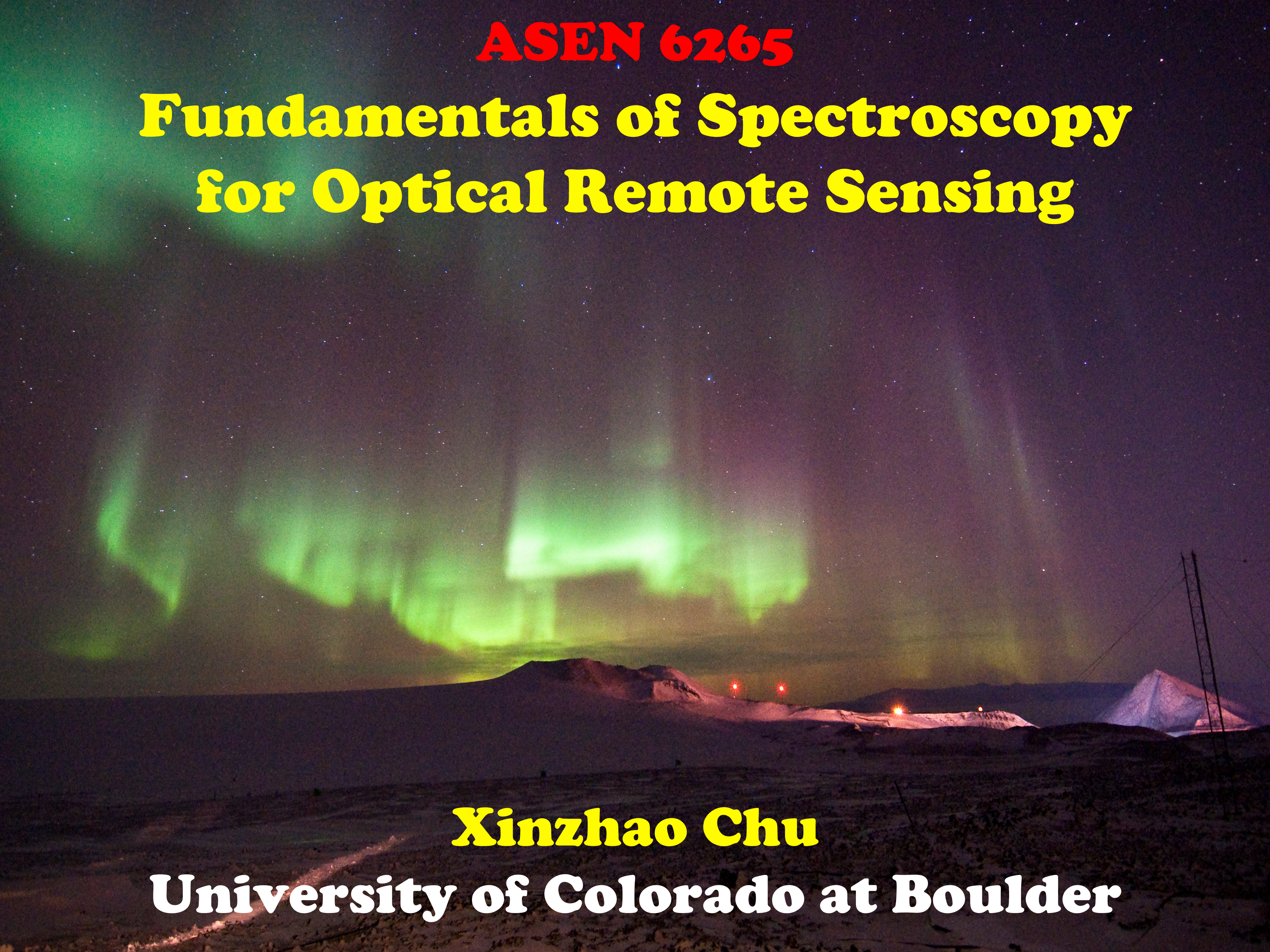
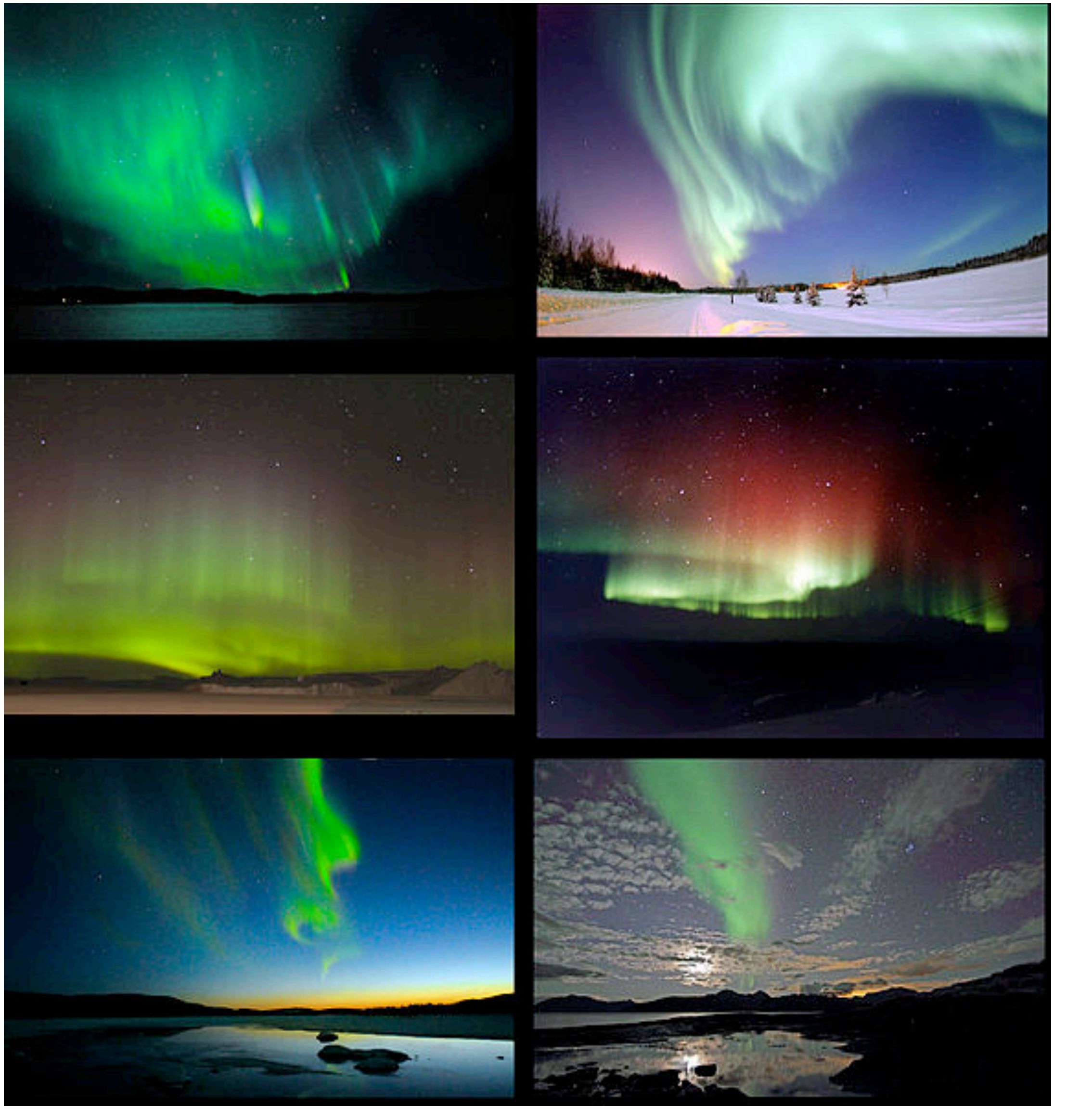


ASEN 6265

Fundamentals of Spectroscopy for Optical Remote Sensing

Xinzhao Chu
University of Colorado at Boulder

Aurora: How is it formed? Why different colors?



From spectroscopy point of view, aurora is simple and nothing more than atomic emission of photons! The answers lie in the O and N spectroscopy.

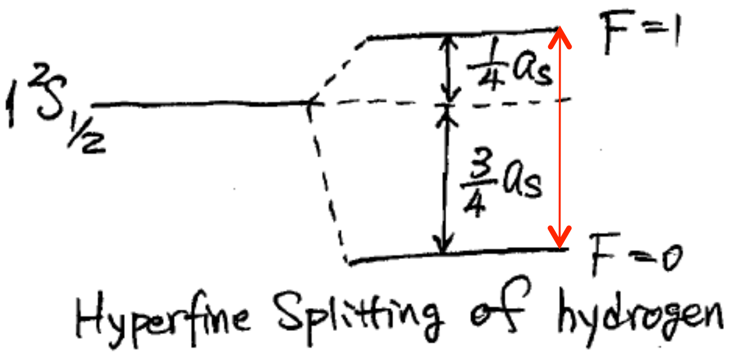
What is spectroscopy about?
Why is spectroscopy important?
How to apply spectroscopy?
How to study spectroscopy?
… …

Instead of traditional teaching sequence, let's discuss first the applications of spectroscopy in various field and how spectroscopy is indispensable to modern physics, chemistry, biology, medicine, material science, astronomy, atmosphere and space sciences, etc.

Then we will introduce the course structures, and attempt to answer the above questions in the first round.

1. How to identify species?

Example 1. How do people know that hydrogen (H) is distributed in the universe and is a major species ?



The frequency corresponding to the transition between these two levels of hyperfine splitting is

$$\nu_H = 1420.405751786 \text{ MHz}$$

Corresponding wavelength is

$$\lambda_H = \frac{c}{\nu_H} \approx 21 \quad cm$$

This is the most famous spectral line in the universe!

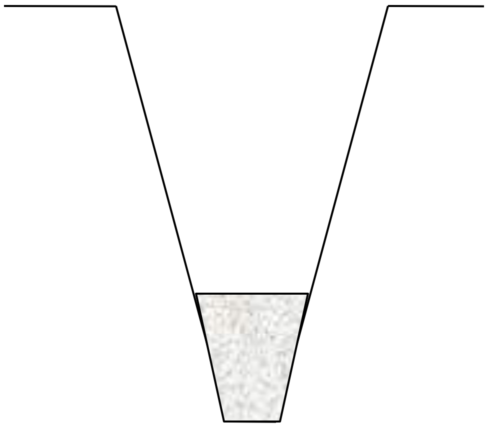
It was the first and also the most frequently used frequency/wavelength in radio astronomy to detect the distribution of hydrogen (H) atoms in the universe. (H is > 70%)

By measuring the Doppler shift of the Hydrogen spectral line, the moving velocities of objects in the universe can be determined.

→ leading to the discovery of expansion of the universe

1. How to identify species?

Example 2. How to find out what gas is in the "death" dip?



A chicken would pass out after being dropped to the dip for about 1 min. How do you find out the killer?

Collect a bottle of gas from the dip, and then analyze it by

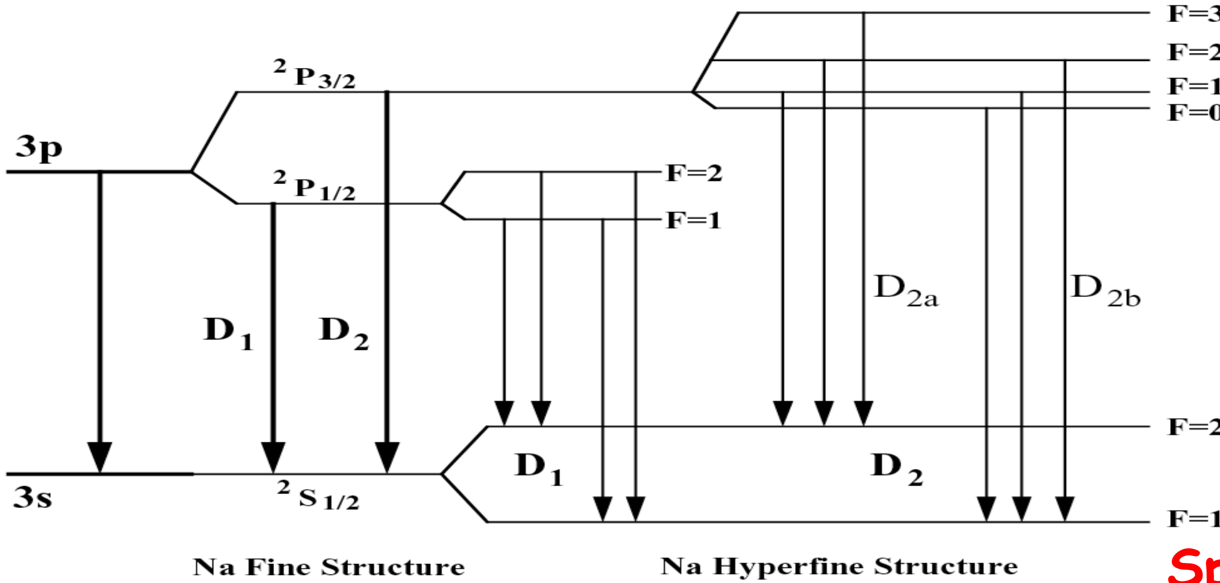
Mass spectroscopy

Optical spectroscopy

The killer is CO_2

1. How to identify species?

Example 3. How do we explore the species in the atmosphere/space?

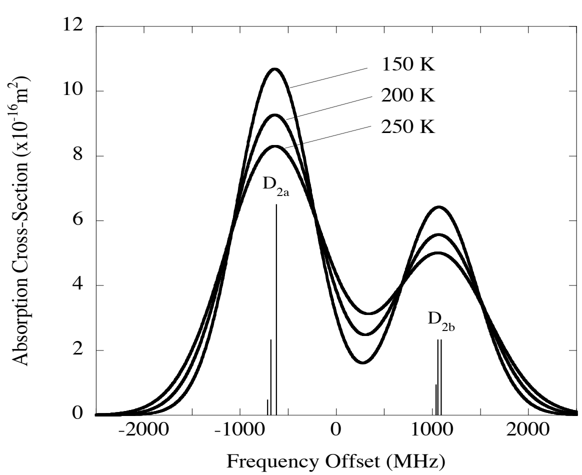


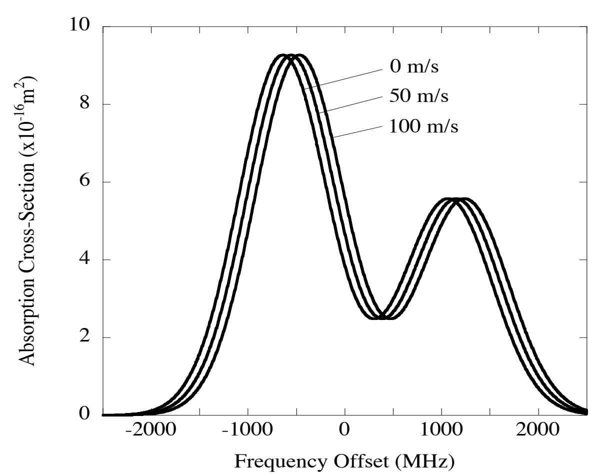
Na D_2 line absorption 589.15826 nm

Spectroscopy signature is utilized.

Energy Level Diagram of Atomic Na

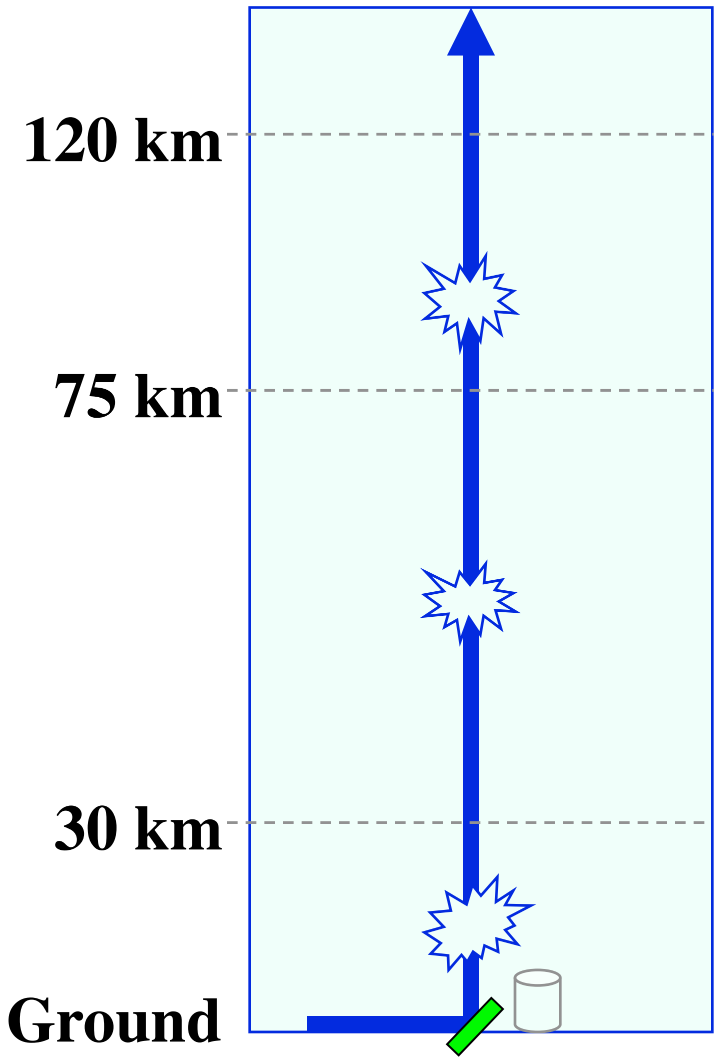
$$\sigma_D = \sqrt{\frac{k_B T}{M \lambda_0^{\,2}}}$$

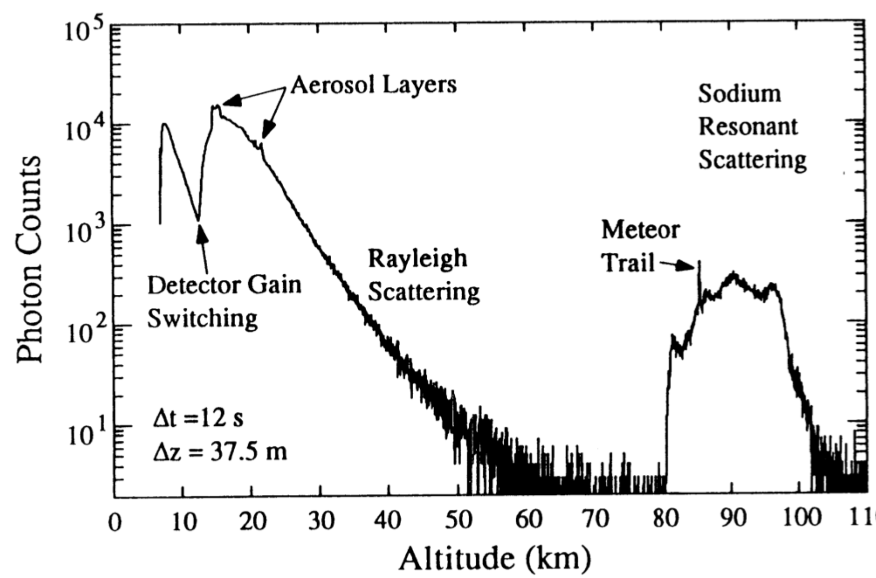




$$\nu' = \nu\left(1 - \frac{V_R}{c}\right)$$

Light Detection And Ranging

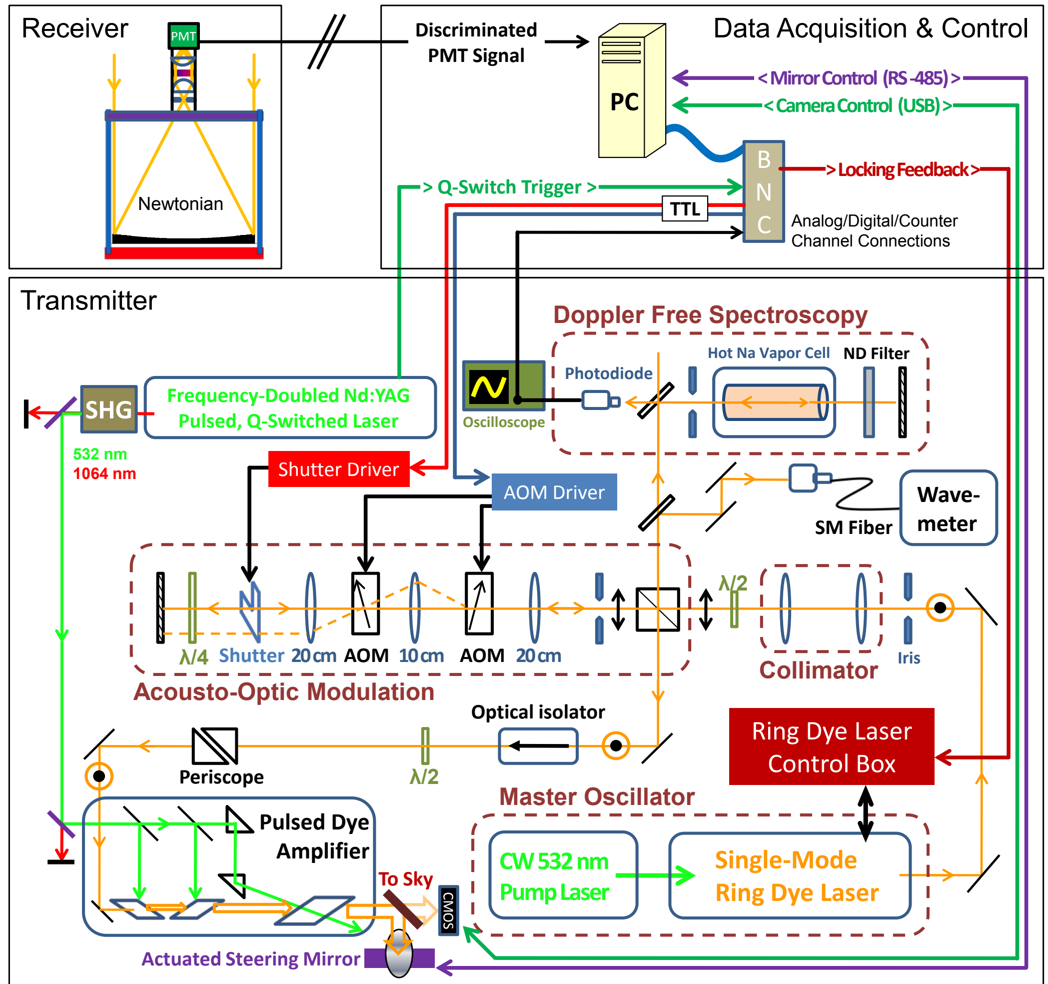




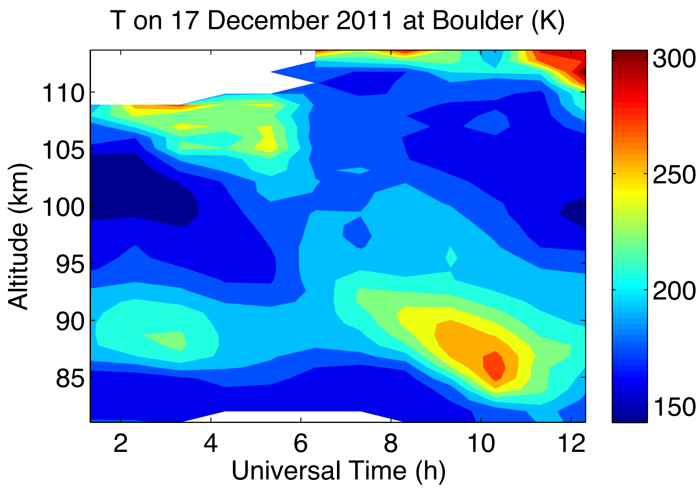
Time of Flight ⇨ Range / Altitude R = C Δt / 2

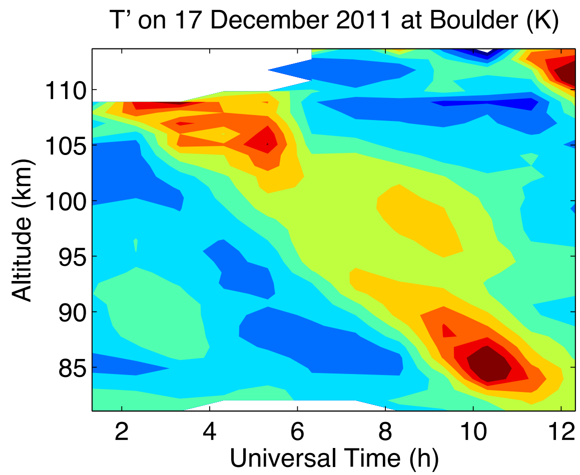
STAR Na Doppler Lidar

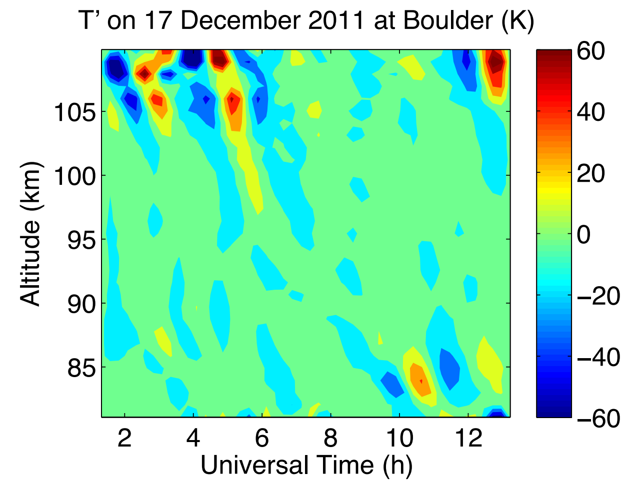
Student Training and Atmospheric Research (STAR) lidar developed by graduate students [Smith, Fong, et al., ILRC, 2012]



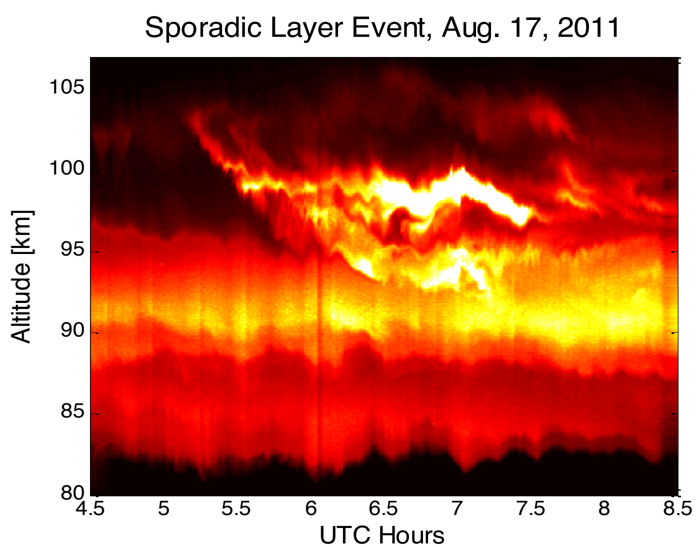
Very High Resolution Achieved by Students



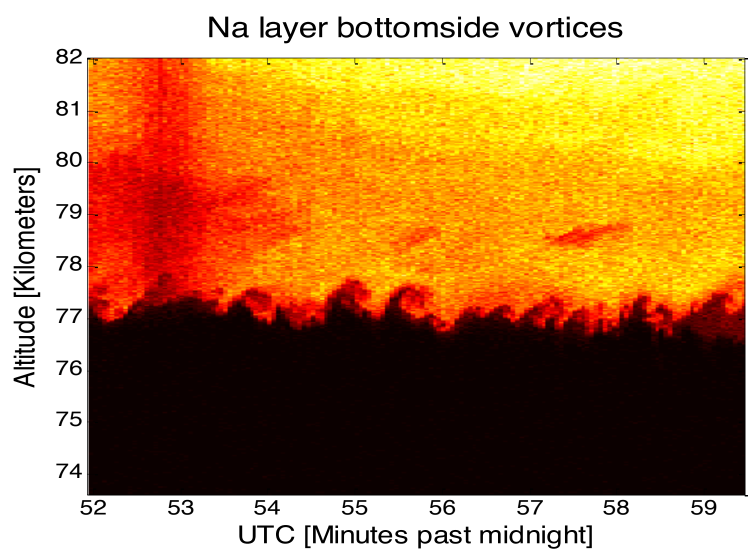




[Figure Credits: John Smith, Xian Lu and Wentao Huang]



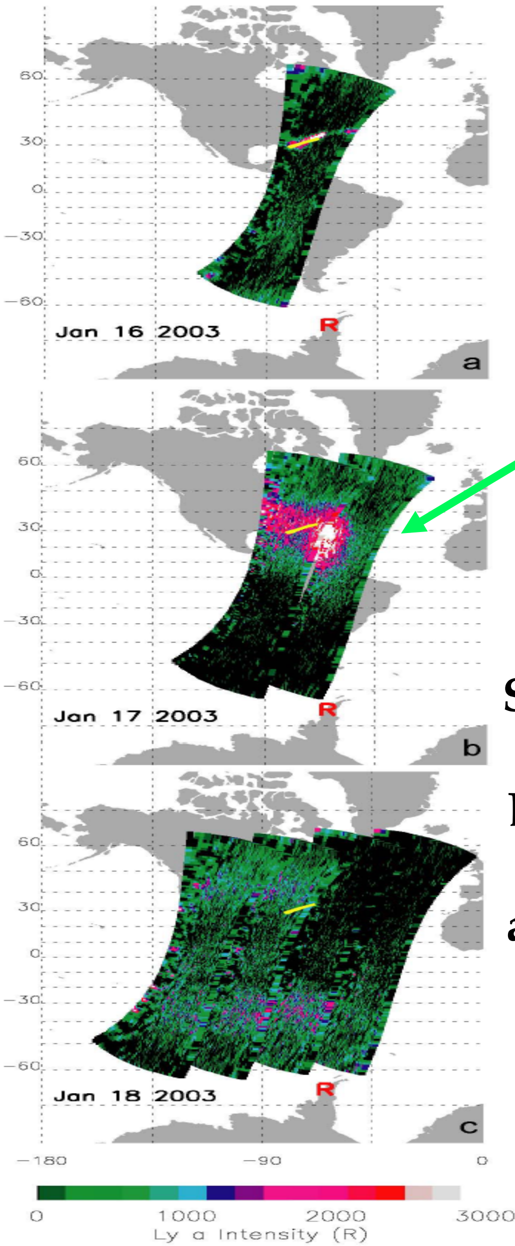
Δz=48 m, Δt=30 sec



Δz=24 m, Δt=3 sec

Eddy flux measurements may be within the reach [Smith and Chu, AO, 2015]

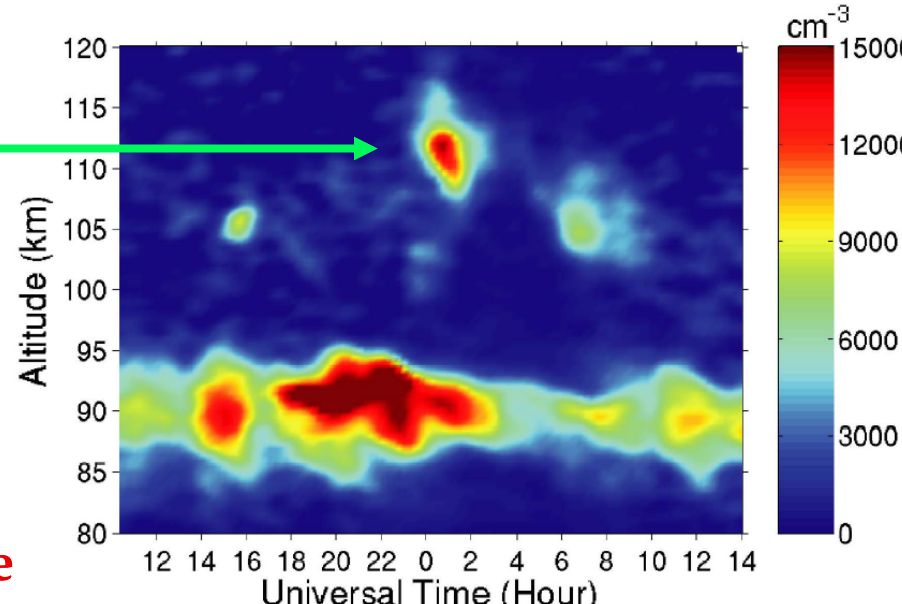
Shuttle Formed High-Z Sporadic Fe



Columbia Space Shuttle launched on Jan 16, 2003

Lyman α Images from GUVI/ TIMED

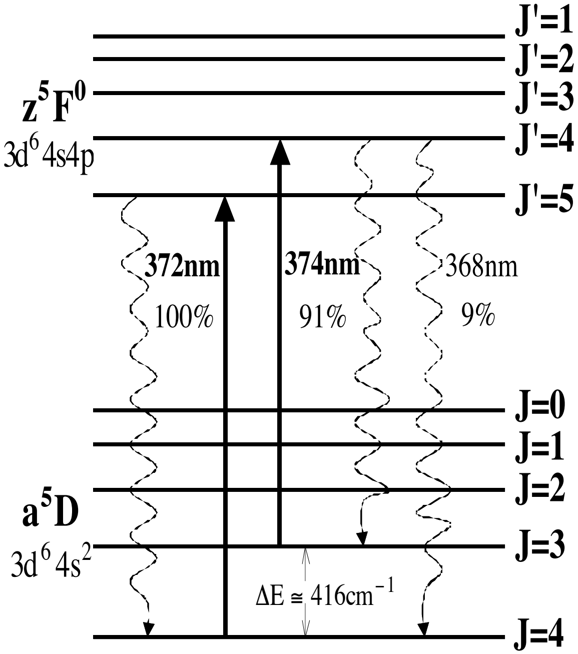
High-Altitude Sporadic Fe layer detected by Fe Boltzmann Lidar on Jan 19, 2003 at Rothera (67.5S)



Causes: Shuttle Engine Ablation!

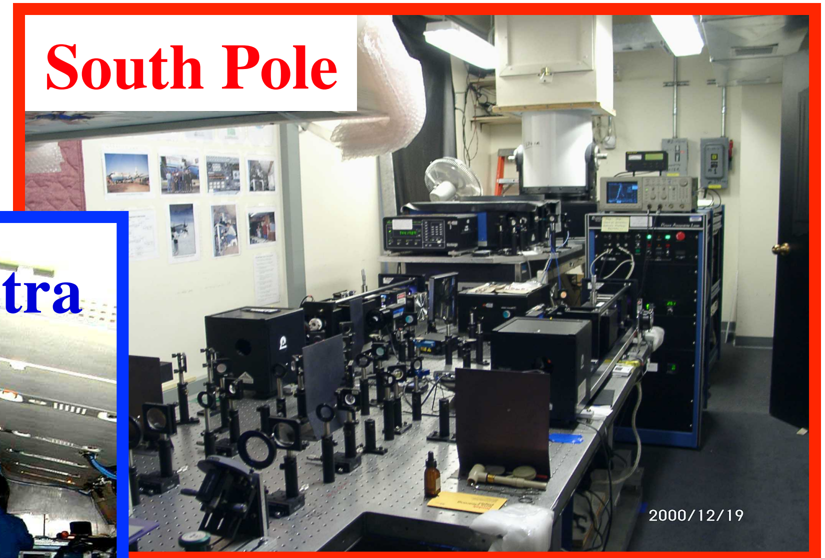
[Stevens et al., GRL, 2005]

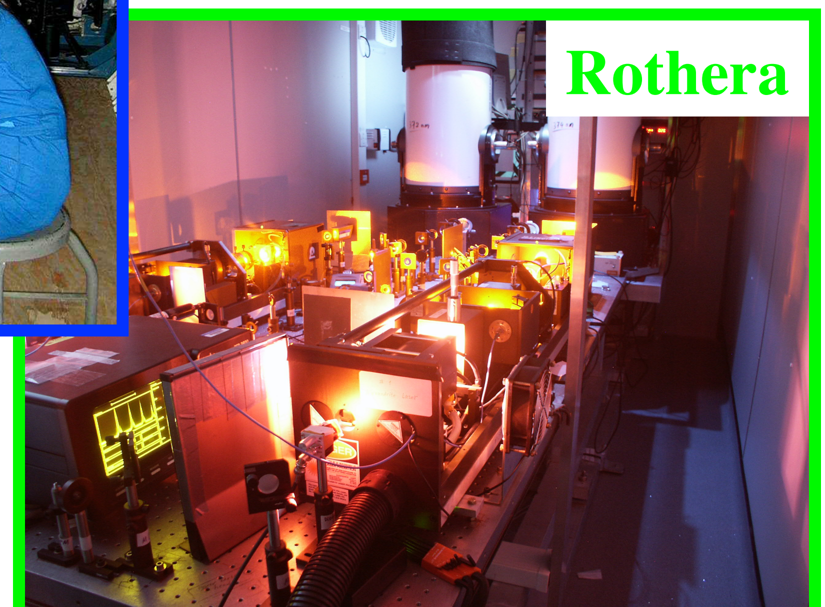
Fe Boltzmann Temperature LIDAR



$$\frac{P_2(J=3)}{P_1(J=4)} = \frac{g_2}{g_1}\exp(-\Delta E/k_B T)$$

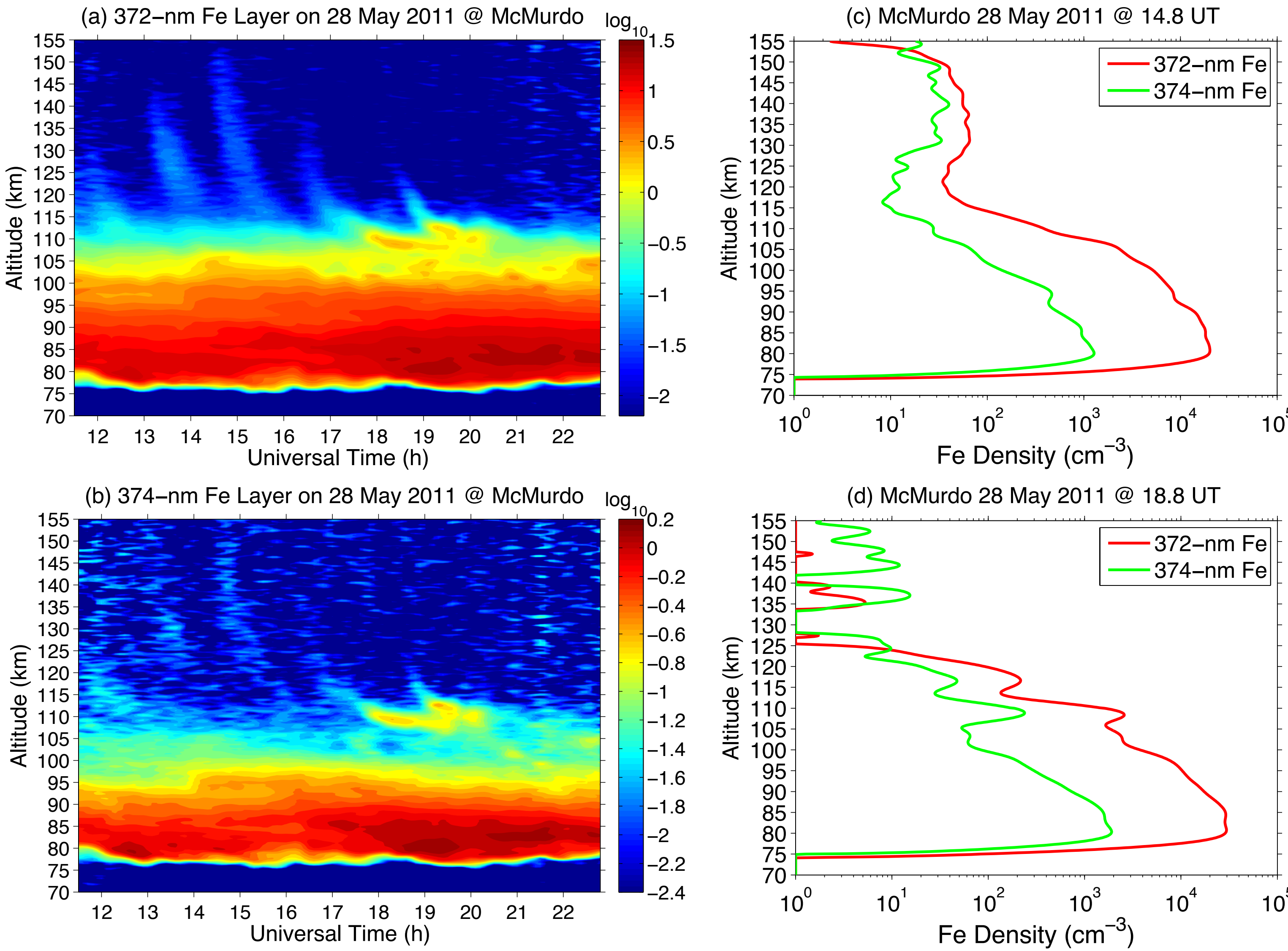
$$T = \frac{\Delta E / k_B}{ln\left(\frac{g_2}{g_1}\cdot\frac{P_1}{P_2}\right)}$$





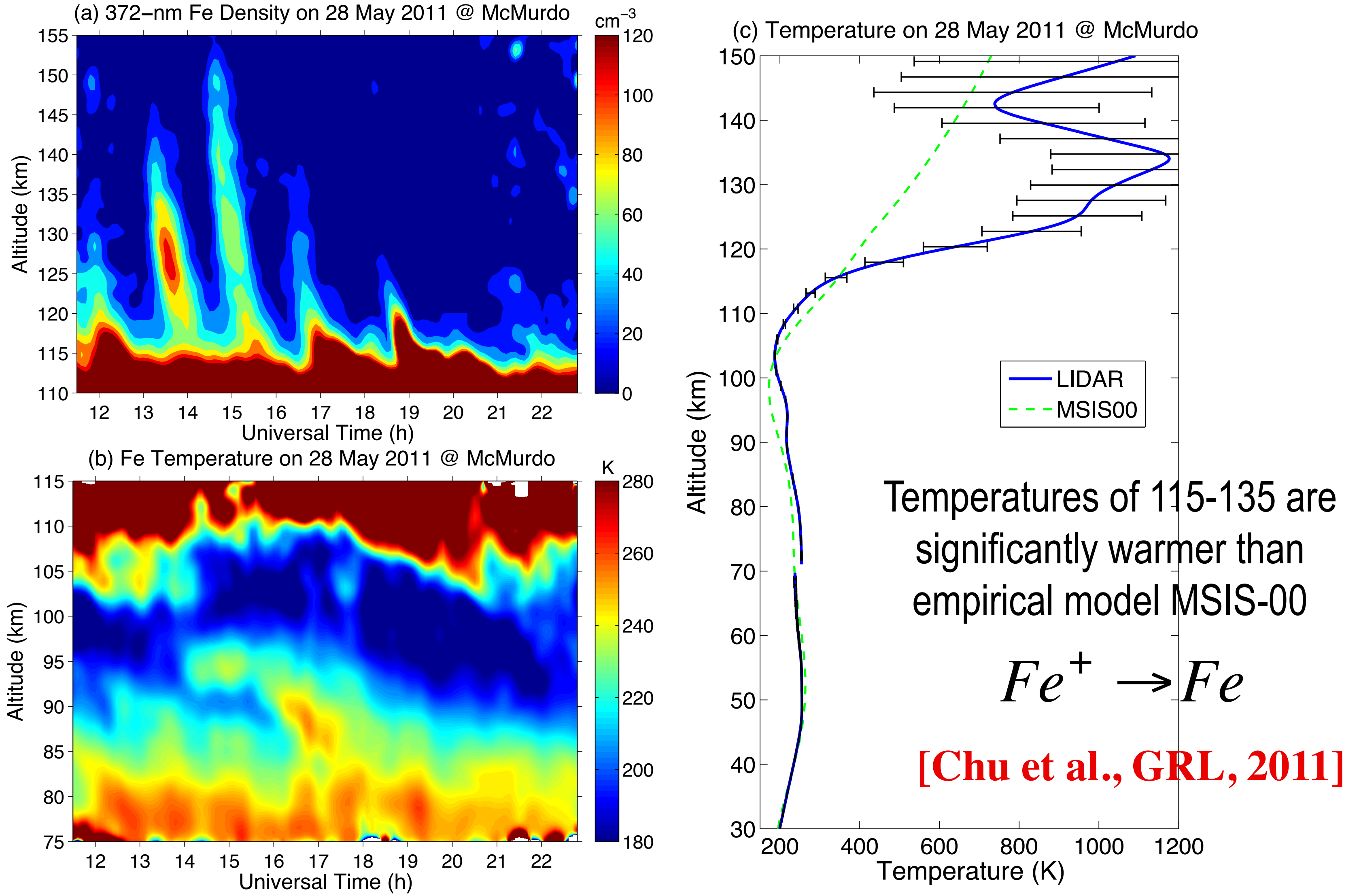
[Gelbwachs, 1994; Chu et al., 2002]

A New Discovery: Thermosphere Fe Layer



[Chu, Yu, Gardner, Chen and Fong, Lidar observations of neutral Fe layers and fast gravity waves in the thermosphere (110-155 km) at McMurdo, Antarctica, *GRL*, 2011]

Temperature Profiling (30-150 km)



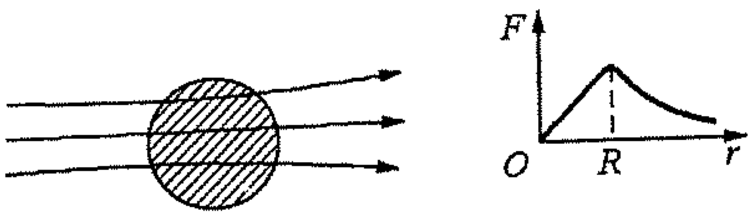
Fe density of 20-120 cm^{-3} from 120-155 km with clear wave signatures

Elevated temp appears to be related to the aurora-enhanced Joule heating

2. How to study structures of atoms/molecules?

Example 1. Models of atomic structure by Thomson and by Rutherford

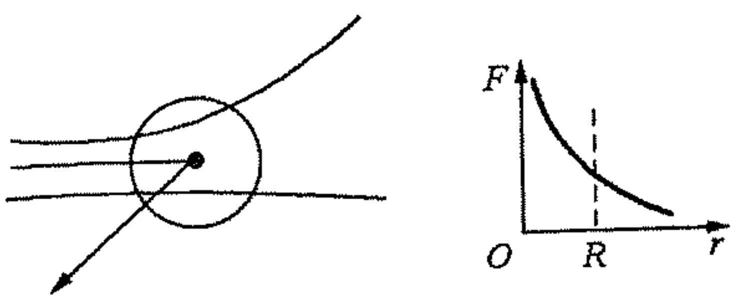
Because atoms are so small that their internal structures cannot be observed directly, we must influence atoms externally and then observe their reactions. Through analyzing the experimental results, we can acquire the atomic structures.



(a)

Thomson model

α-particle scattering by an atom



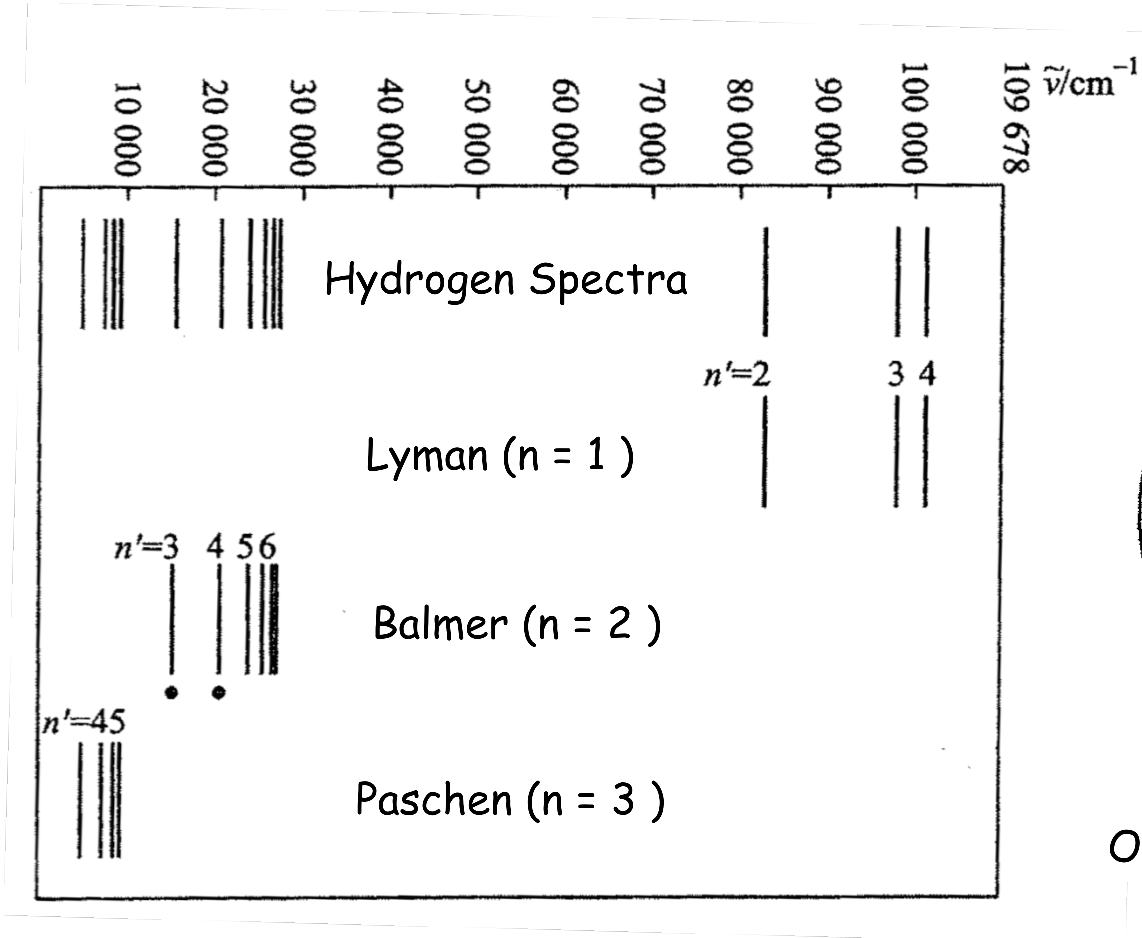
(b)

Rutherford model

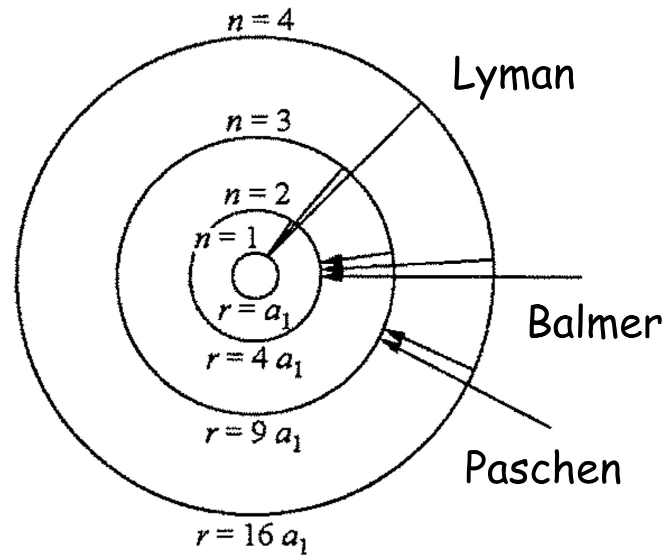
Collision is one important method to study structures of matter.

2. How to study structures of atoms/molecules?

Example 2. Hydrogen Spectra



$$\nu_B = Rc\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$



Orbits of electron inside H-atom

Spectroscopy is another important method to study structures of matter.

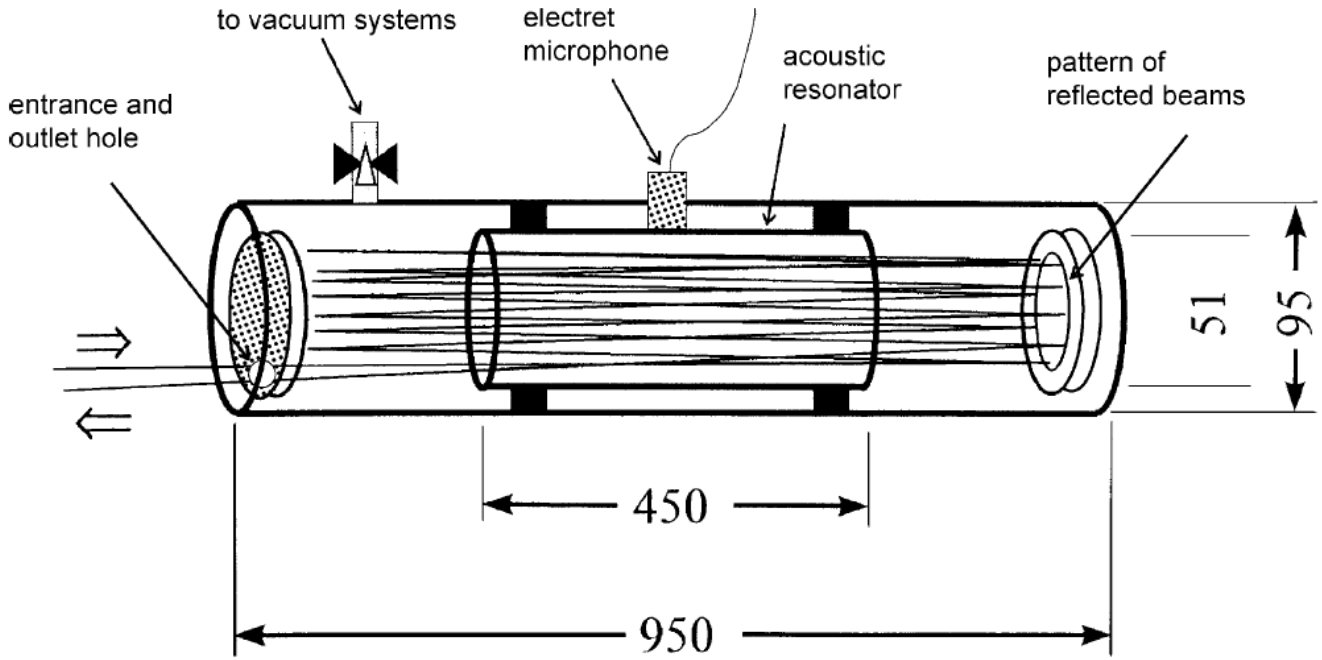
Amazing Applications of Spectroscopy

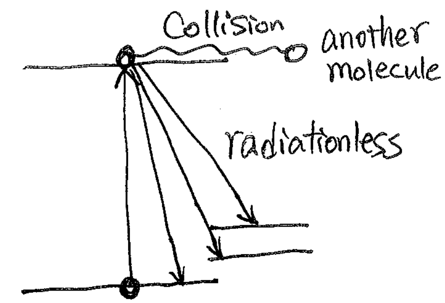
Applications of Laser Spectroscopy
-- Applications in Physics
-- Applications in Chemistry
-- Applications in Biology
-- Applications in Medicine
-- Applications to Material Science
-- Applications to Technical Problems
-- Applications in Environmental Research

Applications of Atoms and Molecules Spectroscopy
-- MRI / CT / X-ray
-- Atomic Clock / Quantum Frequency Standard
-- Bose-Einstein Condensation (BEC)

Applications of Wider Spectroscopy
-- Doppler shift and broadening
-- Boltzmann distribution
-- Mass Spectrometer

Applications in Analytical Chemistry





Collision with other atoms / molecules to transfer energy out

Fig. 10.1. Multipass cell of an optoacoustic spectrometer. All laser beams pass through regions in the acoustic resonator where the radial acoustic resonance has maximum amplitude. Measurementss are in millimeter

Excitation energy → thermal energy of surrounding molecules

→ Temperature or pressure change

→ Detection by microphone

Applications in Analytical Chemistry

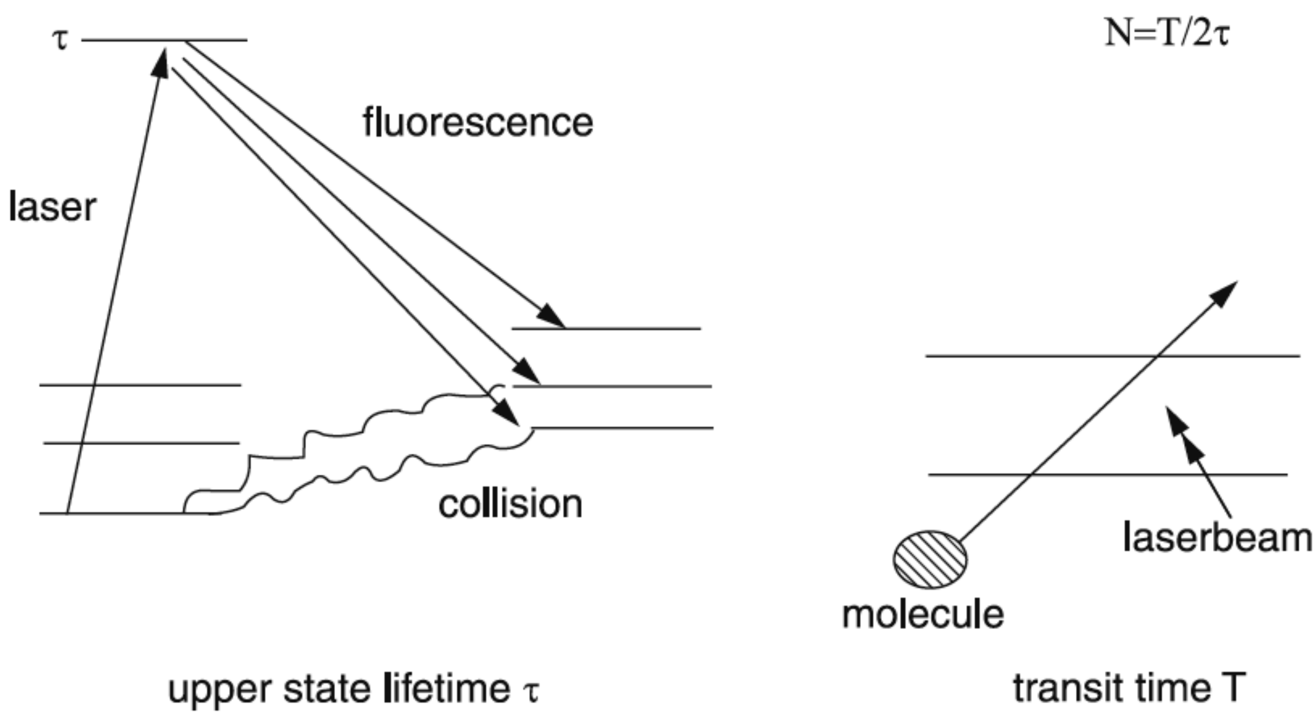


Fig. 10.2. Single-molecule detection

Photon burst → single-atom/molecule detection

Coherent Control of Chemical Reactions

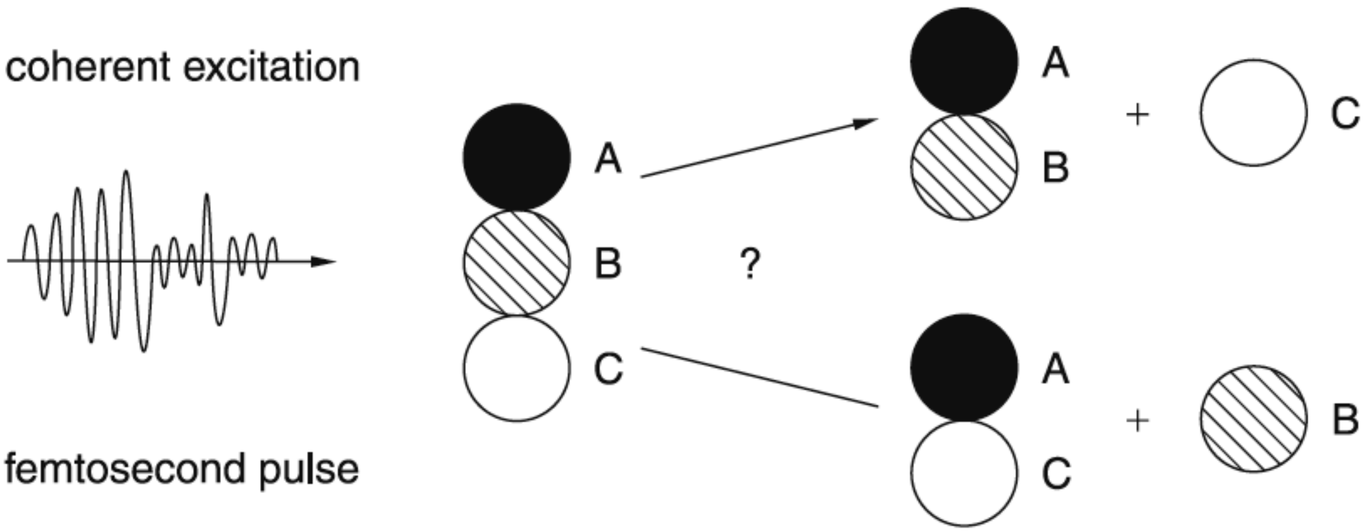


Fig. 10.9. Selection of the reaction channel by the controlled coherent excitation of a molecule

Coherent control means the coherent preparation of a molecular wavefunction through the absorption of coherent radiation. The dream of chemists is the controlled selection of wanted reaction channels and the suppression of unwanted channels in a photoinduced reaction. This is illustrated by Fig. 10.9, where the excitation of the triatomic molecule ABC can induce either of the reactions AB + C or AC + B, depending on the wavefunction in the excited state of ABC, which is controlled by the form of the excitation pulse.

Laser Femtosecond Chemistry

Chemical reactions are based on atomic or molecular collisions. These collisions, which may bring about chemical-bond formation or bond breaking, occur on a time scale of 10^{-11} to 10^{-13} s. In the past, the events that happened in the transition state between reagents and reaction products could not be time resolved. Only the stages "before" or "after" the reaction could be investigated [10.54].

The study of chemical dynamics concerned with the ultrashort time interval when a chemical bond is formed or broken may be called *real-time femtochemistry* [10.55]. It relies on ultrafast laser techniques with femtosecond time resolution [10.56].

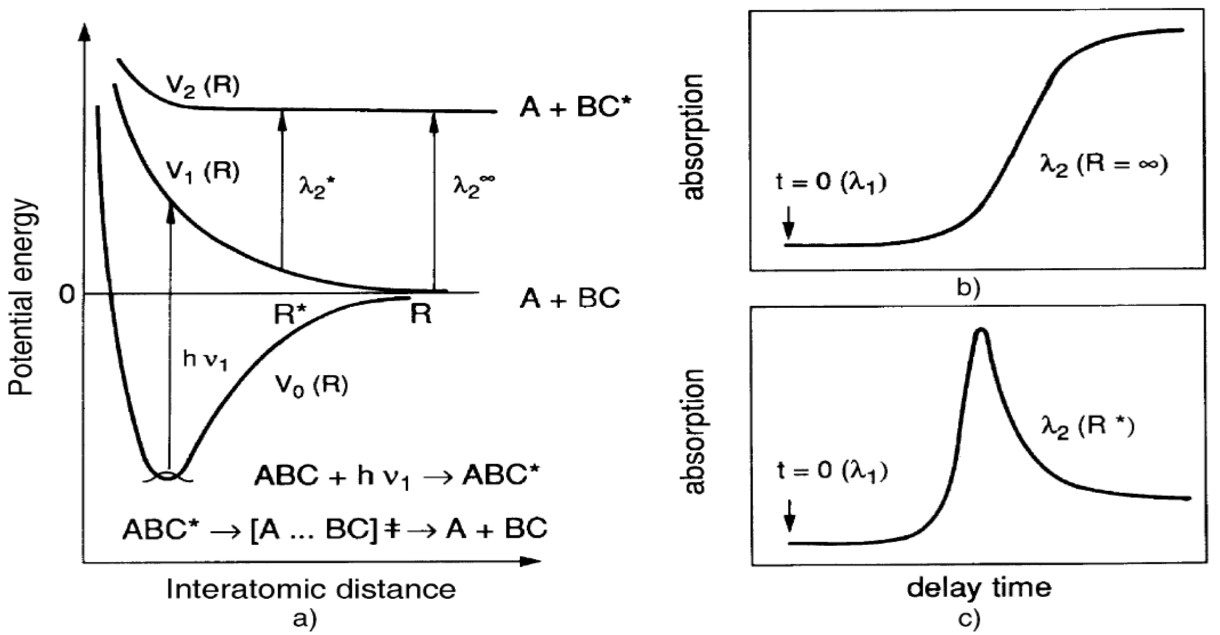


Fig. 10.12. (**a**) Potential energy curves for a bound molecule (V_0) and the first and second dissociative curves V_1, V_2; (**b**) the expected femtosecond transient signals $S(\lambda_2, t)$ versus the delay time t for $\lambda_2(R = \infty)$ and (**c**) for $\lambda_2(R^*)$ [10.55]

Applications in Material Science

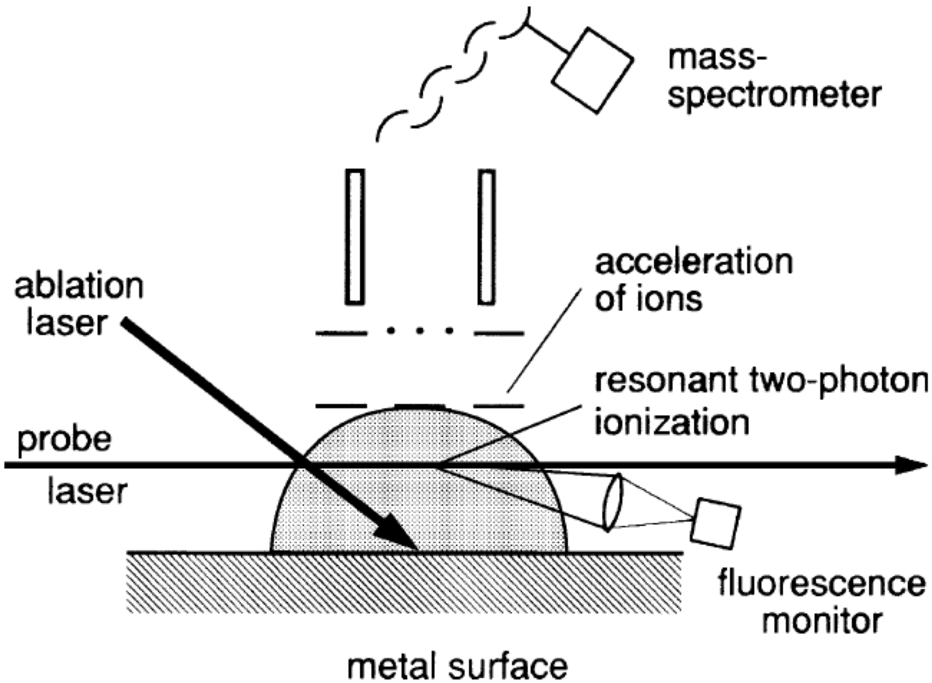


Fig. 10.27. Detection of atoms and molecules sputtered by ion bombardment or laser ablation from a surface and measurements of their energy distribution

Irradiating the surface of a solid with a laser, material can be ablated in a controlled way by optimizing intensity and pulse duration of the laser (*laser ablation* [10.130]). Depending on the laser wavelength, the ablation is dominated by thermal evaporation (CO_2 laser) or photochemical processes (excimer laser). Laser-spectroscopic diagnostics can distinguish between the two processes. Excitation spectroscopy or resonant two-photon ionization of the sputtered atoms, molecules, or fragments allows their identification

Laser-induced breakdown spectroscopy (LIBS)

Applications in Biology

The detailed knowledge of the different steps of biological processes on a molecular level is one of the ambitious goals of molecular biology. The importance of this field was underlined by the award of the Nobel Prize in chemistry in 1988 to J. Deisenhofer, R. Huber, and H. Michel for the elucidation of the primary steps in photosynthesis and the visual process [10.147]. This subsection illustrates the importance of time-resolved Raman spectroscopy in combination with pump-and-probe techniques (Sect. 6.4) for the investigation of fast biological processes.

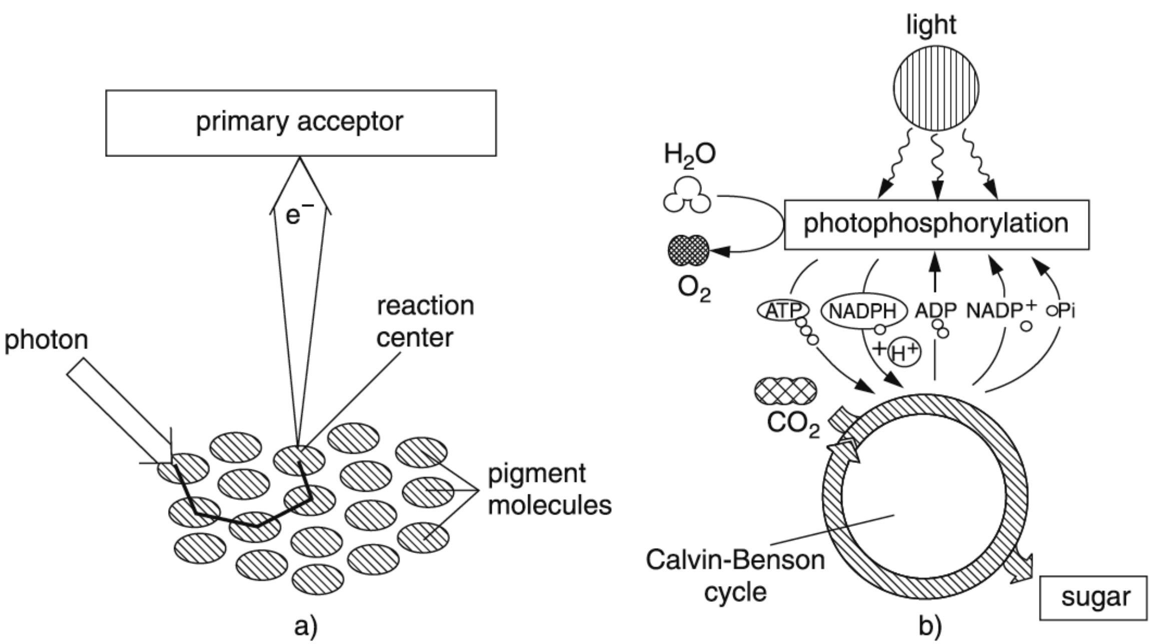
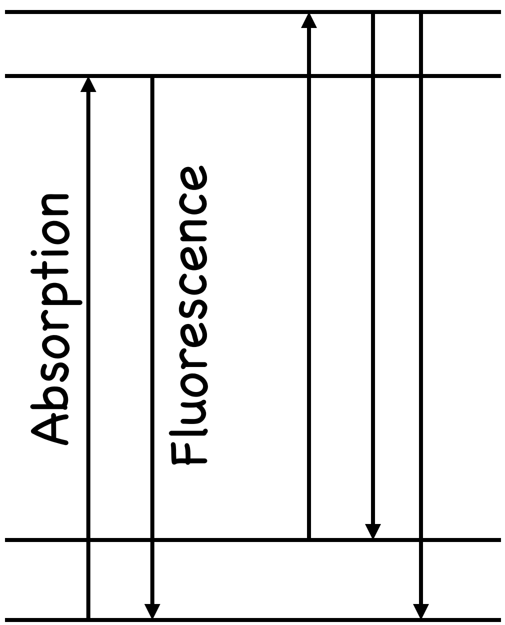


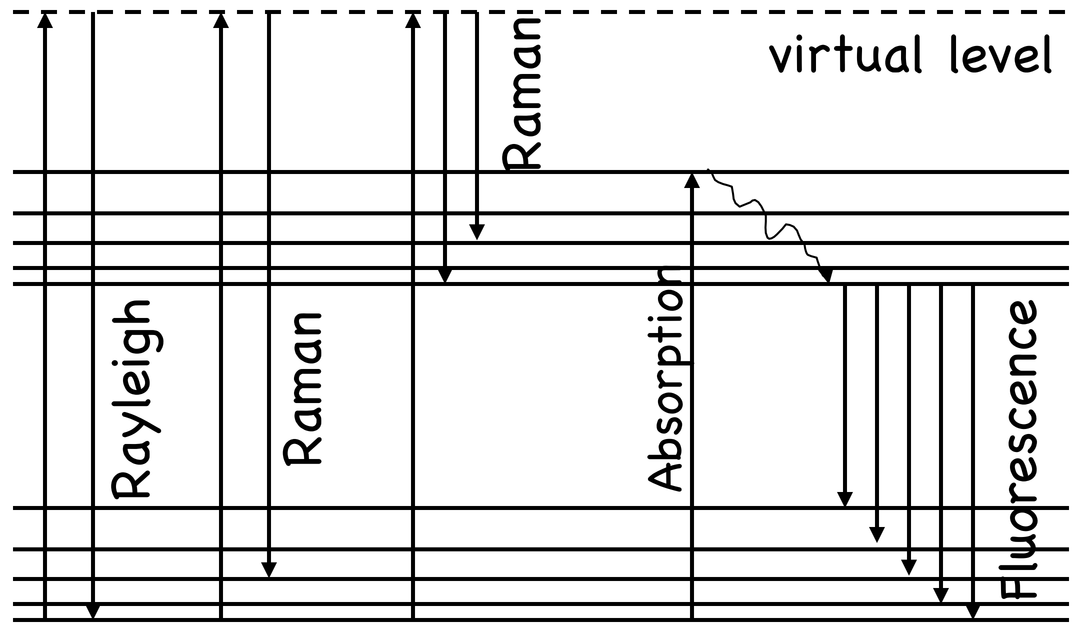
Fig. 10.31a,b. Photosynthesis. (**a**) Primary process; (**b**) reaction cycle [10.193]

Photosynthesis within the chlorophyl cells in green plants studied by time-resolved laser spectroscopy

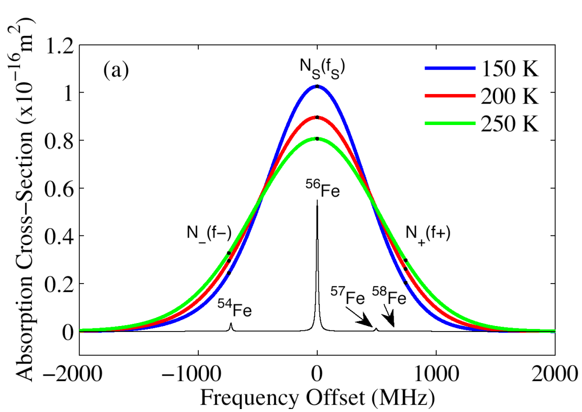
Elastic and Inelastic Scattering

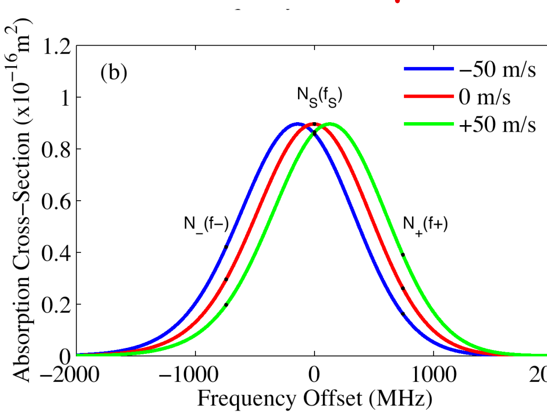


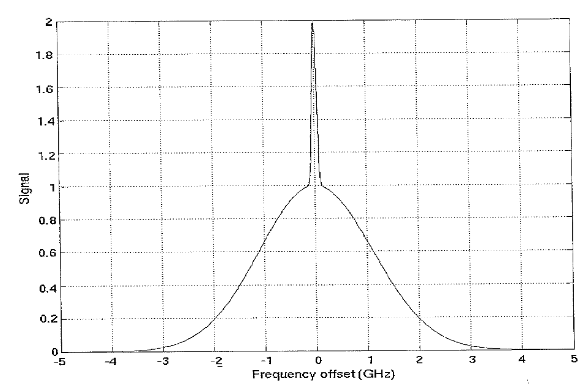
Atomic absorption &
(resonance) fluorescence



Molecular elastic and inelastic scattering,
absorption and fluorescence

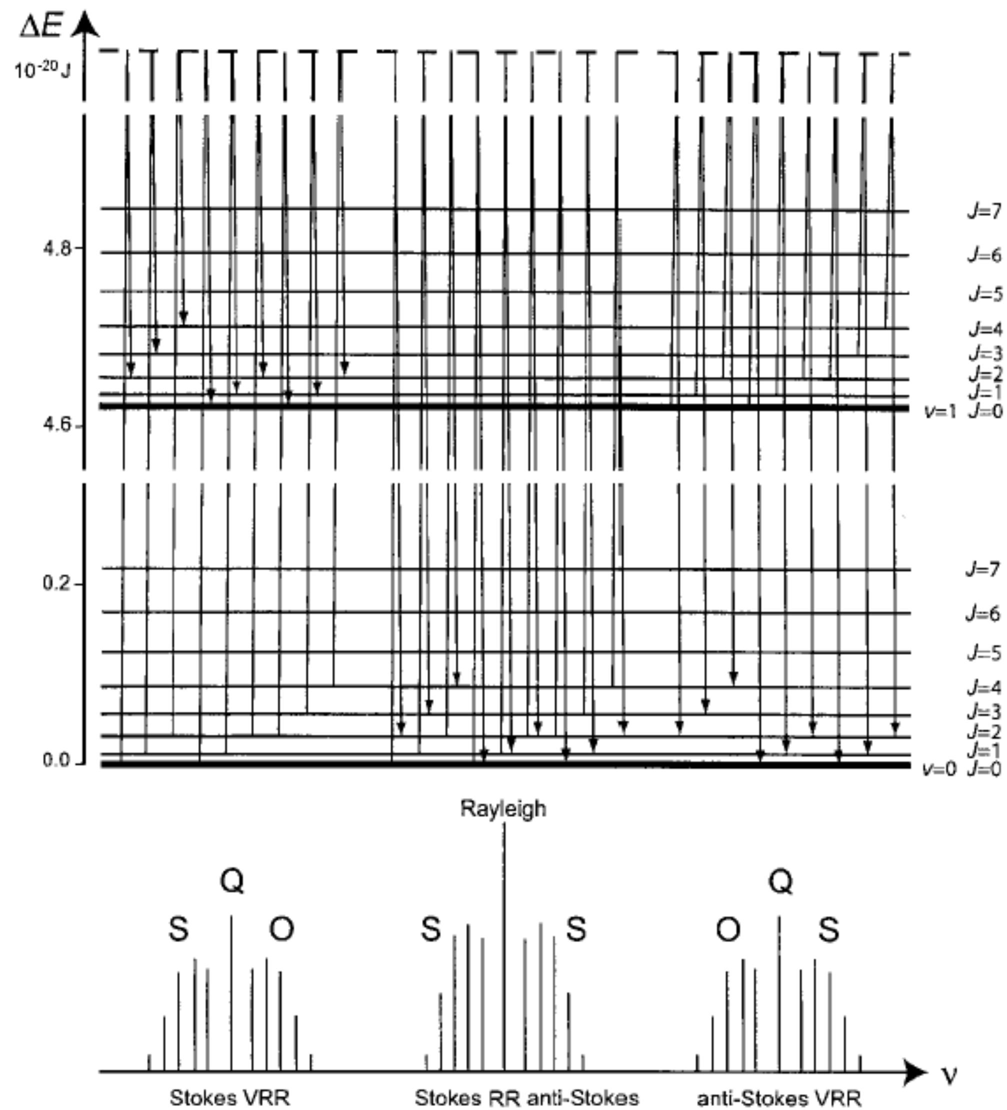




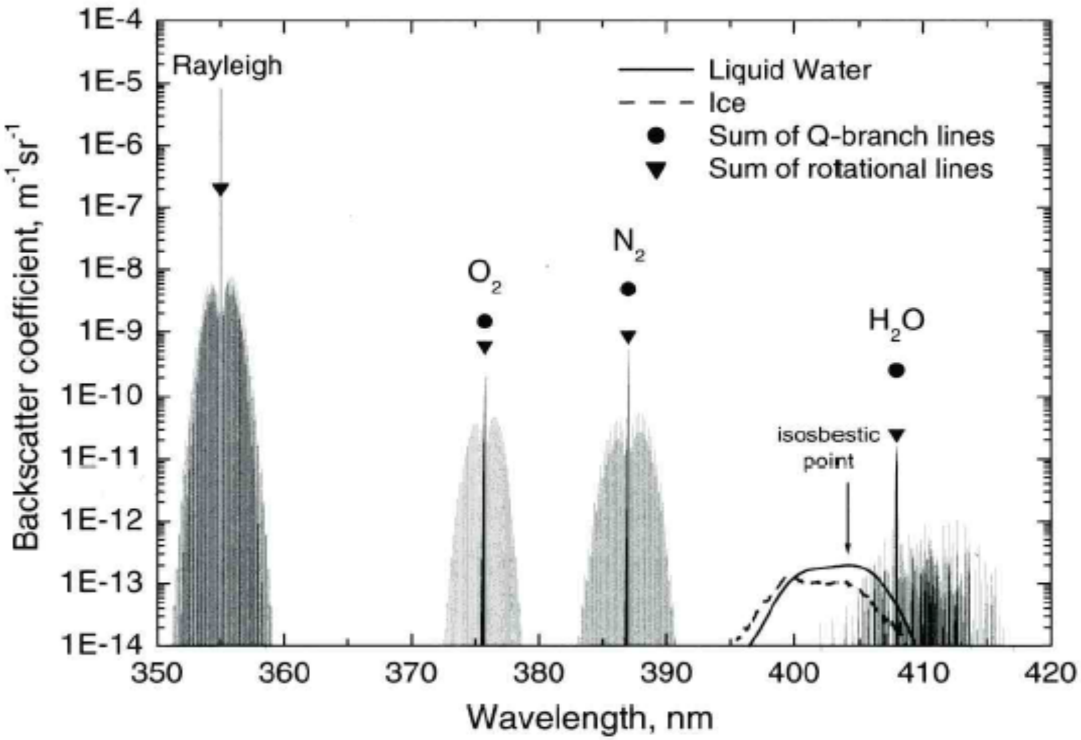


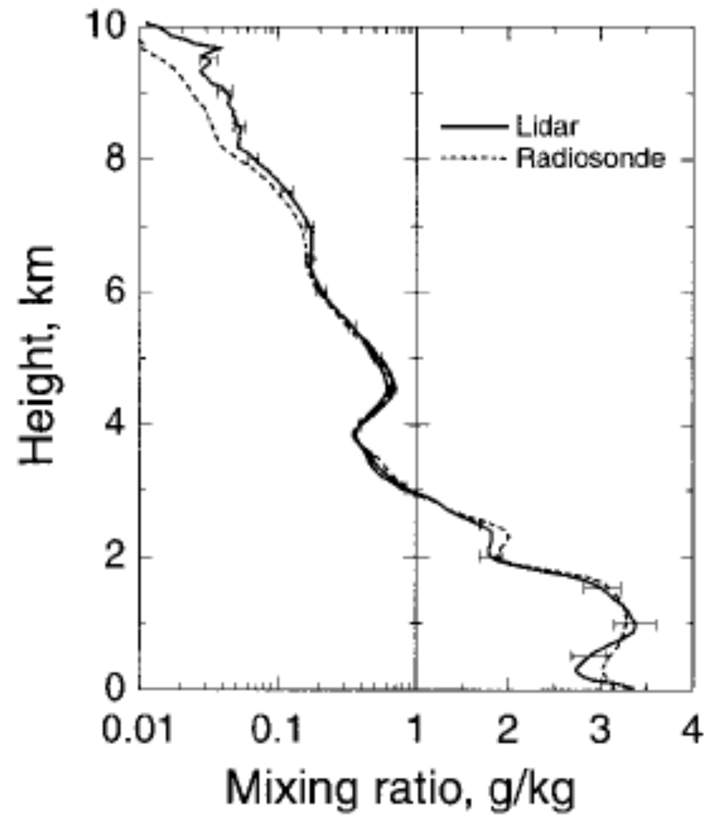
DIAL & Raman Lidar for Trace Gases

- The atmosphere has many trace gases from natural or anthropogenic sources, like H_2O, O_3, CO_2, NOx, CFC, SO_2, CH_4, NH_3, VOC, etc.
- Can we use resonance fluorescence to detect them?
- Quenching effects due to collisions make fluorescence impossible in lower atmosphere for molecules.
- We still need spectroscopy detection - differential absorption and Raman lidars!



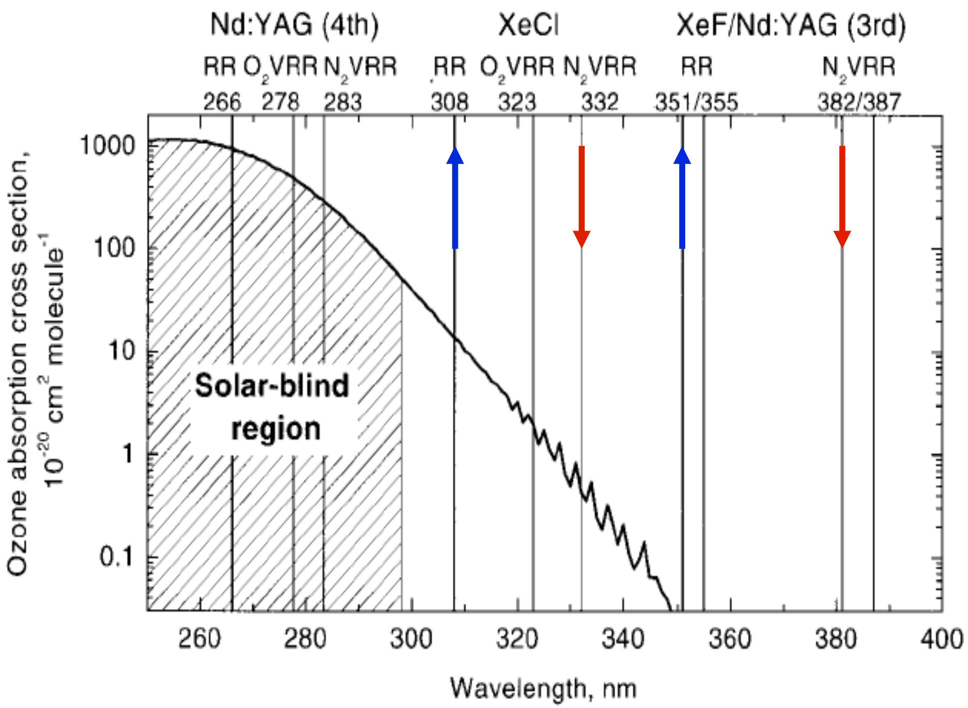
Raman Lidar for Water Vapor





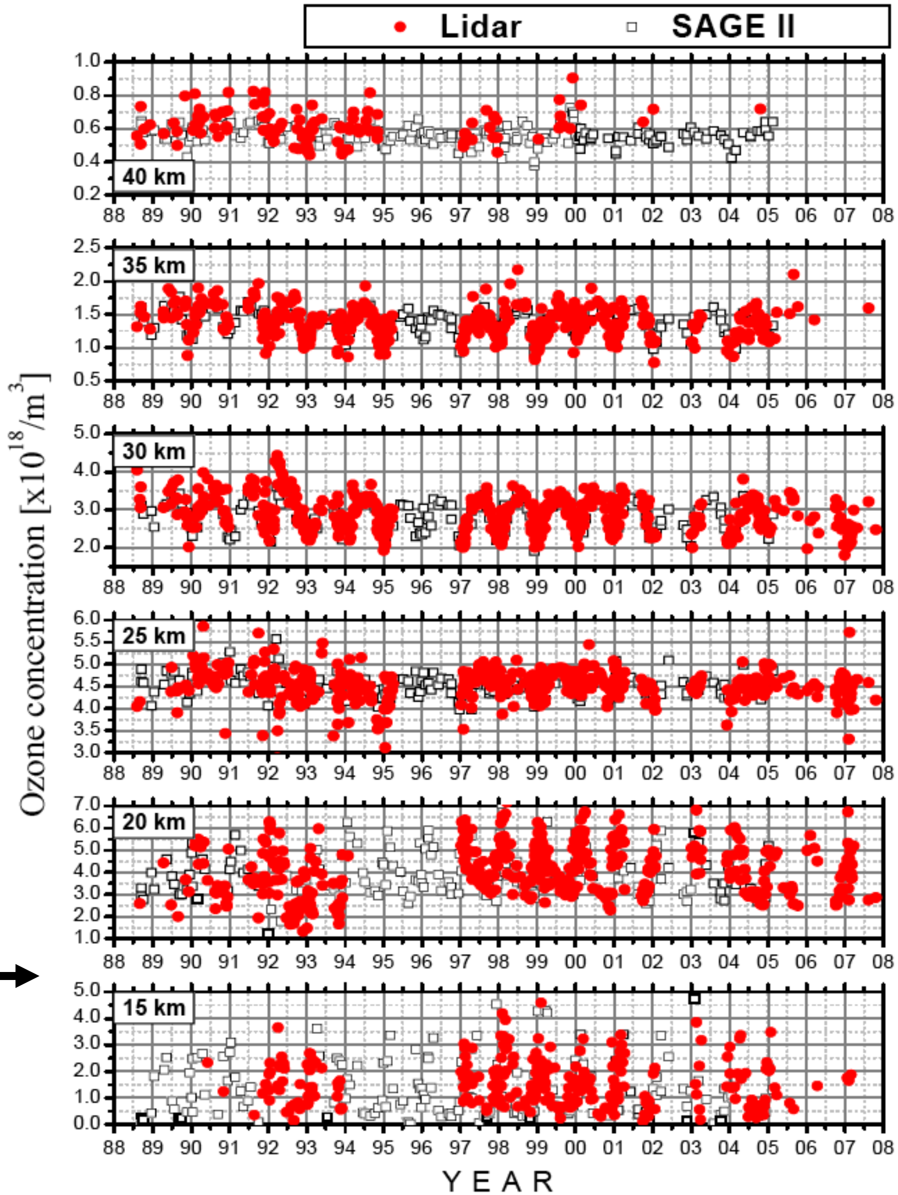
- H_2O molecules exhibit specific spectra - fingerprints!
- Raman lidar catches this 'fingerprints' and avoid the aerosol scattering in the Raman-shifted channel. Thus, only aerosol extinction will be dealt with in deriving H_2O mixing ratio.

DIAL for Ozone in Two Decades

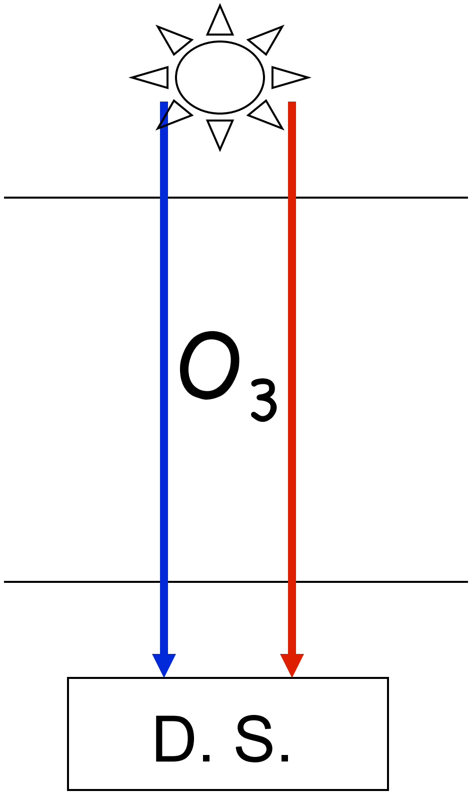


$$\boxed{\Delta\sigma_{abs} = \sigma_{abs}(\lambda_{ON}) - \sigma_{abs}(\lambda_{OFF})}$$

Tsukuba (36N, 140E), Japan
[Tatarov et al., ILRC, 2008]



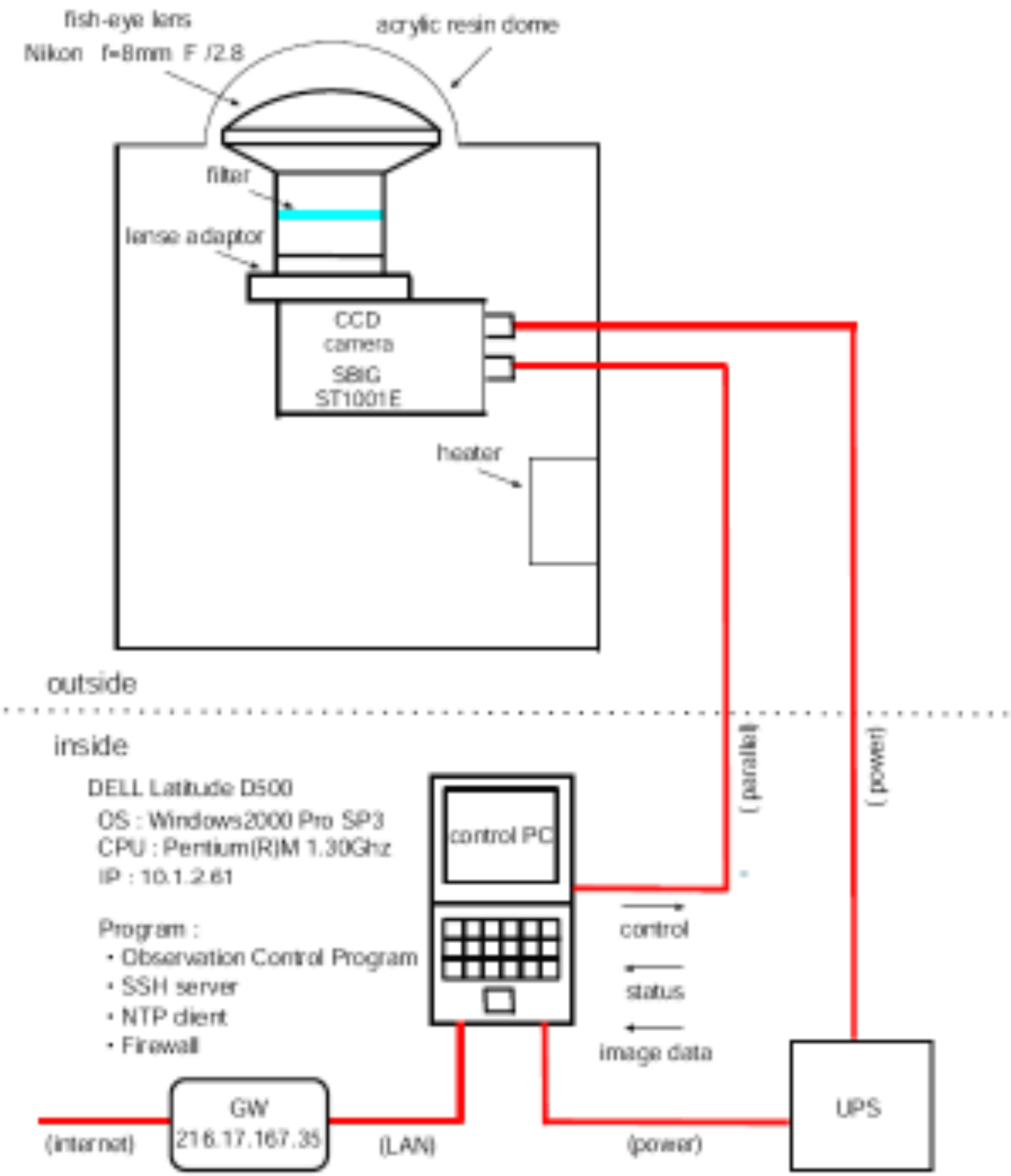
Passive Optical Remote Sensing

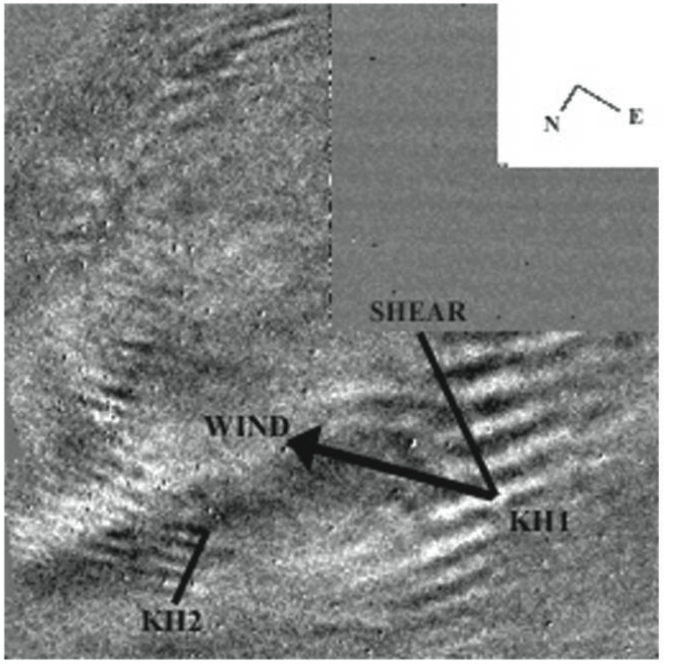


305 and 325 nm

NOAA Dobson Spectrometer
to measure ozone
from the ground

Passive: All-Sky-Camera for Airglow

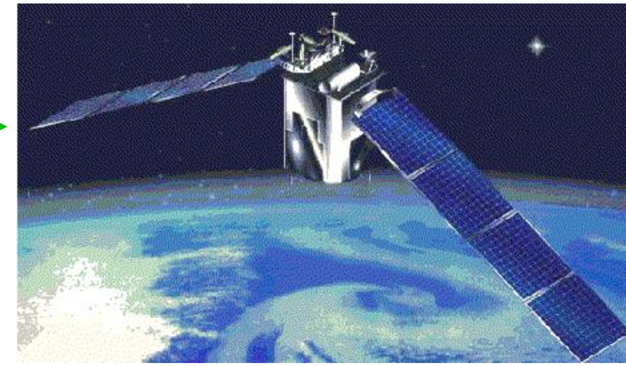




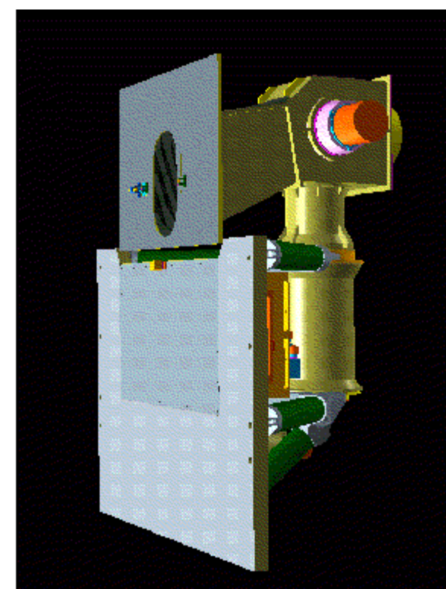
Courtesy of Takuji Nakamura (NIPR) and Jia Yue (CSU)

The SABER Instrument Aboard the TIMED Satellite

TIMED: Thermosphere, Ionosphere, Mesosphere Energetics & Dynamics



SABER: Sounding of the Atmosphere Using Broadband Emission Radiometry



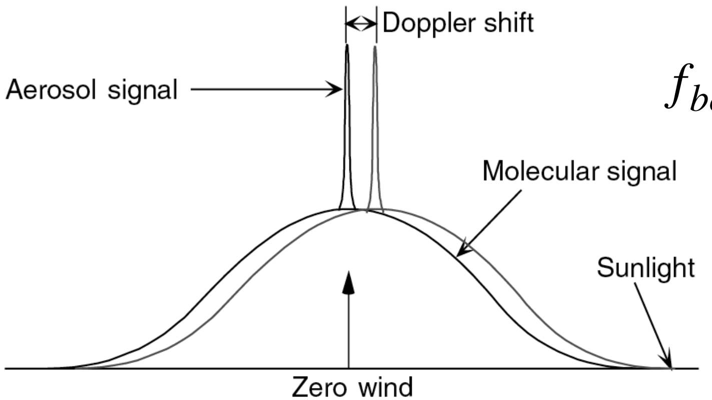
SABER instrument:

- **Limb scanning infrared radiometer**
- **10 broadband channels (1.27-17 µm)**
- **Products: kinetic temperature, CO_2, O_3, H_2O, NO, O_2, OH, O, H**

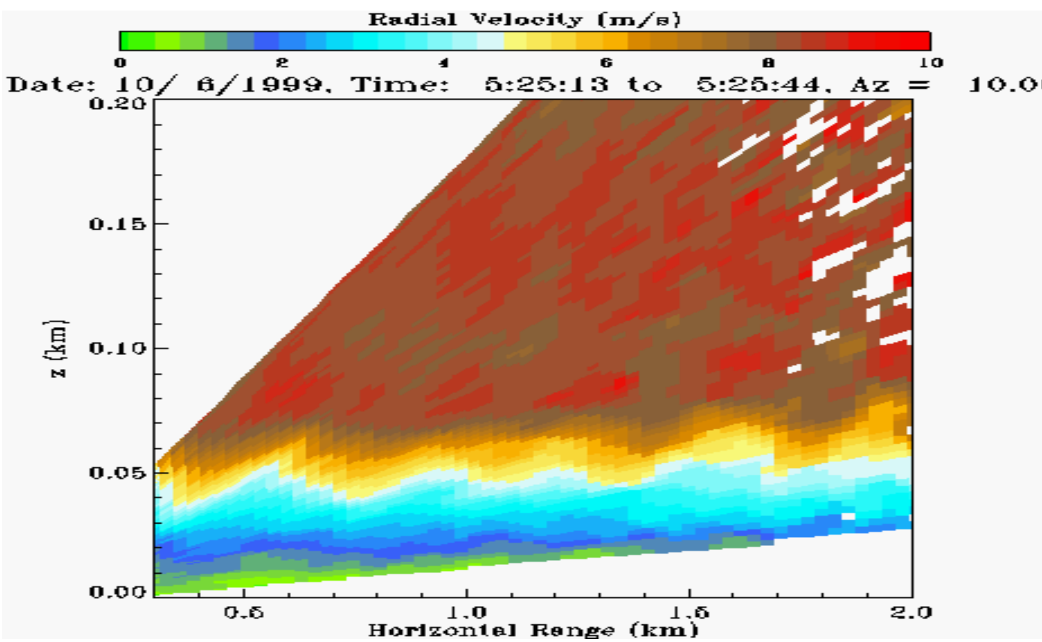
[Courtesy of Dr. *Artem Feofilov et al.*, NASA, 2007]

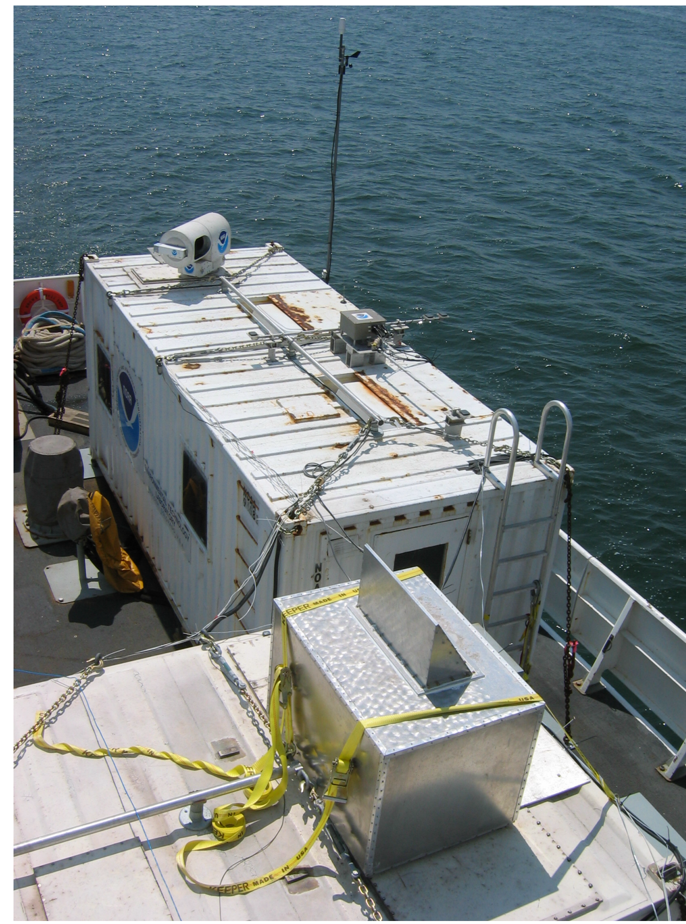
Coherent Doppler Wind Lidar

❑ "Heterodyne" Detection from aerosol scattering: the return signal is optically mixed with a local oscillator laser, and the resulting beat signal has the frequency (except for a fixed offset) equal to the Doppler shift.



$$f_{beat} = \left| f_{LO} - f_{Sig} \right|$$
$$= \Delta f + f_{offset}$$



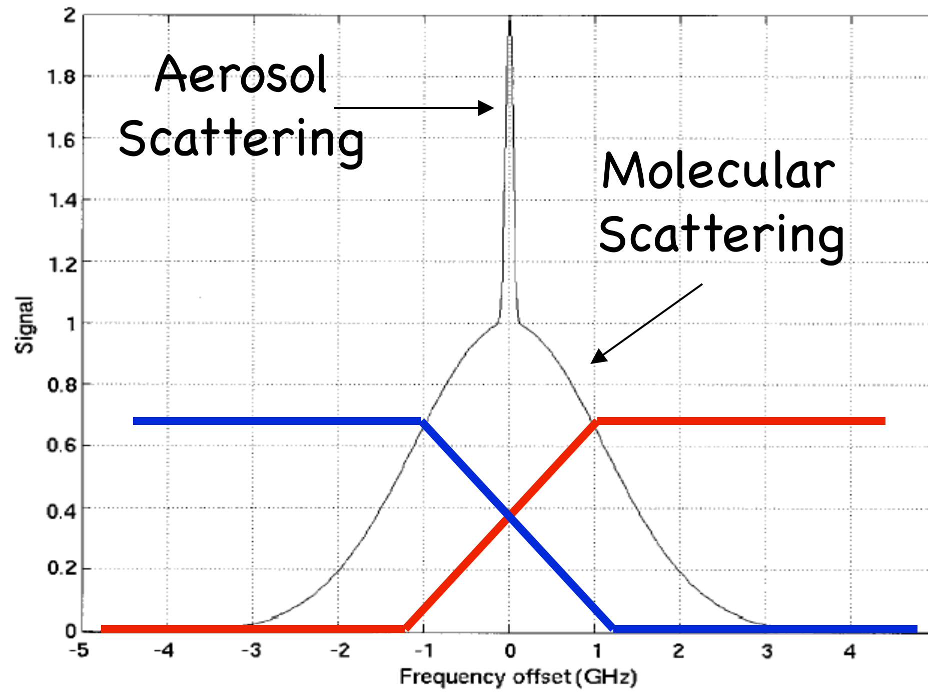


NOAA HRDL

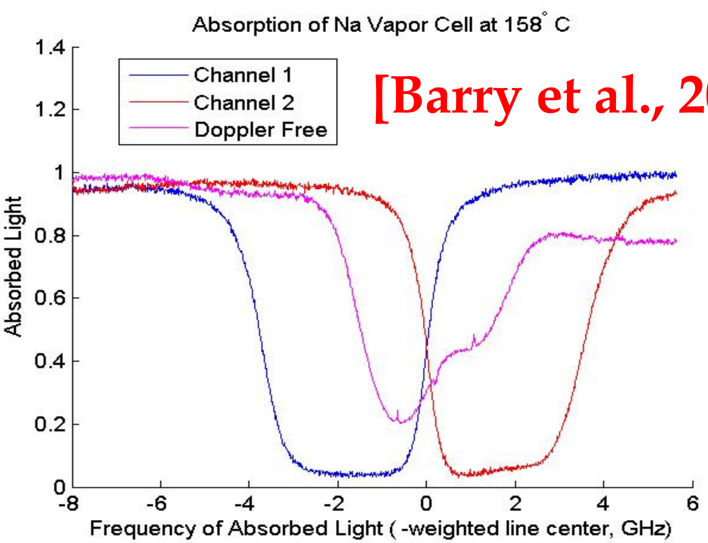
Direction-Detection Doppler Lidar

In lower atmosphere, Rayleigh and Mie scattering experiences Doppler shift and broadening.

However, there is no frequency analyzer in the atmosphere, so the receiver must be equipped with narrowband frequency analyzers for spectral analysis.

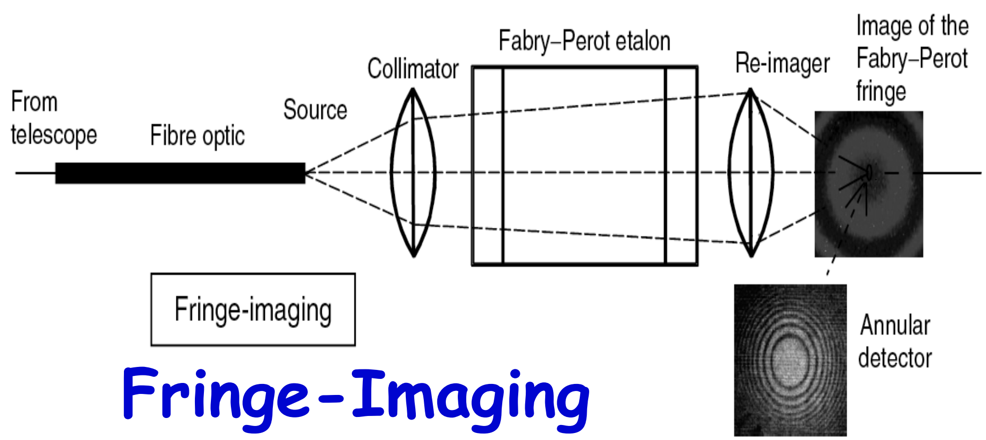


Double-Edge Filter



[Barry et al., 2013]

Na-DEMOF



Fringe-Imaging

Concepts of Spectroscopy

- **Spectroscopy is the study of the interaction between radiation (photons, phonons, or particles) and matter.**
- **Spectroscopy is the study of matter by investigating radiation (photons, phonons, or particles) that is absorbed, emitted, or scattered by the matter under investigation.**
- **The radiation includes all forms of electromagnetic radiation and non-electromagnetic radiation.**

-- EM radiation (photons): radiowaves, microwaves, infrared light, visible light, ultra-violet light, X-ray, etc.

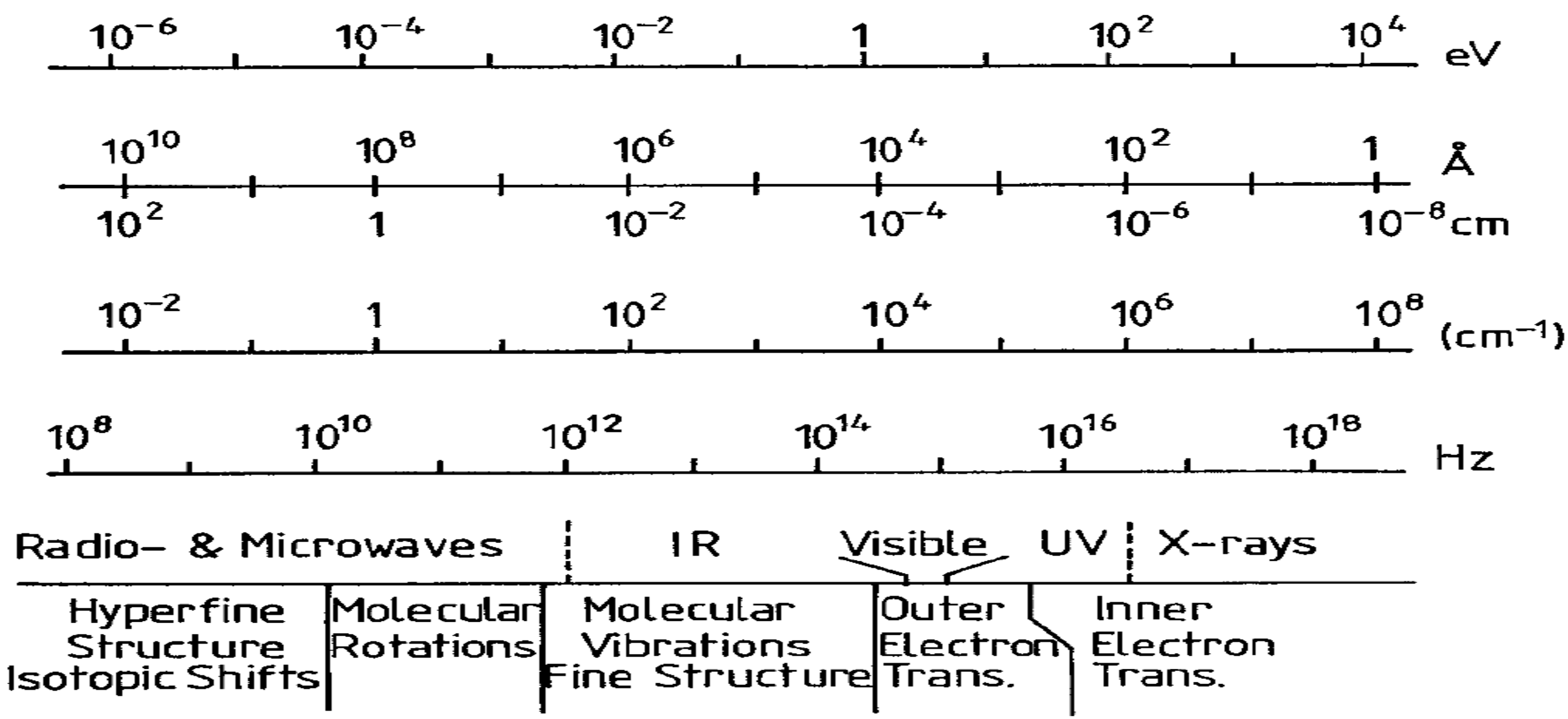
-- Non-EM radiation: phonons (acoustic wave), electrons, etc.

Classification of Spectroscopy

- According to radiation used in the study, spectroscopy can be classified to three main types of spectroscopy:

  EM spectroscopy, Acoustic Spectroscopy, Mass Spectroscopy.

- We deal with EM spectroscopy here.



Major Aspects of Spectroscopy

Three main aspects of spectroscopy study – (modern view)

(1) Fundamental study of matter structure (e.g., atomic or molecular structure) and internal interactions

Spectrum study (wavelength, transition probability, etc.) is the major method to study atomic and molecular structures.

(2) Applied study of environmental properties (e.g., remote sensing of atmosphere parameters, chemical analysis in situ, etc.)

Identification of chemical composition and measurement of their quantity using spectroscopy.

Measurement of environmental conditions like wind and temperature through spectroscopy analysis.

(3) Fundamental study of dynamical processes on a molecular level

Development of time-resolved spectroscopy and femtosecond lasers plays an essential role in the study of fast dynamical processes, allowing better analysis of spectral information and its transformation into models of structures and processes.

Why to Study Spectroscopy?

- Spectroscopy is the fundamental for many modern sciences and technologies. Spectroscopy has found very wide applications.

-- Spectroscopy is an very important approach to study the fundamental matter (fundamental particles, atoms, molecules, etc.) structures and internal interactions, and to study the dynamical processes.

-- Spectroscopy is often used in physics, analytical chemistry, biology, medicine, and material sciences for the identification of substances through the spectrum emitted from them or absorbed in them and for study of fast dynamical processes through time-resolved spectroscopy.

-- Spectroscopy is heavily used in astronomy and remote sensing. They are used either to measure the chemical composition and physical properties of objects or to measure related environmental properties like velocities and temperatures from Doppler shift and broadening of spectral lines.

- Spectroscopy is the fundamental for all remote sensing technologies.
- We want to give students the abilities and fundamental knowledge to learn more things -

"Help students to develop the skills to learn new things".

How to Do Fascinating Spectroscopy?

Fascinating Applications of Spectroscopy, e.g., LIDAR, single-molecule detection, laser femtosecond chemistry and biology, etc.

Need to know the fundamentals of laser spectroscopy, like numerous novel approaches to achieve high sensitivity, high resolution (spectral, spatial, and temporal), high precision, ultra-fast spectroscopy. etc.

Need to understand why and how spectral lineshape, linewidth, and line intensity are formed, and some are allowed while some not, etc.

Need to understand atomic and molecular structures and spectra theories

Need to understand radiation transition / quantum transition theories

Start with the basics of quantum physics, quantum mechanics, electromagnetism, lasers, etc.

Our Spectroscopy Course Structure

Introduction to Quantum Physics (Concepts of quantum, experimental facts leading to quantum physics, wave-particle duality, basics of quantum mechanics) – Read QM and laser materials on your own

Atomic structures and spectra theories

Radiation transition / quantum transition theories

Atomic spectral lineshape, line width and intensity, and selection rules

Molecular structures and spectra along with transition selection rules

Fundamentals of laser spectroscopy, like numerous novel approaches to achieve high sensitivity, high resolution (spectral, spatial, and temporal), high precision, ultra-fast spectroscopy. etc.

Concluding Remarks

- Spectroscopy is the fundamental for lidar and passive optical remote sensing, which is very important in full understanding of the principles and technologies, innovation of new technologies and instrumentation, and fully utilizing these remote sensing approaches to study environment, atmosphere, and space.

- Spectroscopy has also found wide applications in many other modern sciences and technologies, making it a "must-learn" knowledge.

- Study of spectroscopy will inspire us for future lidar innovation or even revolution so that we can answer many open questions in atmosphere and space research.

- Through the spectroscopy class, we try to help you to gain the high abilities and skills to learn new things.