

Rotational Raman Spectra of Diatomic Molecules

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Modern Physics Laboratory
(Physics 6180/7180)

The University of Toledo
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**Chandrasekhra
Venkata Raman
1888-1970**

Elastic Light Scattering

For Rayleigh scattering, the particles must be much smaller than the light's wavelength. Occurs when light travels through transmissive solids or liquids; most prominent in gases.

For $x = 2\pi r/\lambda$, particles are considered small when $x \ll 1$.

Rayleigh scattering depends on wavelength through the following relation for the Rayleigh scattering cross section:

$$\sigma_s = \frac{2\pi^5}{3} \frac{d^6}{\lambda^4} \left(\frac{n^2 - 1}{n^2 + 2} \right)^2$$

where d is the particle diameter, n is the particle's refractive index, and λ is the wavelength of the incident light.

A molecule, which lacks a refractive index and a well-defined size, scatters light elastically according to:

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 R^2} (1 + \cos^2 \theta)$$

where α is the molecule's polarizability, θ is the scattering angle, and R is the distance from the scattering molecule.

Rayleigh Scattering (elastic)



Rayleigh scattering is more dramatic after sunset. This picture was taken about one hour after sunset at 500 m altitude, looking at the horizon where the sun had set.

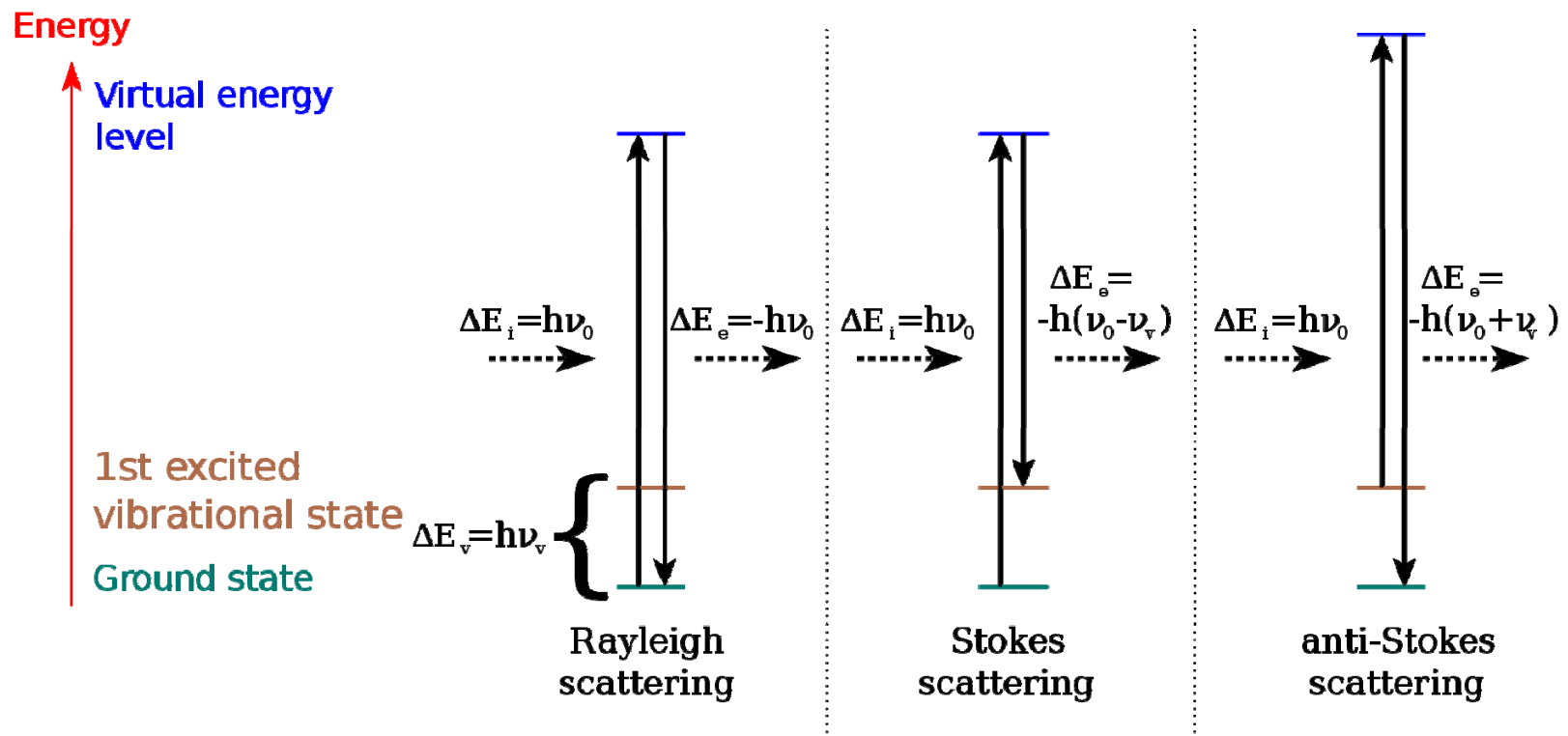
Inelastic light scattering (Raman scattering)

Although Rayleigh (elastic) scattering dominates, a small fraction of the scattered light (approximately 1 in 10 million photons) consists of photons having a frequency different from, and usually lower than, the frequency of the incident photons. In a gas, Raman scattering can occur simultaneously with a change in vibrational, rotational or electronic energy of a molecule. Chemists are concerned primarily with the vibrational Raman effect (see below).

The Raman effect was first reported by C. V. Raman and K. S. Krishnan, and independently by Grigory Landsberg and Leonid Mandelstam, in 1928. Raman received the Nobel Prize in 1930 for his work on the scattering of light. In 1998, the Raman Effect was designated an ACS National Historical Chemical Landmark in recognition of its significance as a tool for analyzing the composition of liquids, gases, and solids.

Raman scattering

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Rotational motion of a diatomic molecule

$$I = \mu R_0^2$$

Moment of inertia, I , where R_0 is the equilibrium internuclear separation, and μ is the reduced mass.

$$E_r = \frac{L^2}{2I}$$

Classical formulation of the rotational energy E_r , where L is the angular momentum (given by $\mu v R_0$).

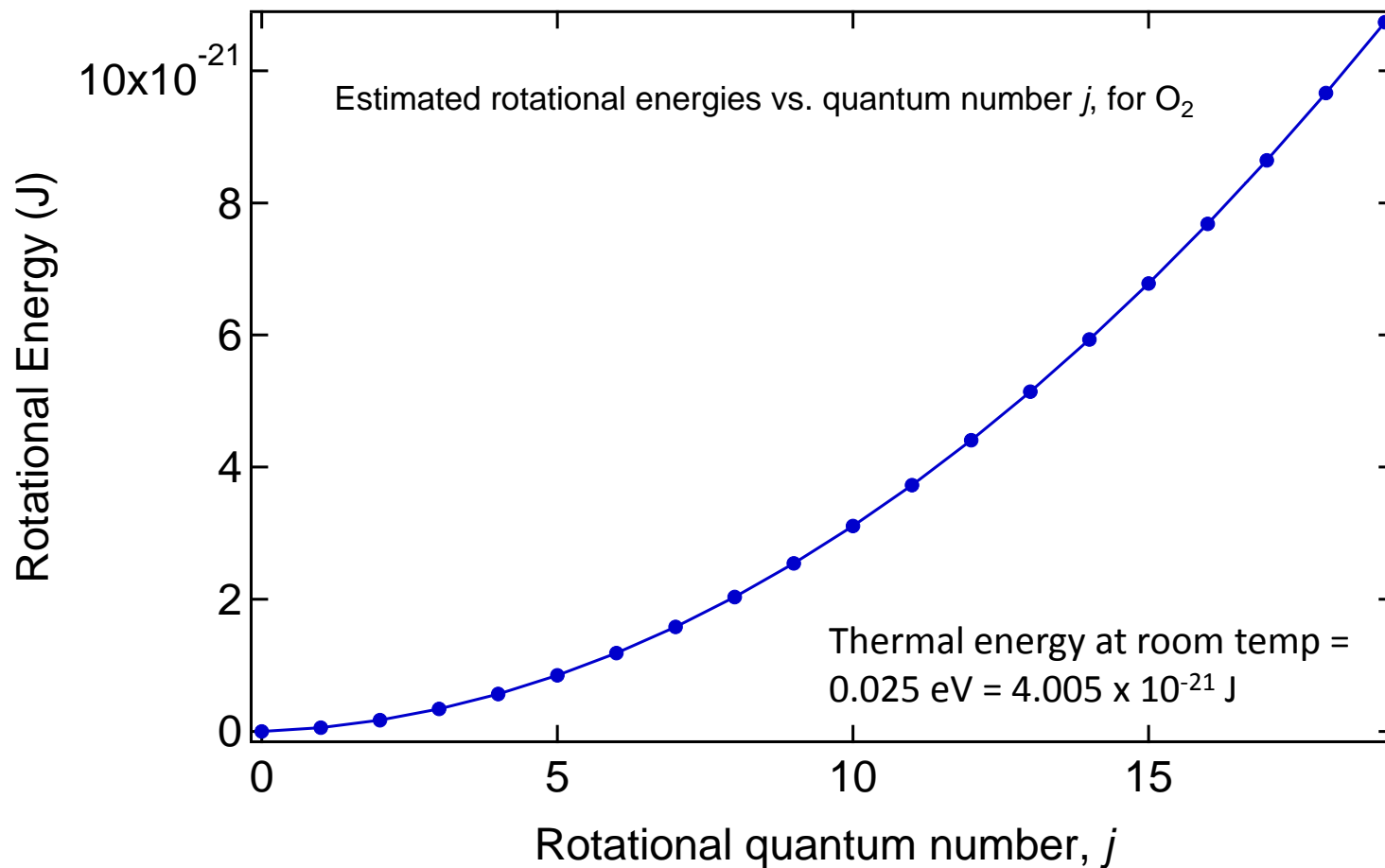
$$L^2 = j(j+1)\hbar^2$$

Quantization of the magnitude of the angular momentum, with the rotational quantum number j .

Rotational energies of a diatomic molecule

$$E_r = \frac{\hbar^2}{2I} j(j+1)$$

Quantum mechanical formulation of the rotational energy. (From Eisberg and Resnick, Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles (1985))



Experimental setup

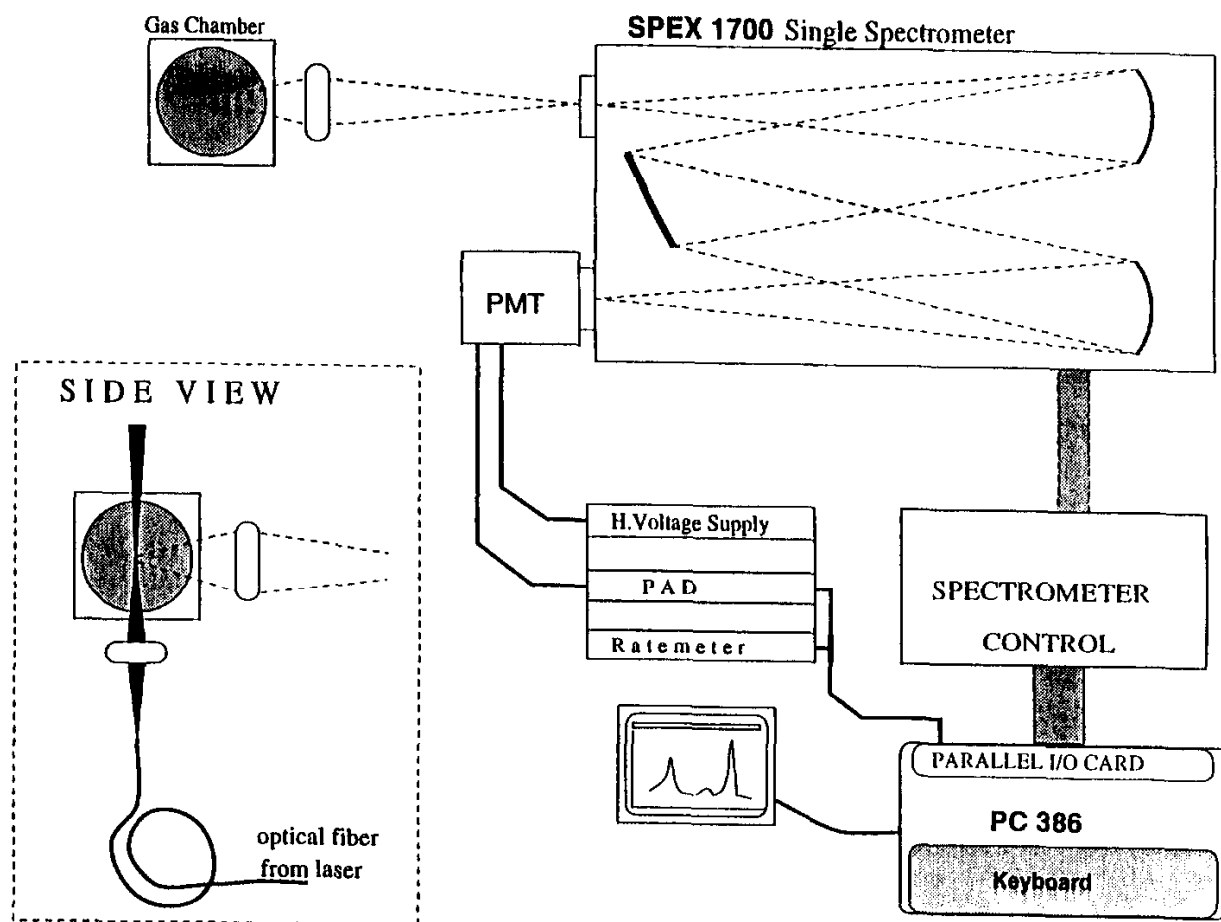
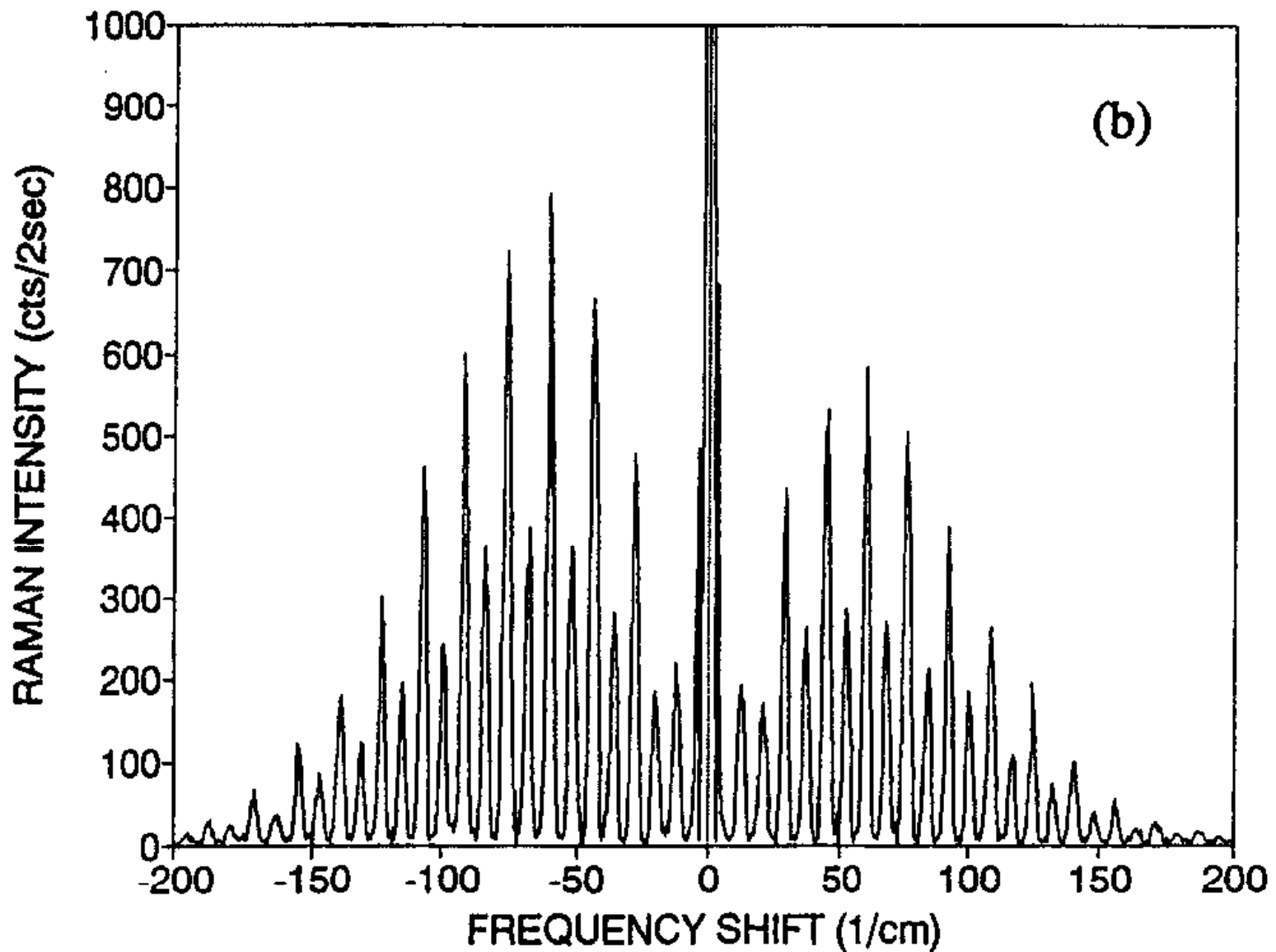
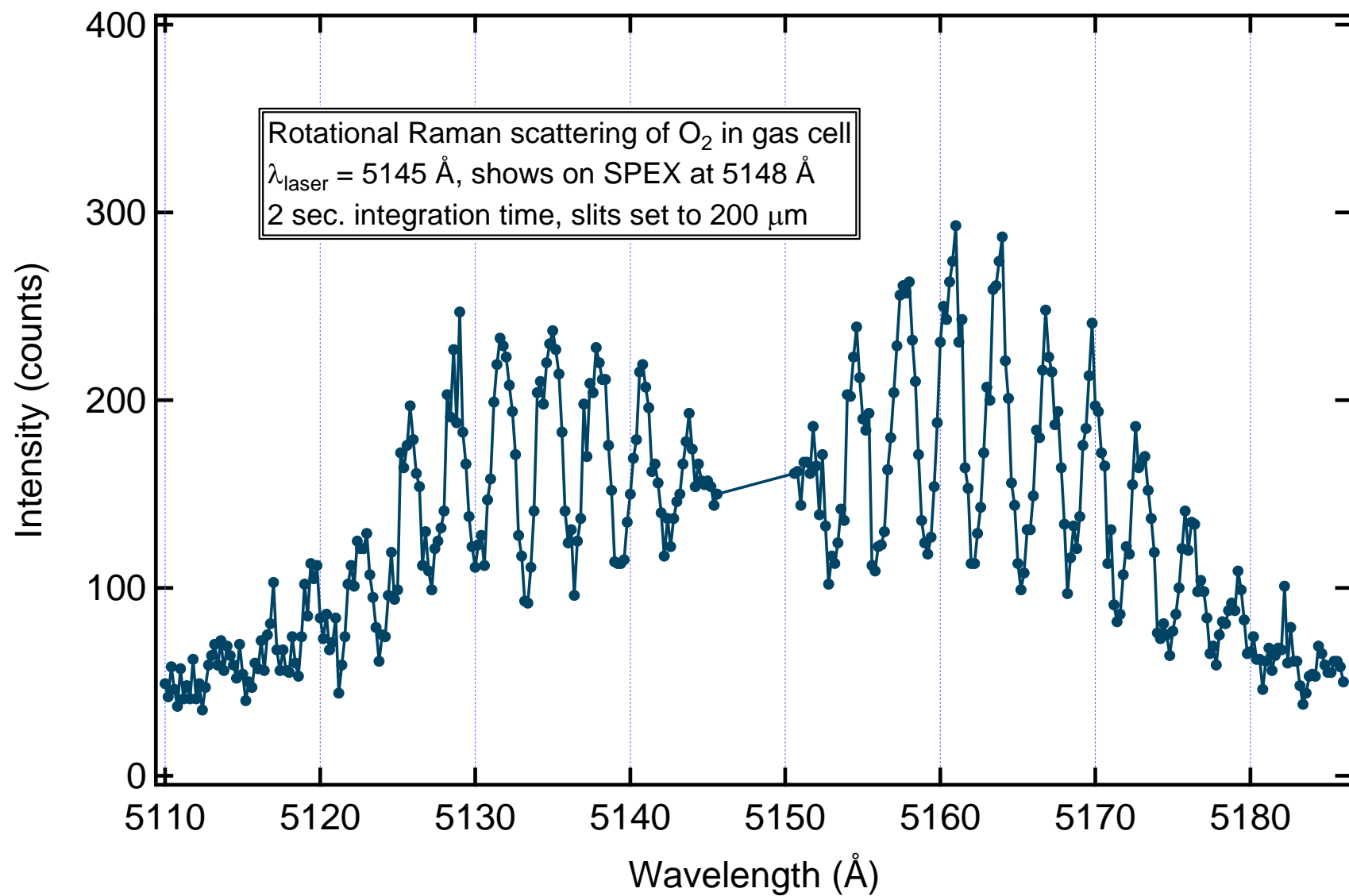


Fig. 1. Experimental arrangement for pure rotational Raman measurements using a single grating spectrometer.

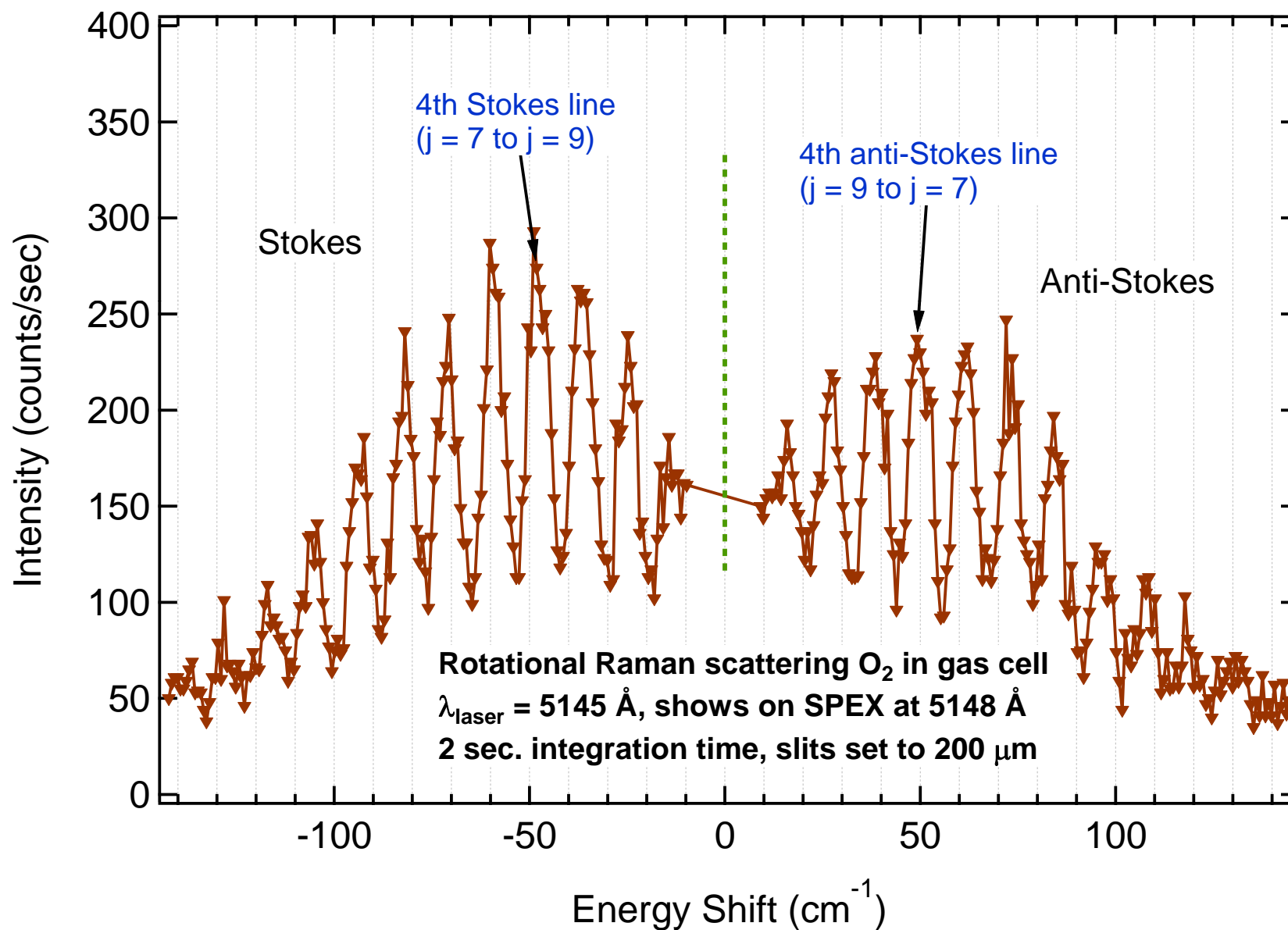
Rotational Raman scattering for N₂ gas



Rotational Raman scattering data for O₂ molecules (raw data)



Rotational Raman scattering data for O₂ molecules (wavenumber shift)

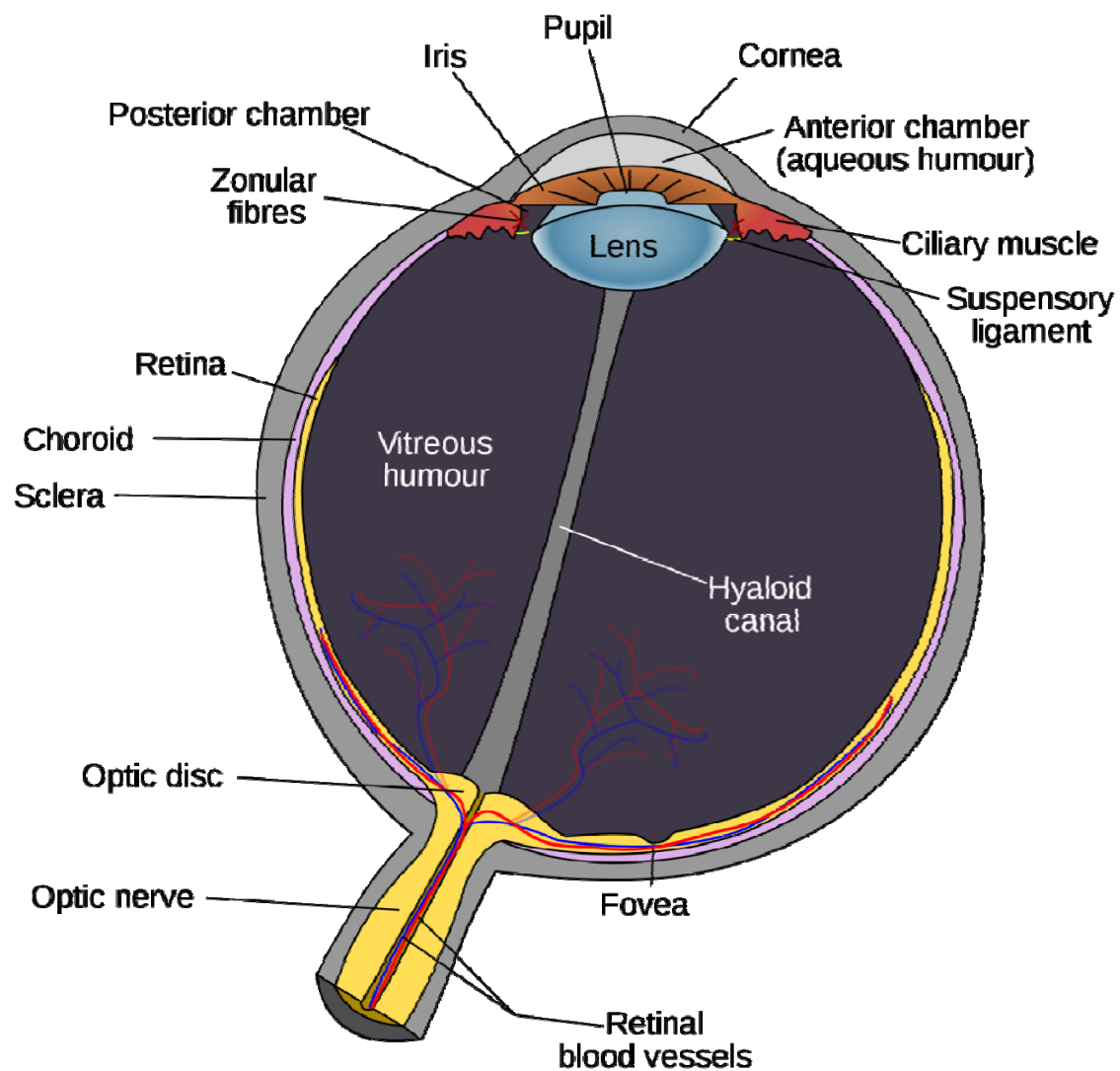


The Ar⁺ laser

An Ion Laser is a gas laser which uses an ionized gas as its lasing medium. Like other gas lasers, ion lasers feature a sealed cavity containing the laser medium and mirrors forming a Fabry-Perot resonator. Unlike HeNe lasers, the energy level transitions that contribute to laser action come from ions. Because of the large amount of energy required to excite the ionic transitions used in ion lasers, the required current is much greater, and as a result all but the smallest ion lasers are water cooled. A small air cooled ion laser might produce, for example, 130mW of light with a tube current of 10A @ 105V. This is a total power draw over 1 kW, which translates into a large amount of heat which must be dissipated.

“Wall efficiency” of $\sim 0.1 \text{ W} / 1000 \text{ W} = 0.02 \%$!

Laser Safety



Laser Safety

General precautions

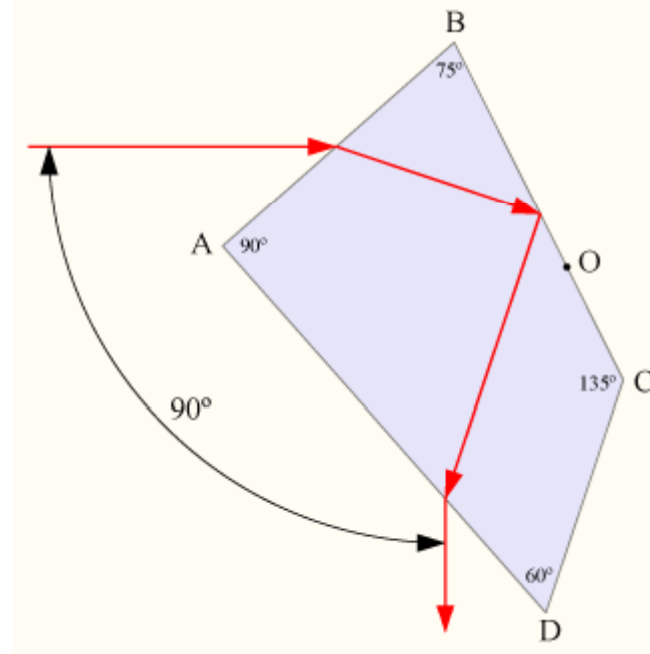
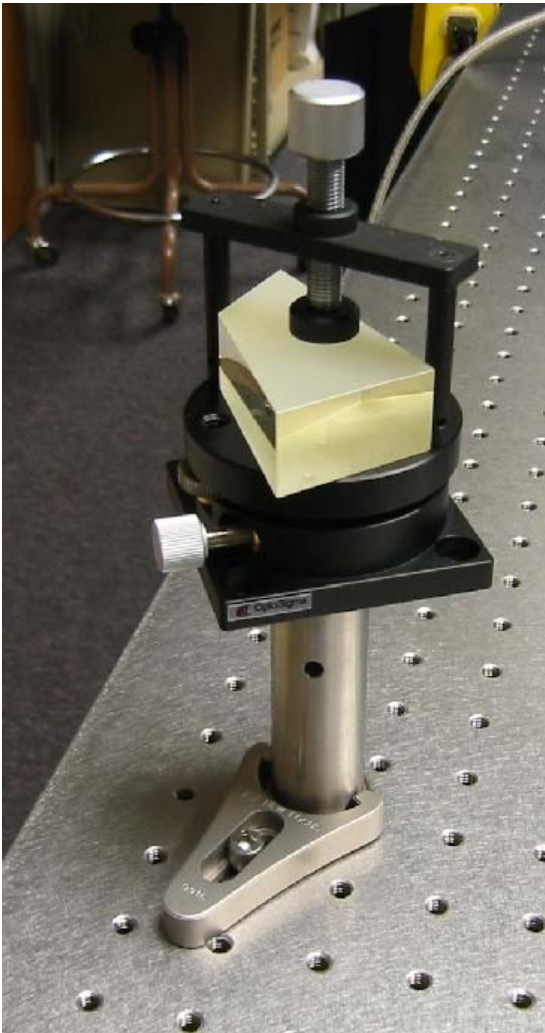
- Everyone who uses a laser should be aware of the risks. This awareness is not just a matter of time spent with lasers; to the contrary, long-term dealing with invisible risks (such as from infrared laser beams) tends to reduce risk awareness, rather than to sharpen it.
- Optical experiments should be carried out on an optical table with all laser beams travelling in the horizontal plane only, and all beams should be stopped at the edges of the table. Users should never put their eyes at the level of the horizontal plane where the beams are in case of reflected beams that leave the table.

Laser Safety

General precautions (continued)

- Watches and other jewelry that might enter the optical plane should not be allowed in the laboratory. All non-optical objects that are close to the optical plane should have a matte finish in order to prevent specular reflections.
- Adequate eye protection should always be required for everyone in the room if there is a significant risk for eye injury.
- High-intensity beams that can cause fire or skin damage (mainly from class 4 and ultraviolet lasers) and that are not frequently modified should be guided through tubes.
- Alignment of beams and optical components should be performed at a reduced beam power whenever possible.

Turning and dispersing the Ar⁺ laser beam



Using a Pellin-Broca prism (shown), we can both turn the laser beam at an approximate right-angle (through the wall-port, as you'll see in lab), and also disperse the different laser lines that operate simultaneously within the laser. A BK-7 glass P-B prism disperses two beam at $0.38\ \mu\text{m}$ and $2.5\ \mu\text{m}$ by just 2° .