Light Interactions with Matter

or

How We Know What We Know

Designing Matter
January 27, 2004

Brooks H. Pate
Department of Chemistry

Outline:

Stage 1: 1900 - 1940

How light tells us about the structure of matter (atoms and molecules)

Stage 2: 1950 – 1980

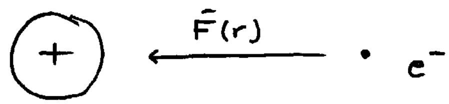
How matter can be used to create a new type of light (LASER)

Stage 3: 1980 – Present

How lasers can be used to create new behavior in matter

How Light Tells Us About the Structure of Matter

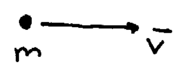
Spectroscopy and Energy Quantization



The Problem of the Hydrogen Atom

1. Accelerating electrons radiate light

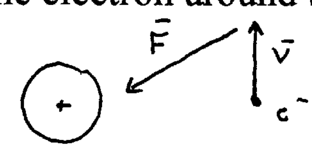
$$\bar{a} = \frac{d\bar{v}}{dt}$$



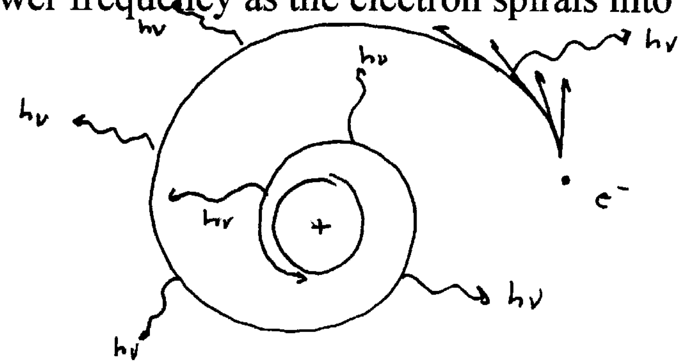
$|\bar{v}|$: SPEED

$\bar{v}$: VELOCITY (DIRECTION)

2. The Coulomb potential of the H-atom causes radial acceleration of the electron around the nucleus



3. The H-atom should continuously emit light of increasingly lower frequency as the electron spirals into the nucleus



OBSERVED H-atom ABSORPTION FREQUENCY PATTERNS

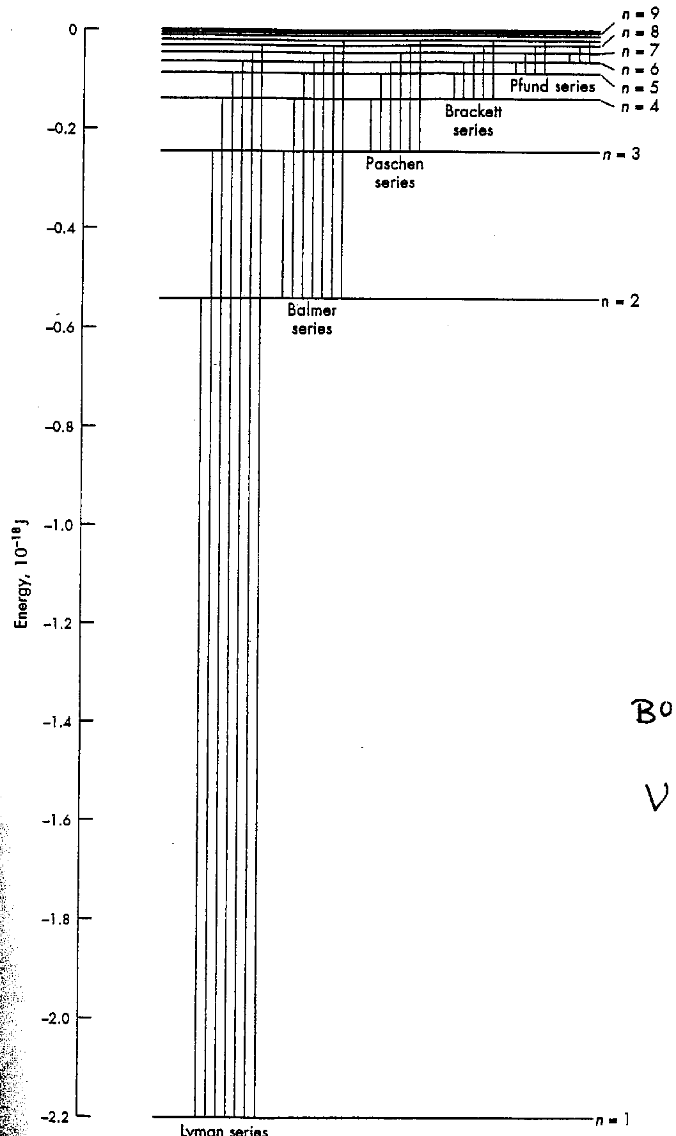


FIGURE 10-2
The hydrogen-atom energy-level diagram showing the Bohr atom quantum-number designations and the spectral series.

BOHR CONDITION:

$$\nu = \frac{E_f - E_i}{h}$$

G. Barrow, Physical Chemistry, 6th Ed.

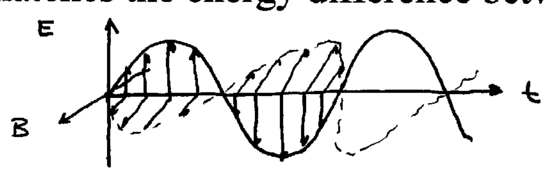
Experimental Result:

The H-atom only emits distinct frequencies of light

Quantum Theory: (Bohr, Physics 1922)

1. The bound states of an atom or molecule have discrete energies: Energy Quantization of the Stationary States

2. Light is emitted or absorbed when the frequency of light matches the energy difference between the quantum states



$$\lambda \nu = c = 3 \times 10^{8} \ m/s$$

Spectroscopy: Interpreting the pattern of the frequencies of light absorbed by matter.

Information: 1) Structure of Matter

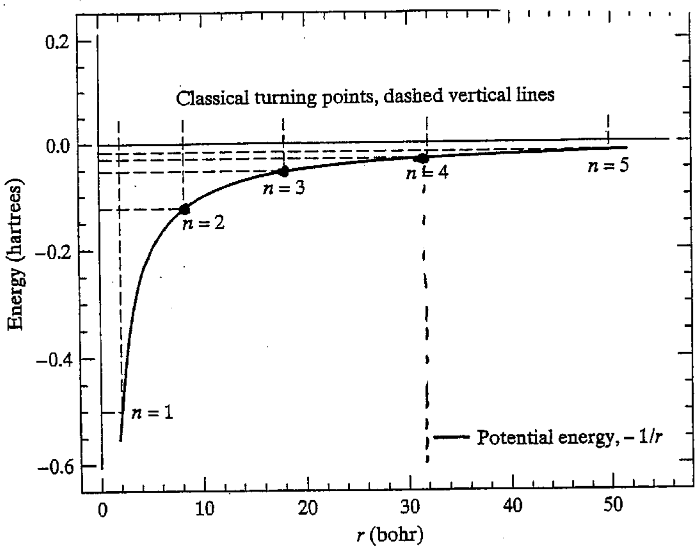
2) Bond Strengths and Ionization Energies

Applications: 1) Medical Diagnostics

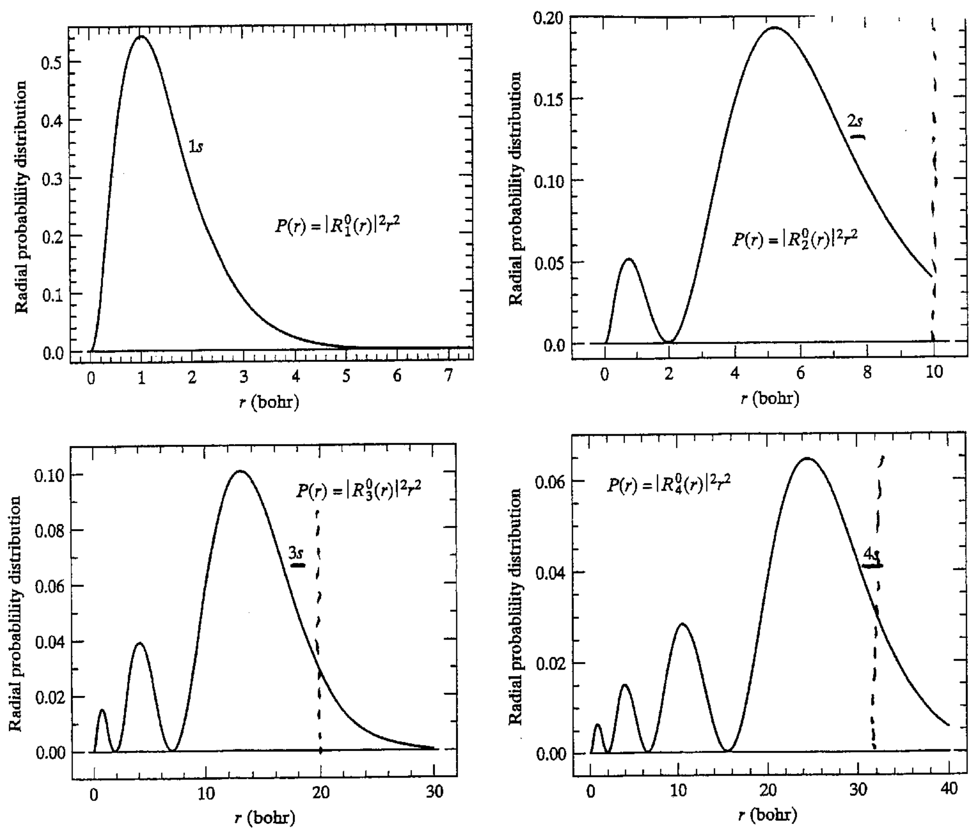
2) Environmental Monitoring

3) Astronomy

QUANTUM MECHANICS OF THE H-atom

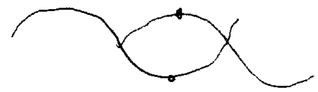


◀ FIGURE 13.6
The coulombic potential in atomic units as a function of radial distance for a hydrogen atom. The hydrogen-atom energy eigenvalues are shown as horizontal dashed lines. The point at which these horizontal lines intersect the potential are the classical turning points, shown by the vertical dashed lines.



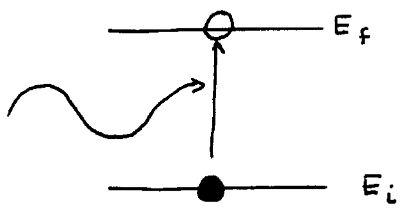
▲ FIGURE 13.7
The radial probability distributions $P(r)$ for 1s, 2s, 3s, and 4s orbitals for the hydrogen atom. Radial distances are expressed in bohr. Each distribution is obtained from Eq. 13.27.

L.M. Raff, Principles of Physical Chemistry



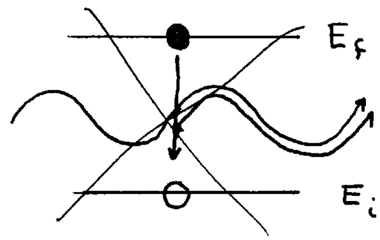
Basic Light – Matter Interactions (Einstein)

Absorption



$$\nu_L = \frac{E_f - E_i}{h}$$

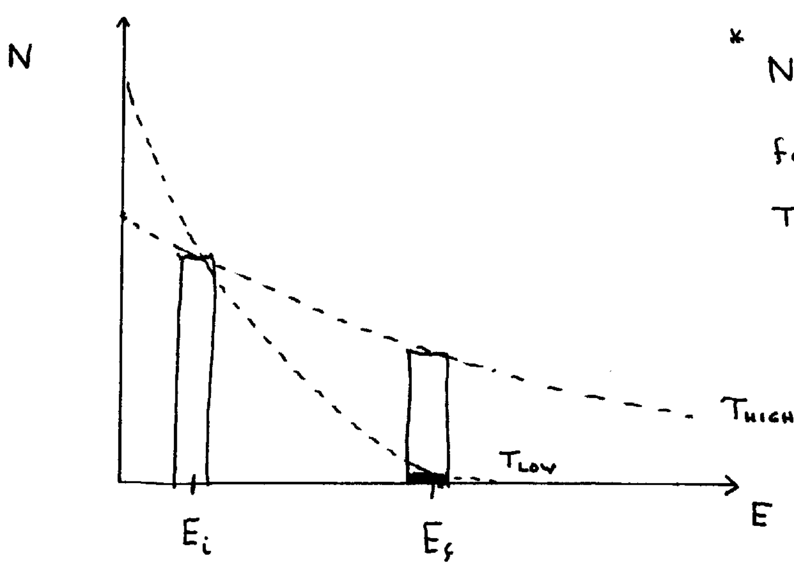
Stimulated Emission



$$\nu_L = \frac{E_f - E_i}{h}$$

Key: At thermal equilibrium, absorption dominates.

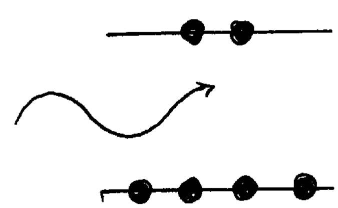
The Boltzmann Distribution $\quad P(E) = \lambda e^{-E/RT}$



* $N_{LOW} > N_{HIGH}$

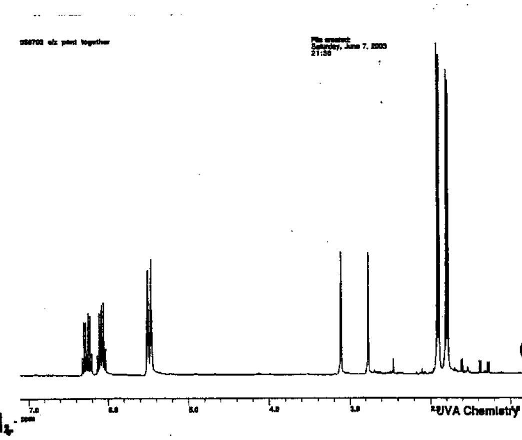
for $T > 0$ at

THERMAL EQUILIBRIUM

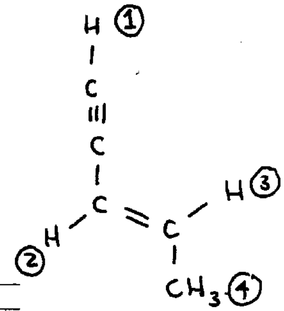


Nuclear Magnetic Resonance (NMR)

Synthesis produces two isomers:

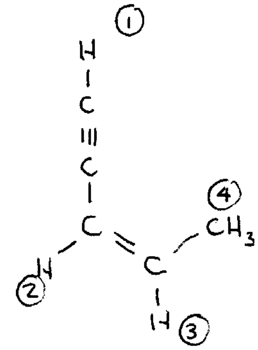


$\nu \approx 300\,MHz$



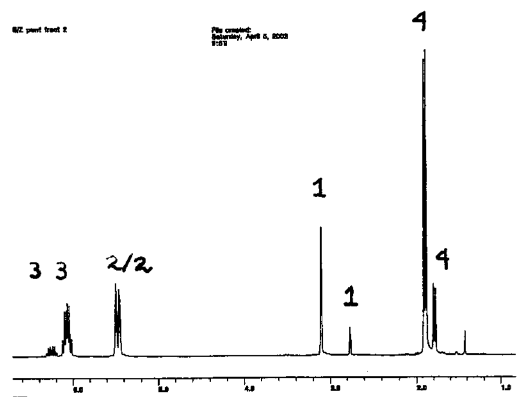
"E" pentenyne

bp 51°C



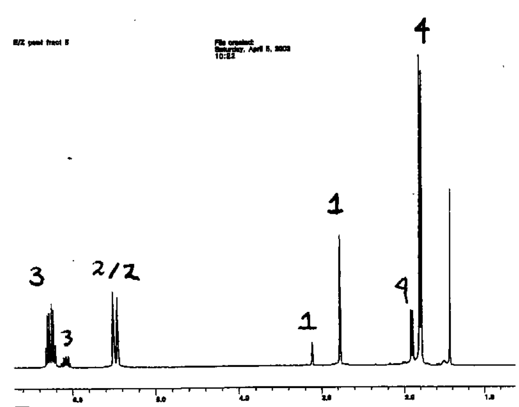
"Z" Pentenyne

bp 43°C



Early in Distillation

(mostly Z - isomer)

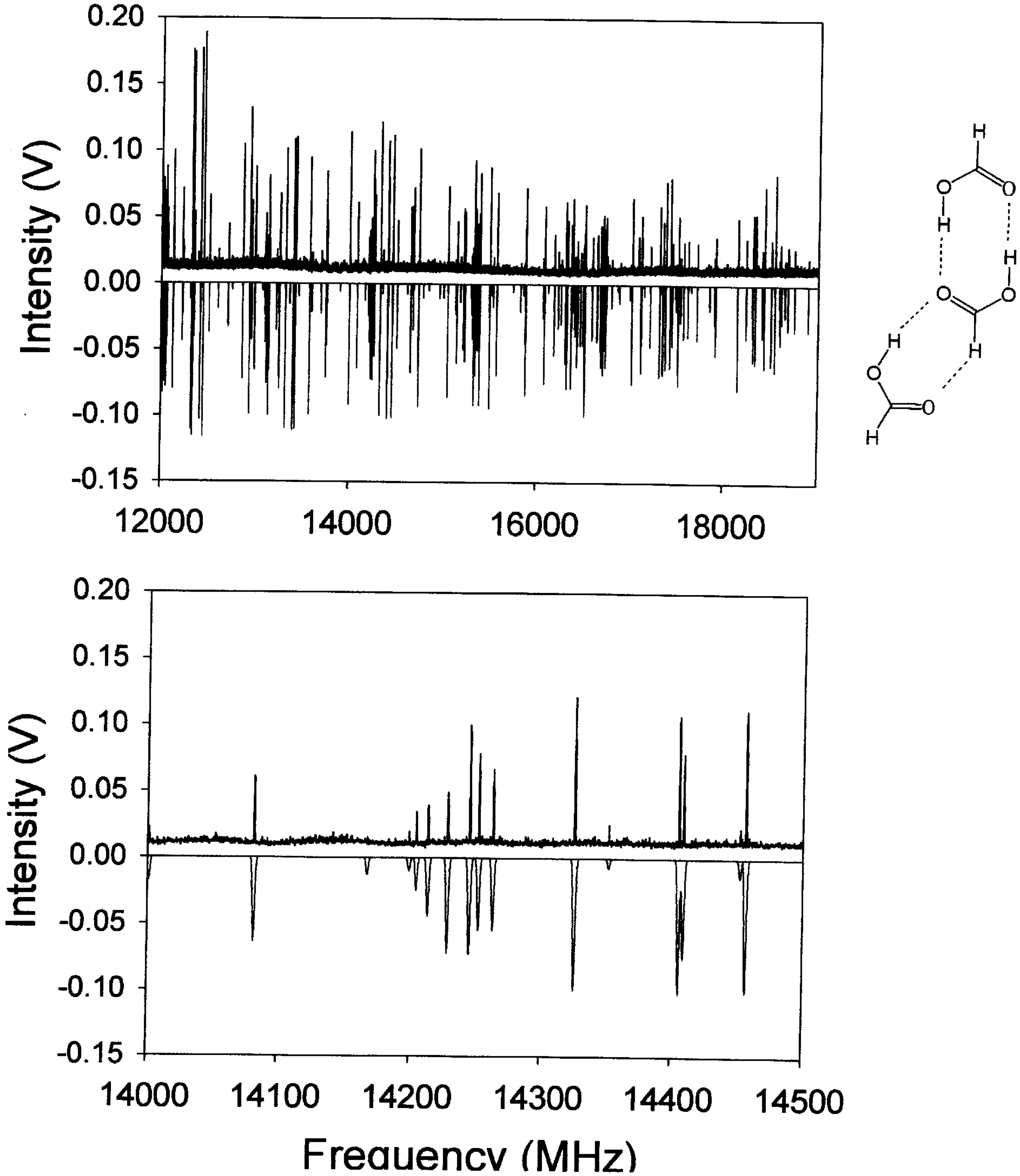


Late in Distillation

(mostly E - isomer)

Frances Rees (UVa)

Formic Acid Trimer
Ground State Rotational Spectrum

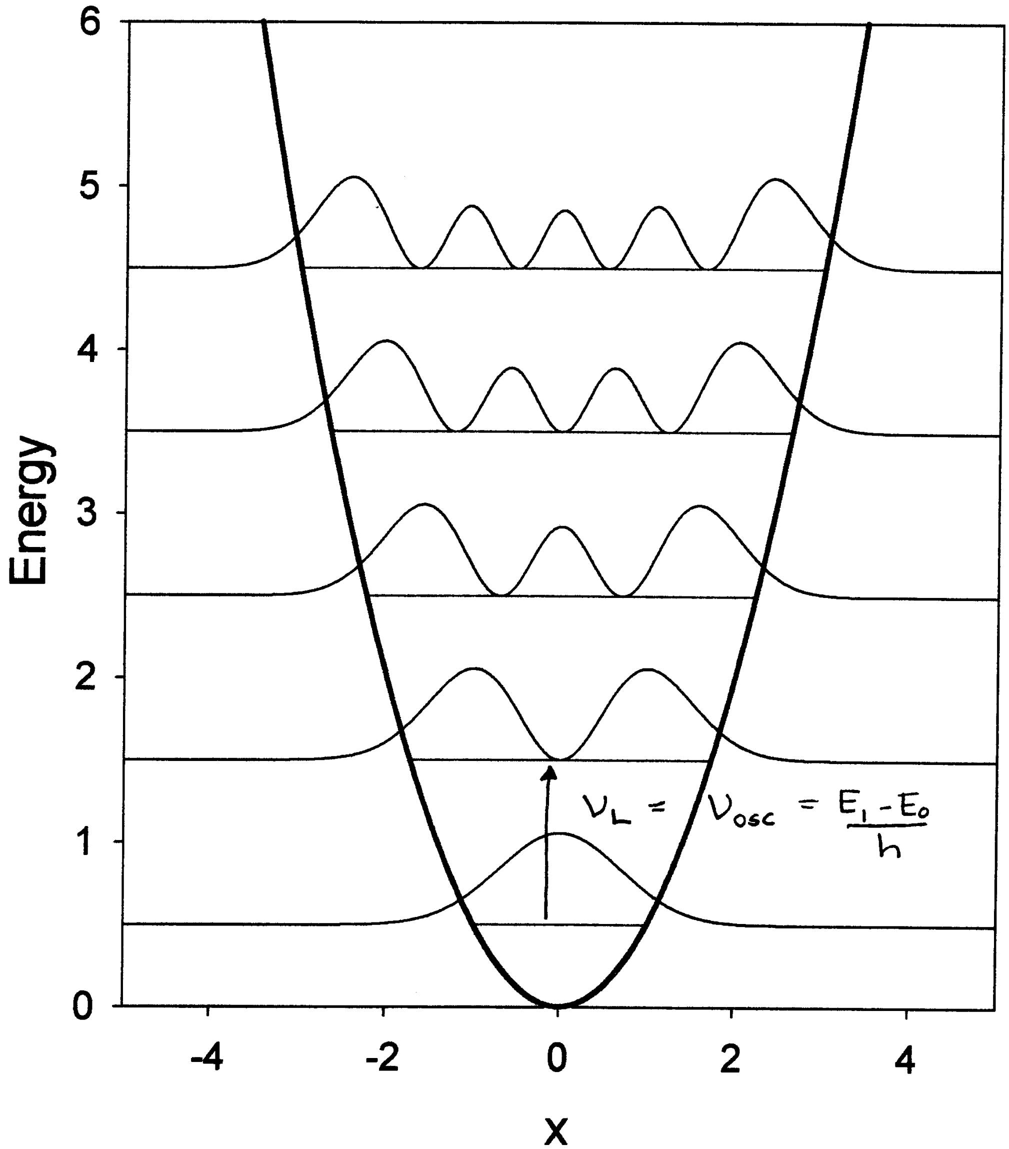


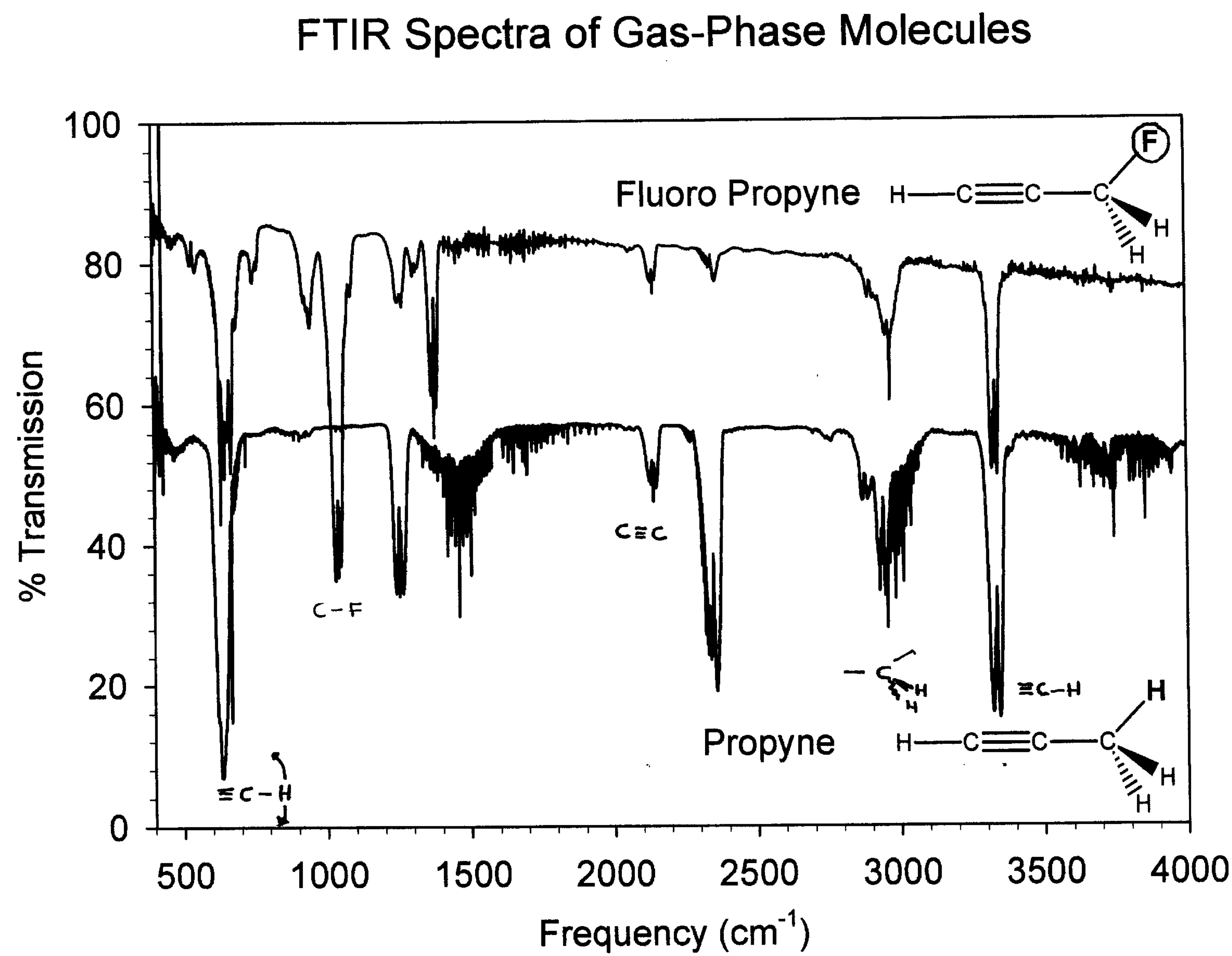
Stationary States of the Harmonic Oscillator

$$V(x) = 1/2\ kx^2$$

$$F(x) = -kx$$

$$E_n = (n + 1/2)\ h\nu$$





FTIR Spectra of Gas-Phase Molecules
Fluoro Propyne
Propyne
C−F
C≡C
≡C−H
% Transmission
Frequency (cm^{-1})
0
20
40
60
80
100
500
1000
1500
2000
2500
3000
3500
4000

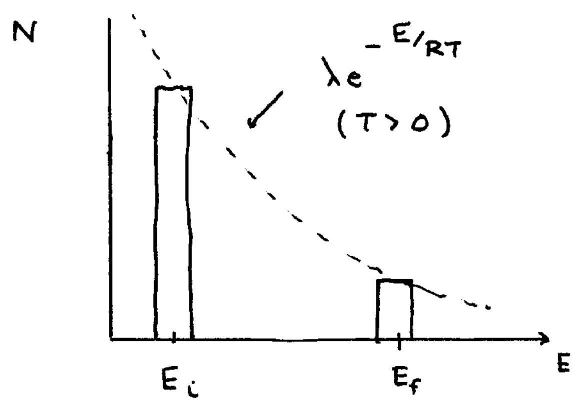
Using Matter to Create a New Type of Light

The Laser

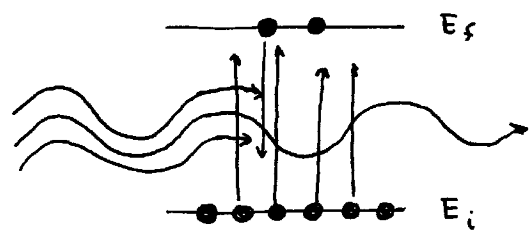
Idea: *Store energy in the stationary states of matter and then release it as light*

Problem: *How do you beat thermodynamics?*

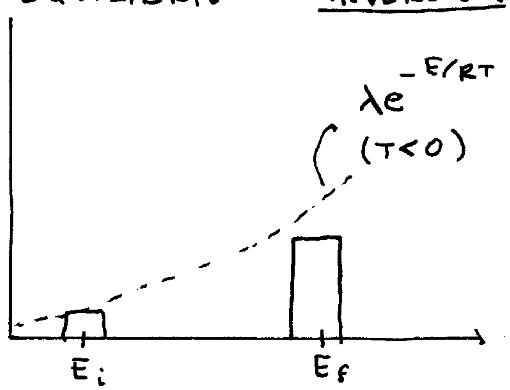
THERMAL EQUILIBRIUM



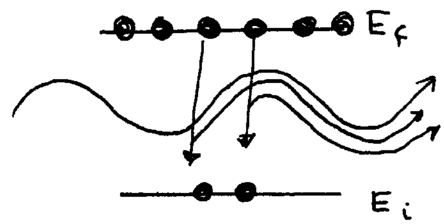
NET ABSORPTION:



"NON EQUILIBRIUM" : INVERSION



NET LIGHT AMPLIFICATION :



$T=0^+ \longrightarrow +\infty, -\infty \longrightarrow T=0^-$

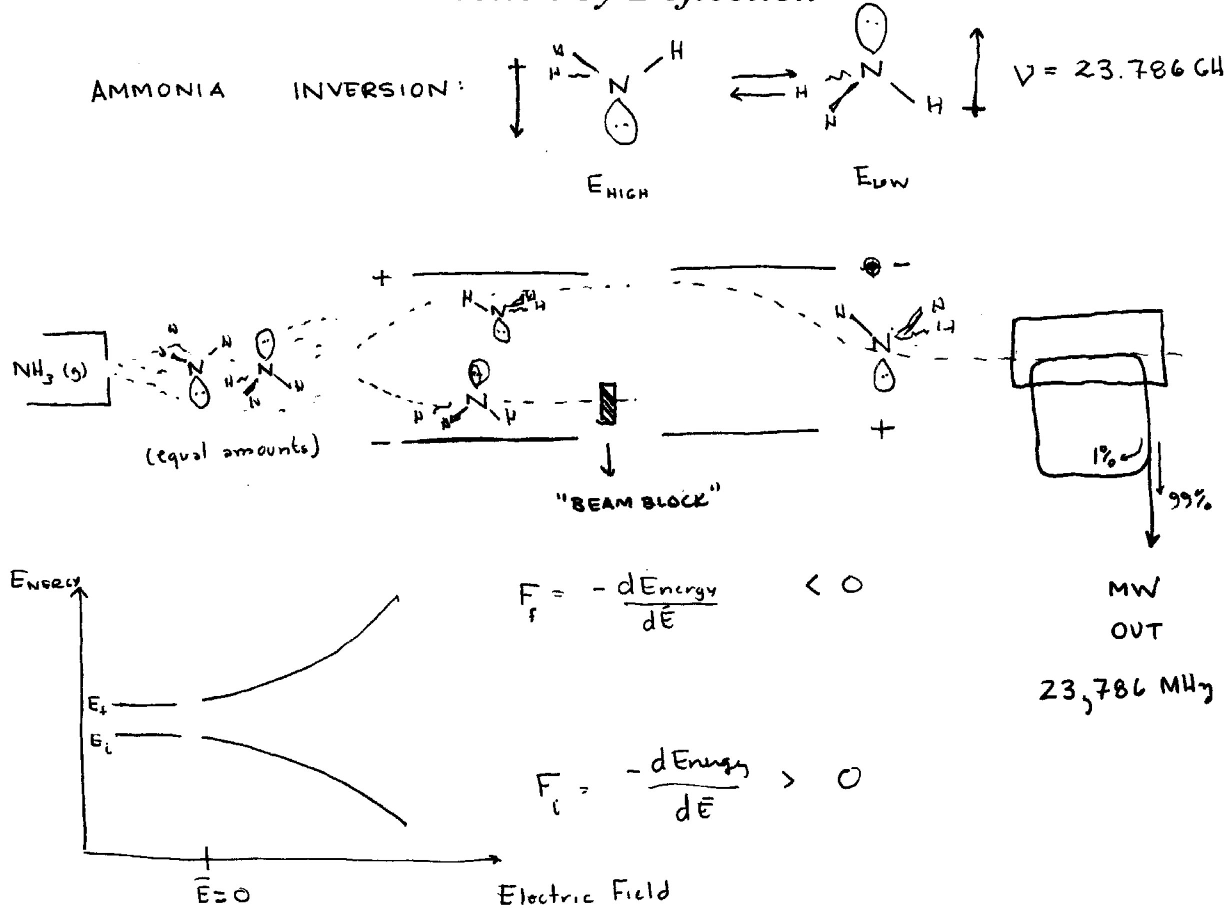
COLD $N_i > N_f$ $(N_i = N_f)$ $N_i < N_f$ HOT

Microwave Amplification by Stimulated Emission of Radiation (MASER)

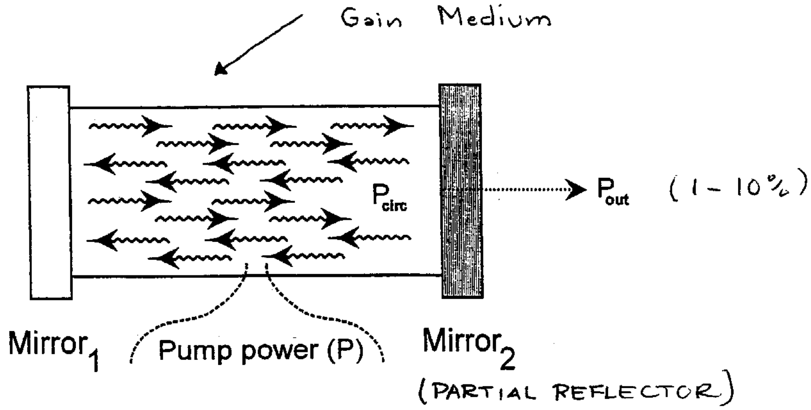
1954

(C.H. Townes, Physics 1964, A.L. Schawlow, Physics 1981, S. Chu, Physics 1997)

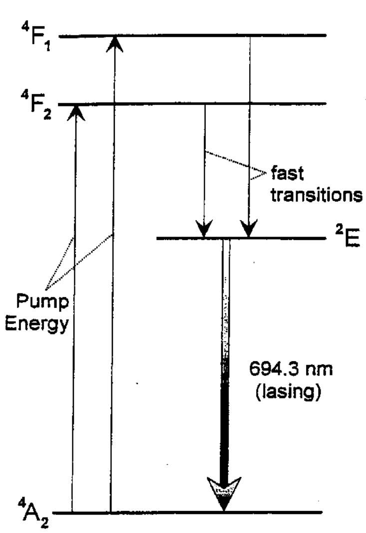
Physical Separation of Higher Energy Molecules: *"Selection by Deflection"*



Laser Basics:



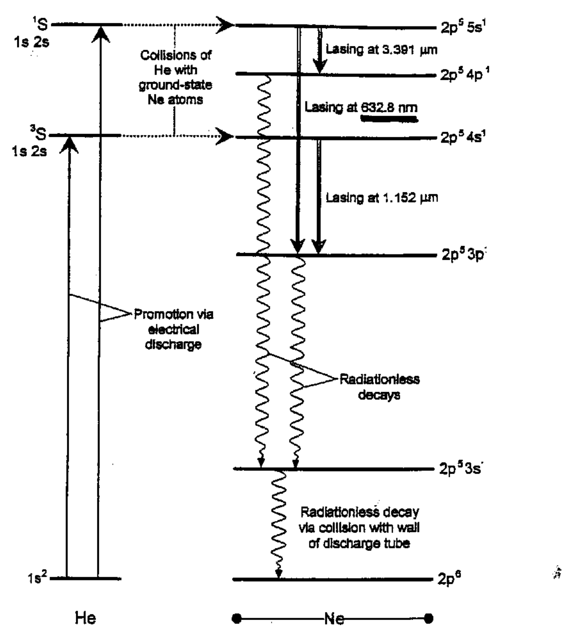
RUBY LASER



Ted Maiman 1960

(3 LEVEL)

He/Ne Laser



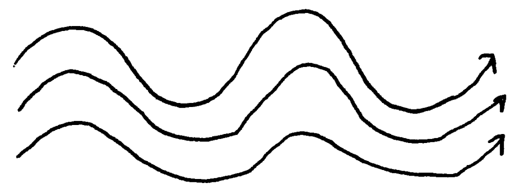
Javan, Bennett, and Harriott 1961

(4 LEVEL)

G.R. van Hecke and Kerry K. Karukstis, "A Guide to Lasers in Chemistry" (Jones and Bartlett, Boston, 1998).

Special Properties of Light
Created from Matter

1. The light is *coherent*

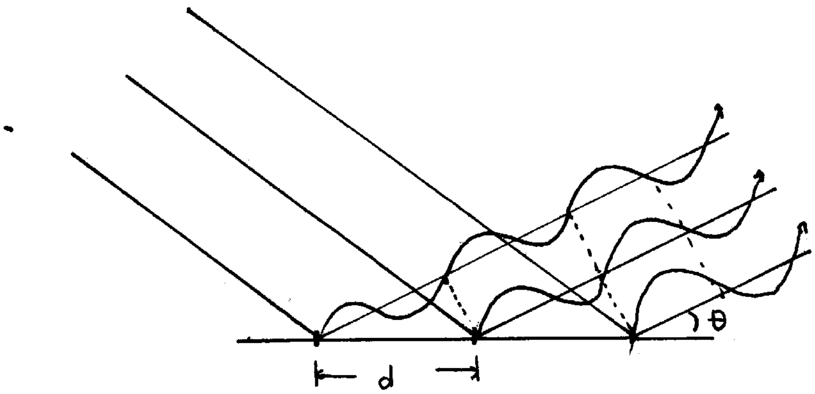


COHERENCE LENGTH:	LIGHT BULB	25×10^{-6} m (0.000025 m)
	Hg Lamp	0.08 m
	He/Ne Laser	50 m

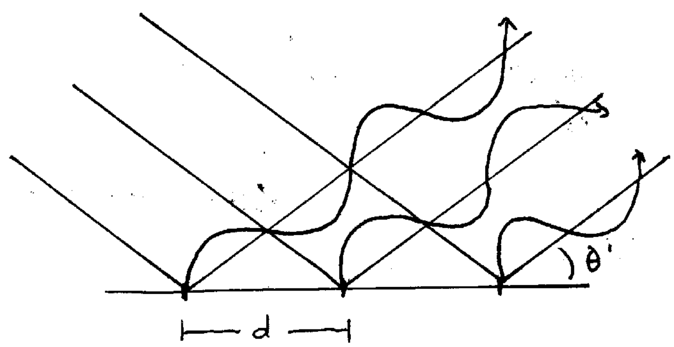
2. The light can be made "monochromatic" (narrow range of frequencies.

3. The "spectral brightness" greatly exceeds any thermal source (lightbulb).

LIGHT COHERENCE : DIFFRACTION



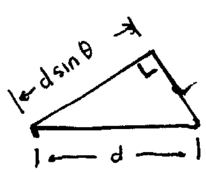
BRIGHT SPOT at θ

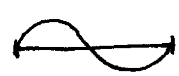


NO SPOT AT θ'

CONSTRUCTIVE INTERFERENCE

BRAGG CONDITION

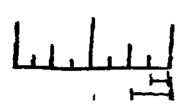




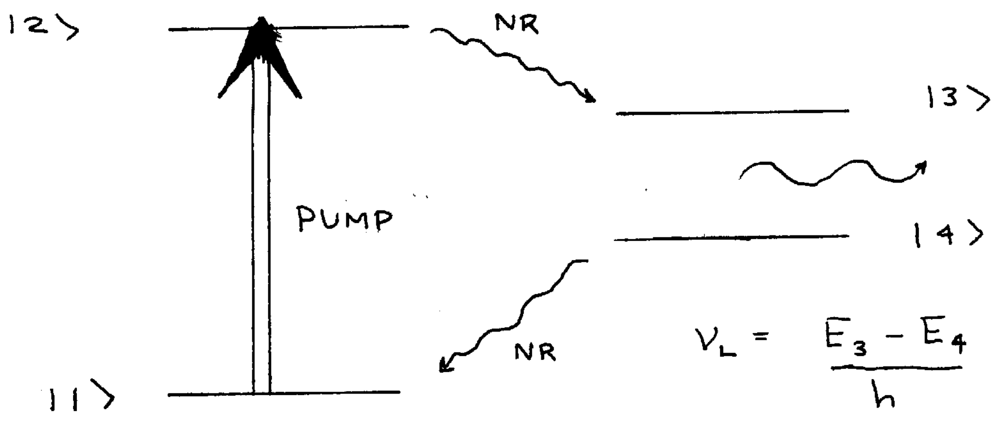
$$d\sin\theta = n\lambda$$

$$\sin\theta \approx \theta = \frac{n\lambda}{d} \qquad \theta_{NEXT} = \frac{(n+1)\lambda}{d} \qquad \overbrace{(\theta_{NEXT} - \theta)}^{\text{SPOT SPACING}} = \frac{\lambda}{d}$$

RULER BLAZES:



Common LASER Level Scheme
The Four Level System



$\nu_L = \dfrac{E_3 - E_4}{h}$

Issues:

1. Efficiency : $\nu_{PUMP} > \nu_{LASER} \Rightarrow E_{PUMP} > E_{LASER}$

2. Tunability

3. Total Power

Using Lasers to Create New Behavior in Matter: *How do molecules work?*

(Zewail, Chemistry 1999)

- Nanotechnology
- Biological Systems

Key: Remove the energy stored in matter in a very short time: ~ 10^{-15} s (femtosecond)

Advantages:

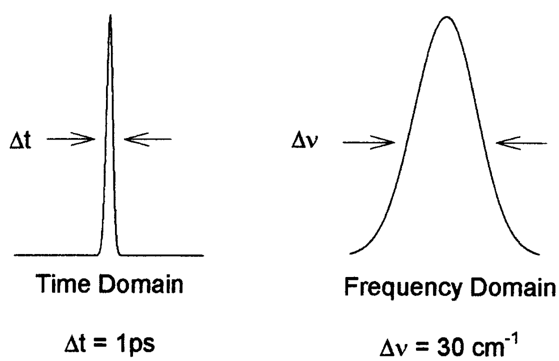
1. Very strong peak field strengths (rips matter apart)

2. Short pulses have a large frequency spread: *Quantum Dynamics*

Ultrafast Laser Spectroscopy

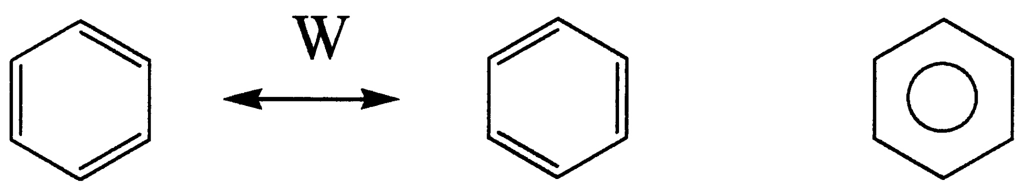
(picosecond (10^{-12} s) and femtosecond (10^{-15} s))

- High time resolution of quantum dynamics
- Studies of coherent superpositions of many eigenstates

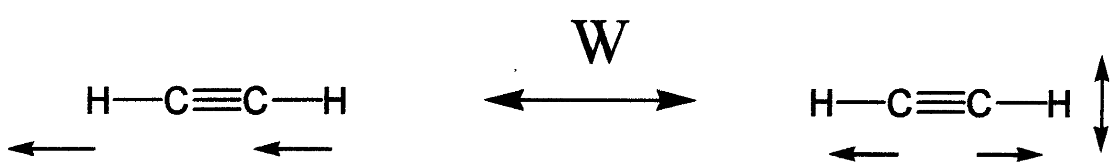


Quantum Mechanical Resonance

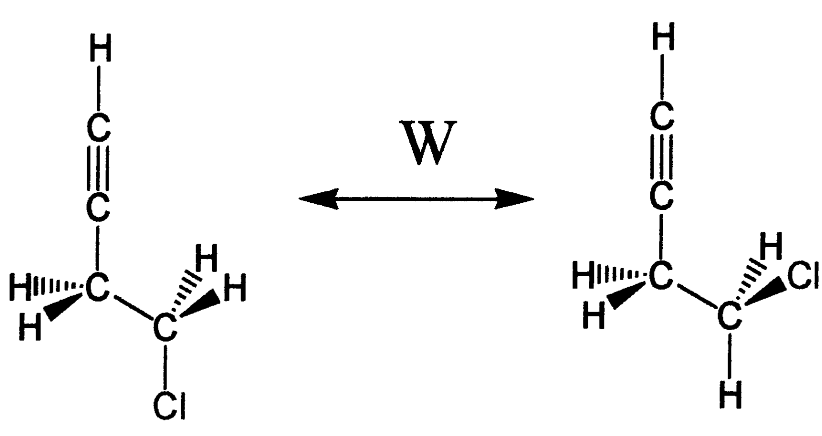
Electron Motion



Vibrational Motion



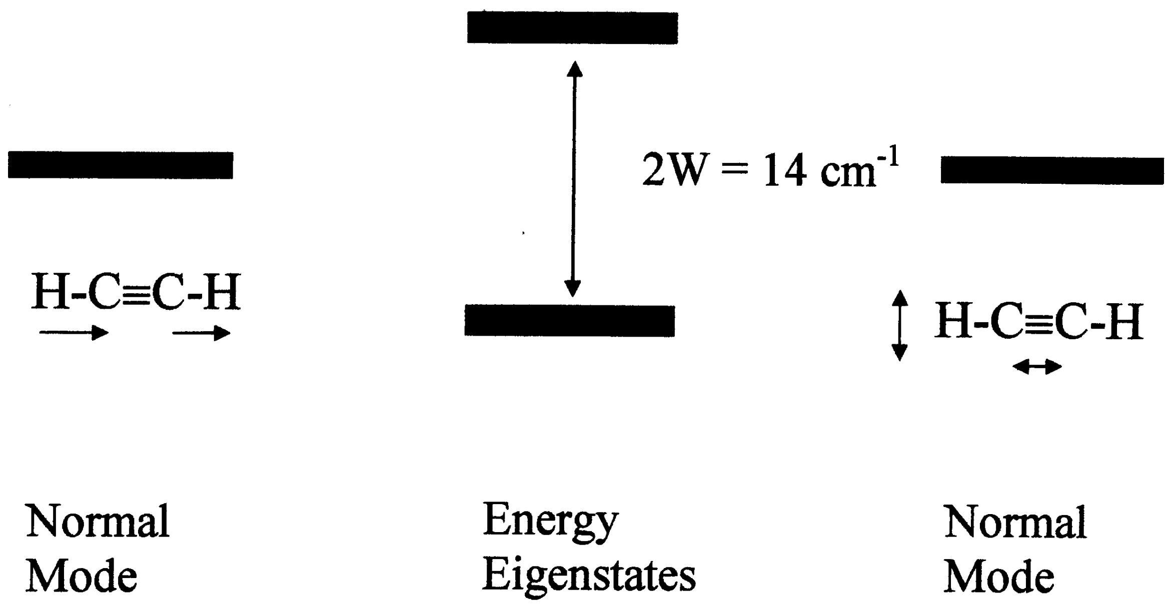
Conformational Structure

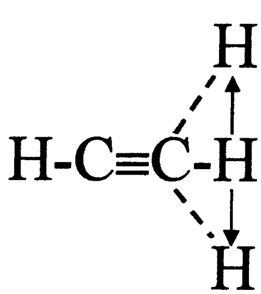


Perturbations and Quantum Dynamics

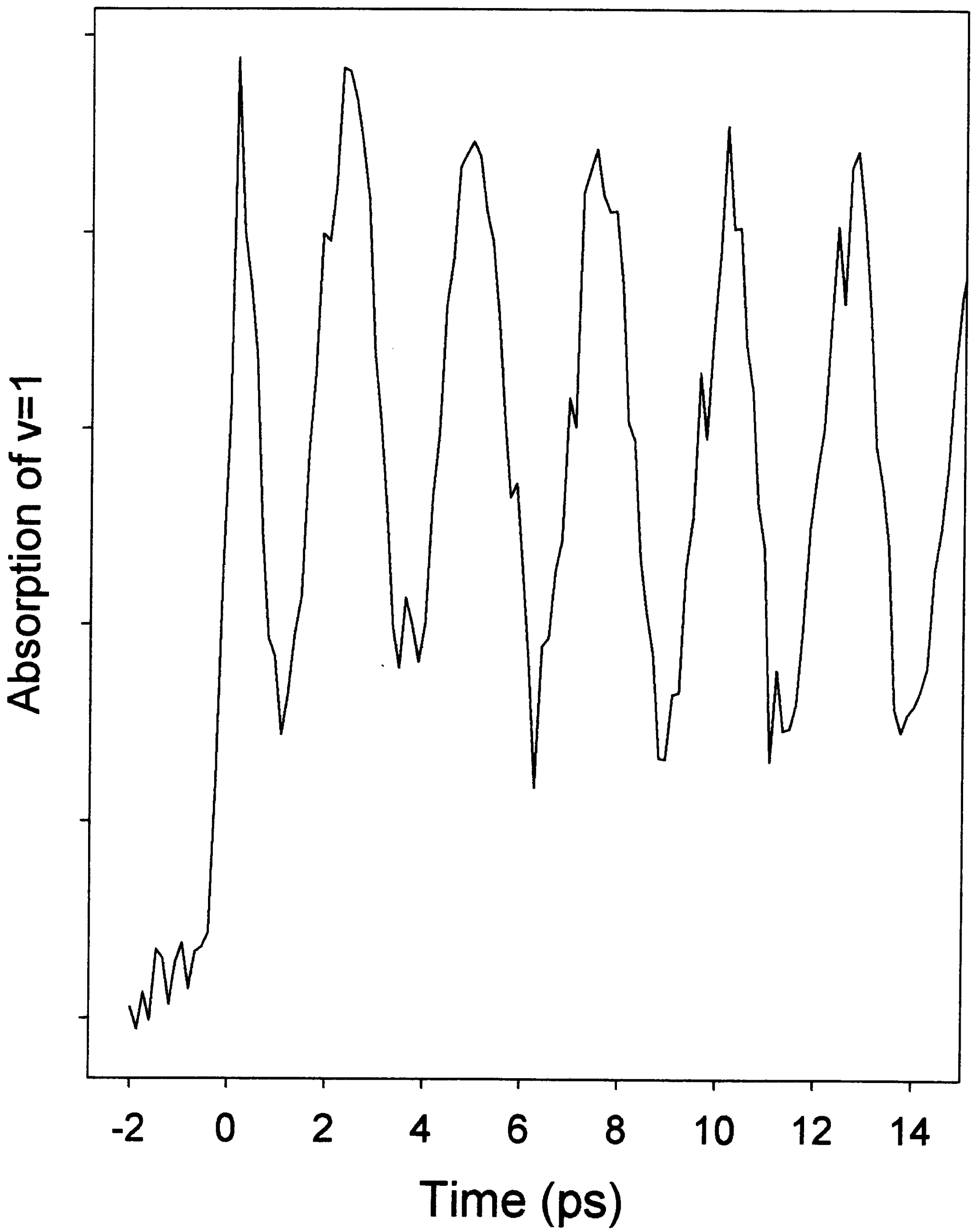
Acetylene: H-C≡C-H

Stretch-Bend Interaction:

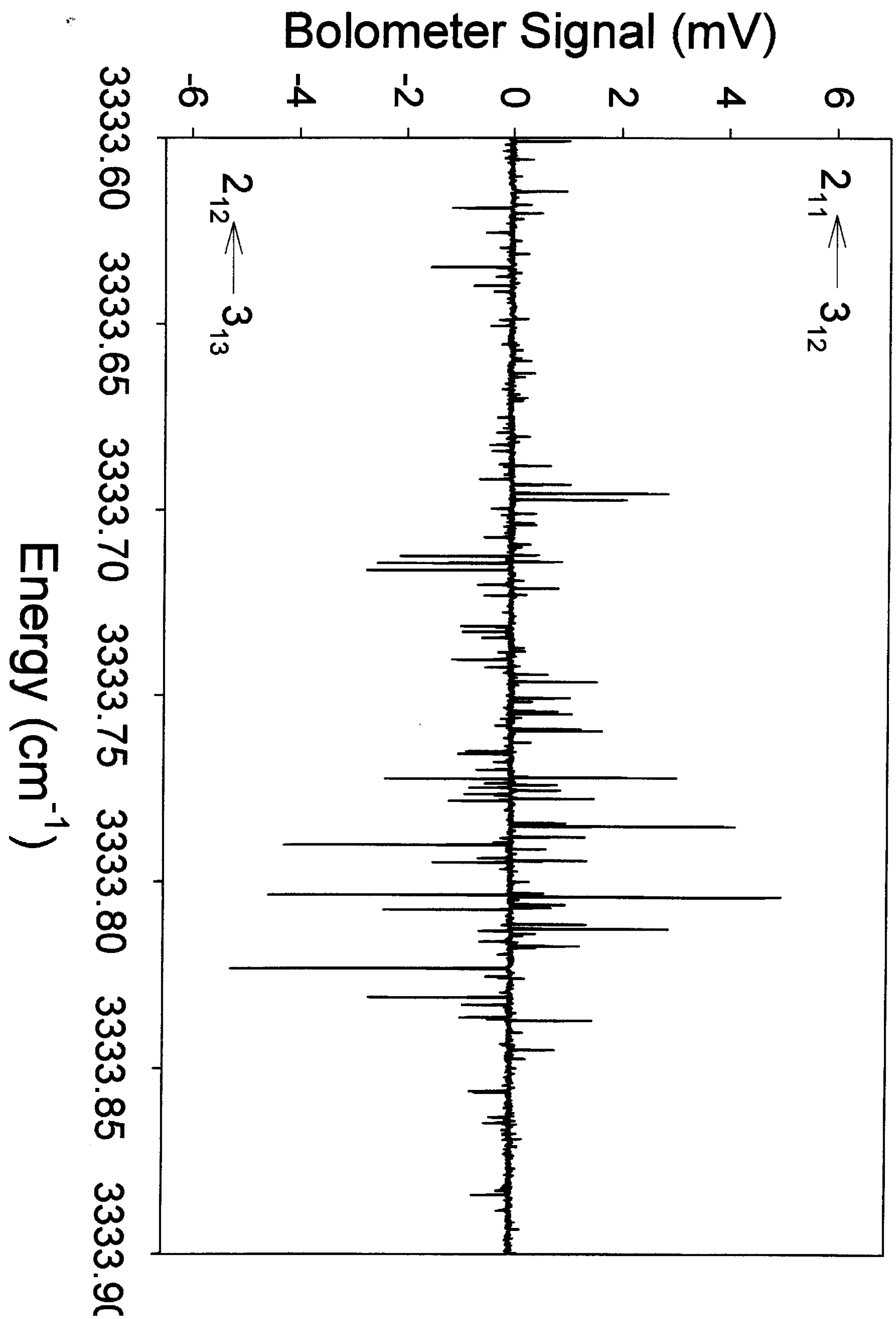




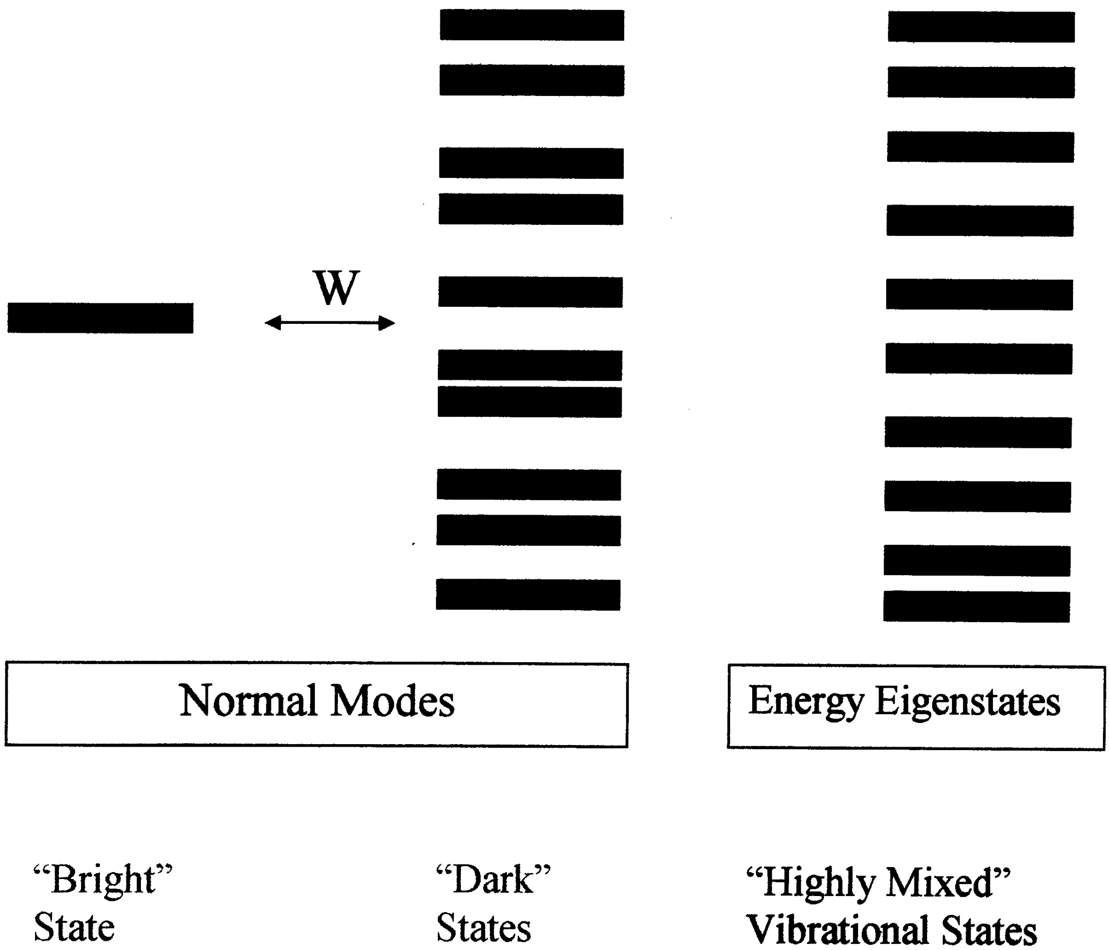
Acetylenic CH Stretch Dynamics of Gas Phase Acetylene (C_2H_2)



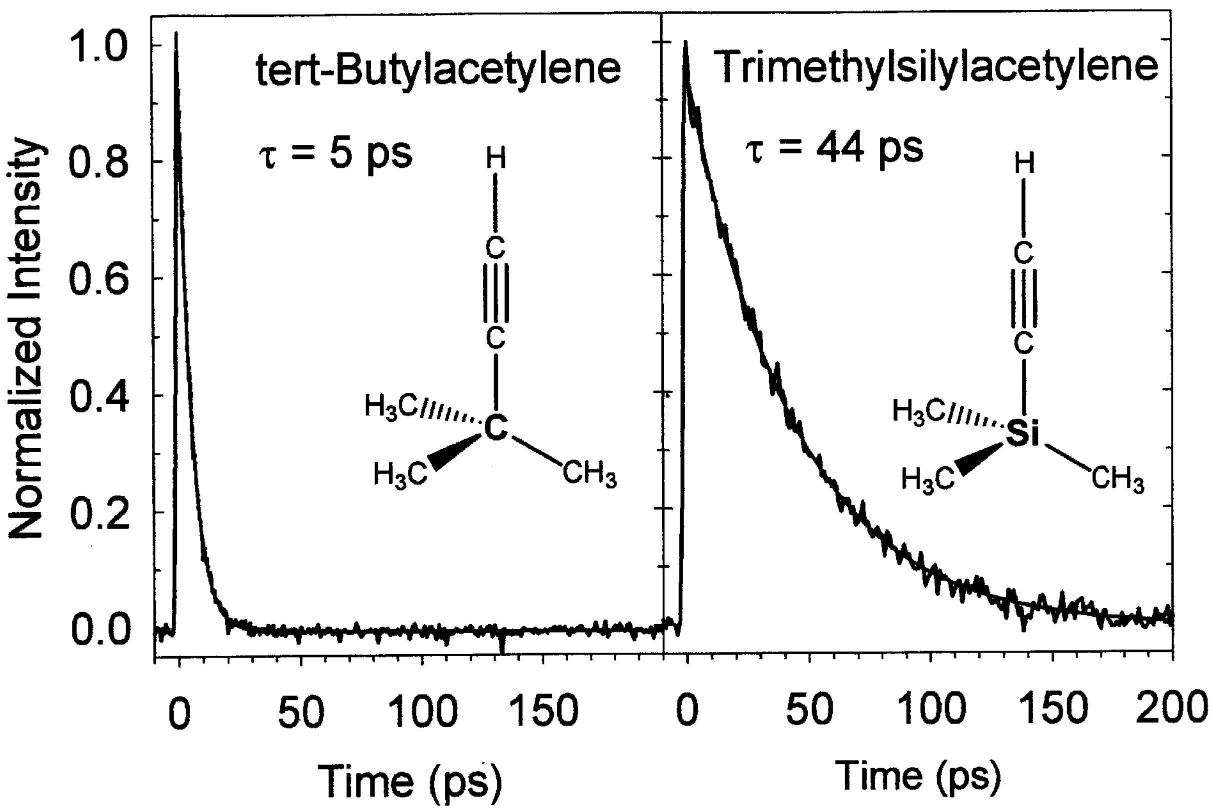
Hyun Yoo (UVa)

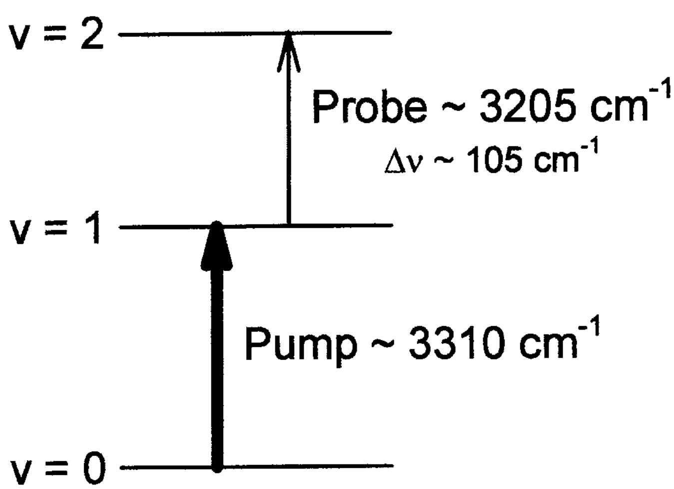

Bolometer Signal (mV)
6
4
2
0
-2
-4
-6
$2_{11} \leftarrow 3_{12}$
$2_{12} \leftarrow 3_{13}$
3333.60
3333.65
3333.70
3333.75
3333.80
3333.85
3333.90
Energy (cm^{-1})

Many Perturbations: Intramolecular Vibrational Energy Redistribution



Relaxation of the Excited State Population
in Dilute Carbon Tetrachloride (CCl_4) Solution





Hyun Yoo (UVa)

Coherent Nuclear Motion: "Wavepackets"

Shape of the laser pulse influences the motion

Approaches:

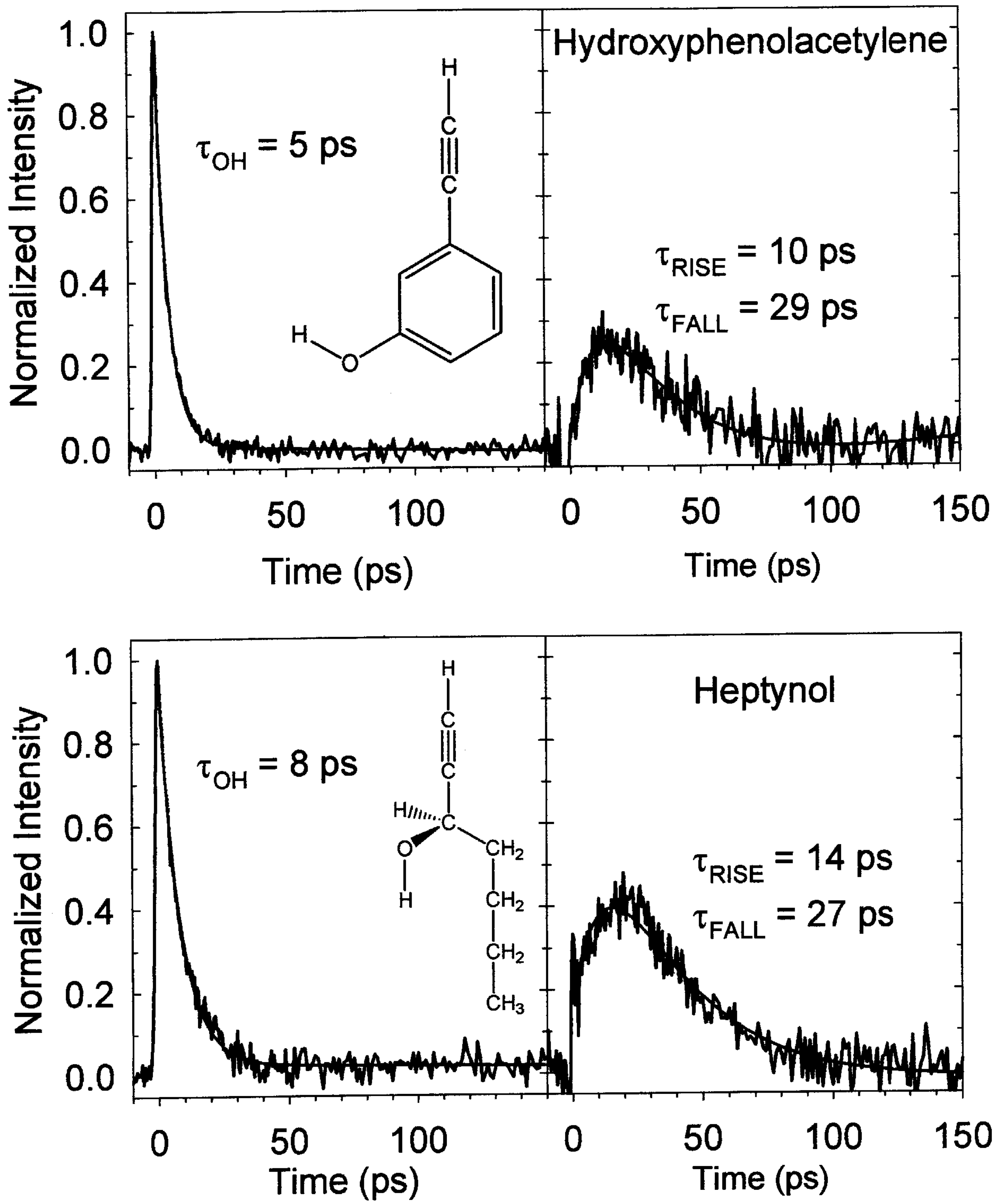
1. Use strong laser fields to dictate the molecular motion

2. Use a sequence of pulses to intercept the motion at an opportune time

3. Start with highly excited molecules and use quantum interference to shape the properties

Intramolecular Energy Flow

in Dilute Carbon Tetrachloride (CCl_4) Solution



Control of Chemical Reactions by Feedback-Optimized Phase-Shaped Femtosecond Laser Pulses

A. Assion, T. Baumert,* M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, G. Gerber