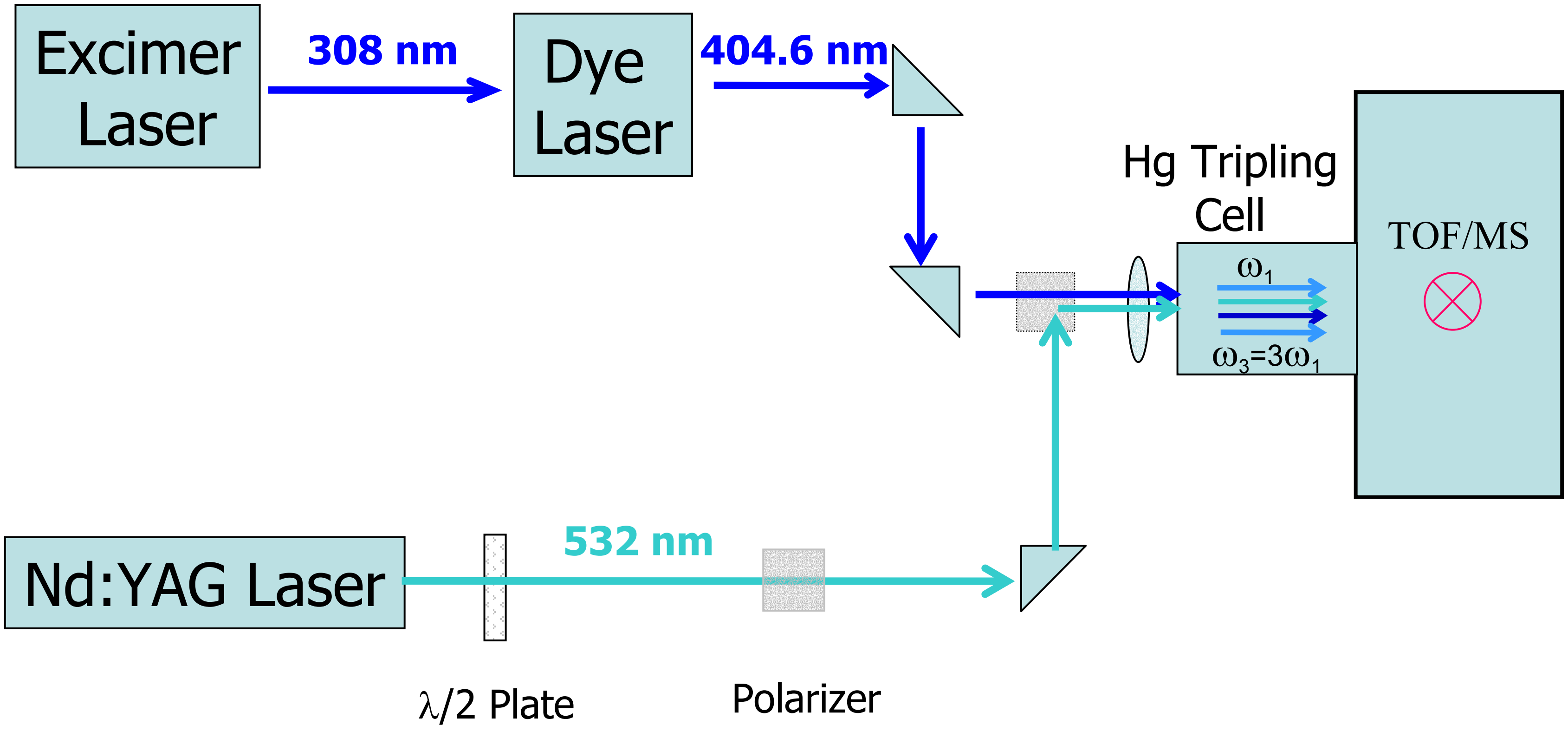
# Coupling Schemes

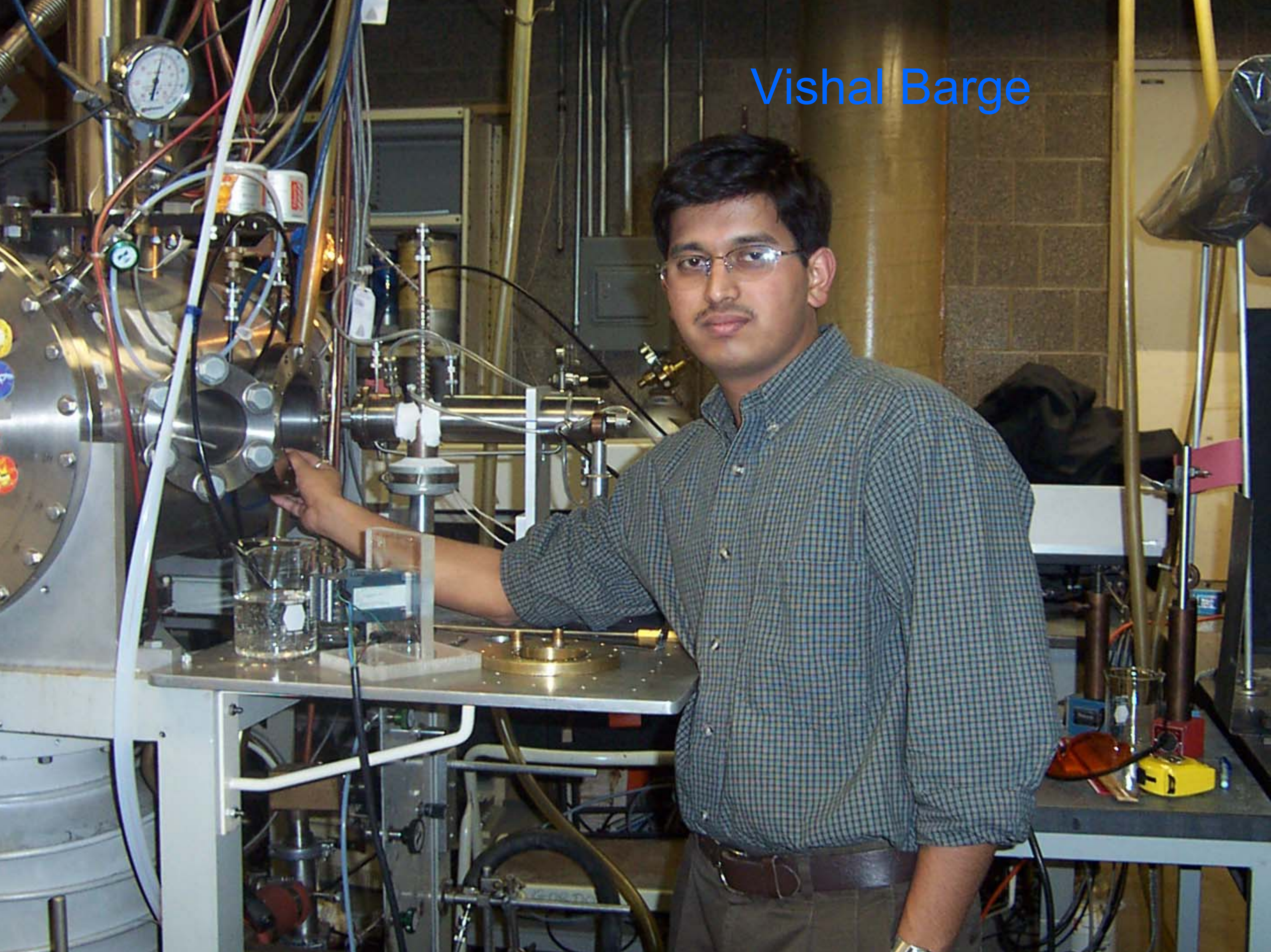


$CH_2{=}CHCl + \omega_3,\ 3\omega_1 \rightarrow$

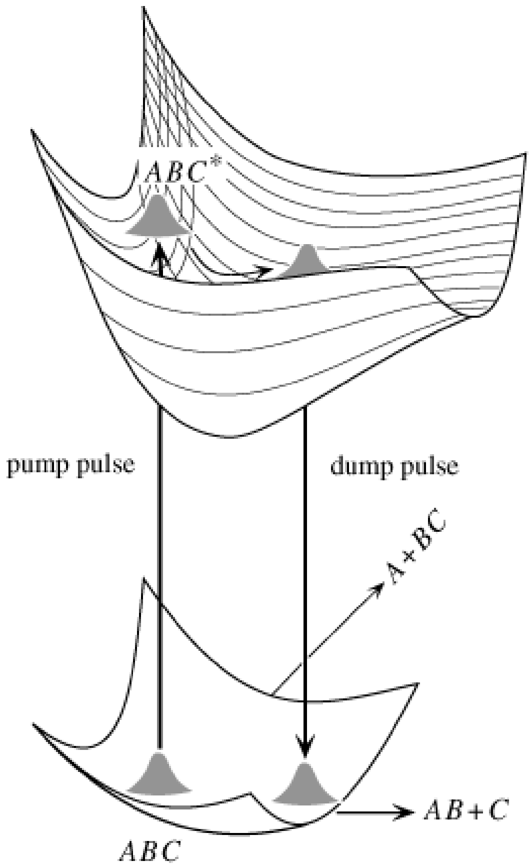
- Cl
- H
- HCl
- $H_2$

# VCl Experimental Setup




Vishal Barge

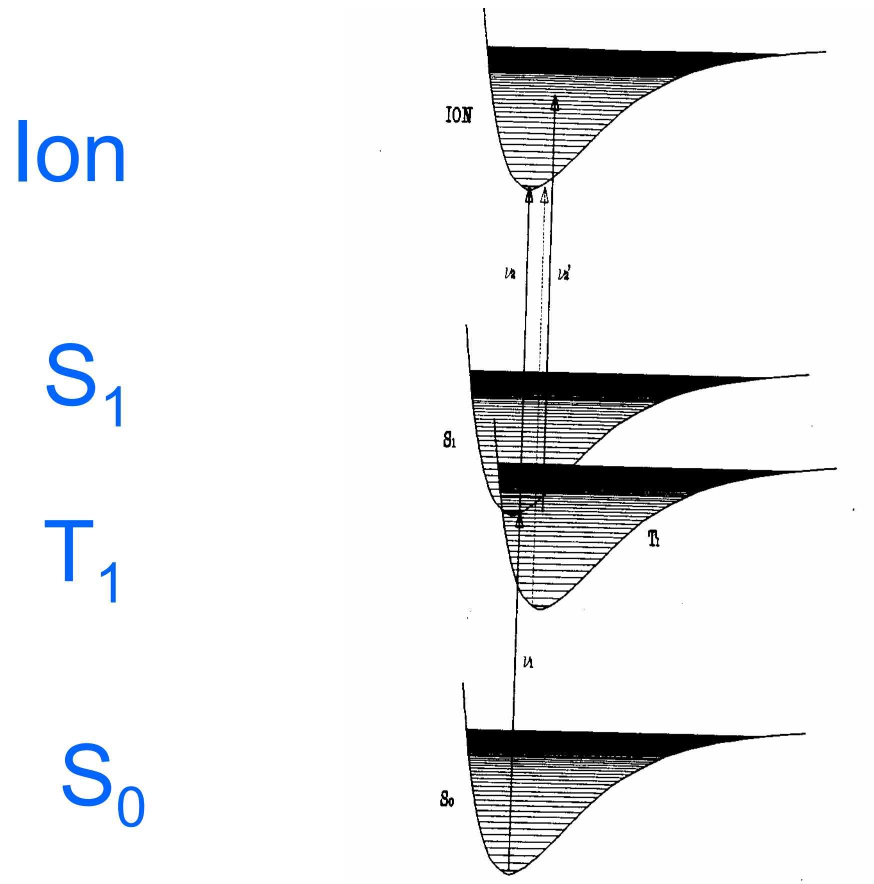
# Wave Packet Control



# Possible FEL Experiment

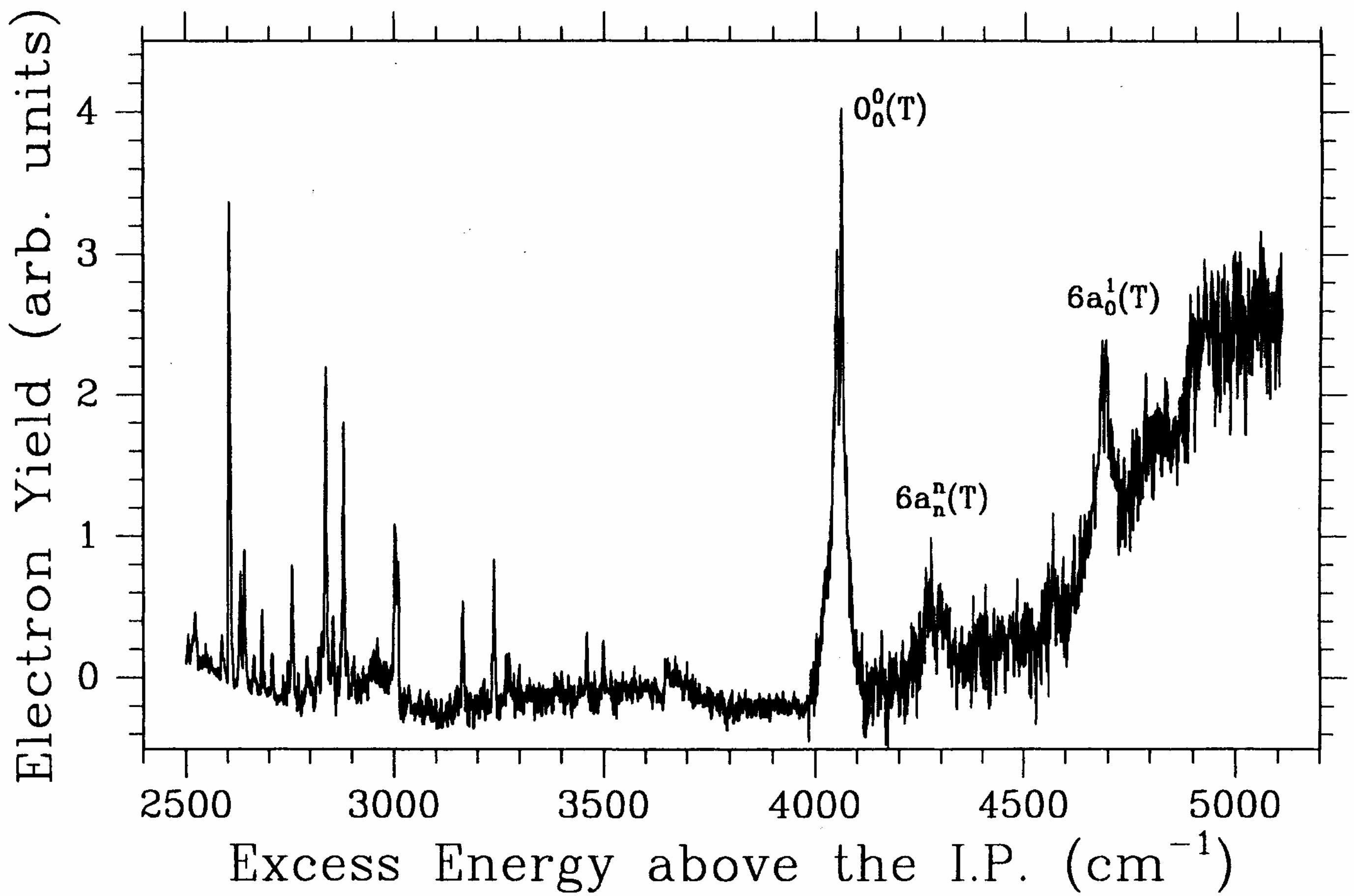
- Pump-probe study of time-resolved intersystem crossing in pyrazine
- Wave packet control of ISC

# Pyrazine Intersystem Crossing




$C_4N_2H_4$

# Photoelectron Spectrum of Pyrazine




Reprinted with permission from S. Hillenbrand, L. Zhu, P. Johnson, JCP **95**, 2237 (1991). Copyright 1991 American Institute of Physics.

# Material Processing

- Biomedical applications
- Microfluidics
- Nano-fabrication