

Rotational Raman Spectra of Diatomic Molecules

Week of November 1, 2010

**Atomic and Nuclear Physics Laboratory
(Physics 4780)**

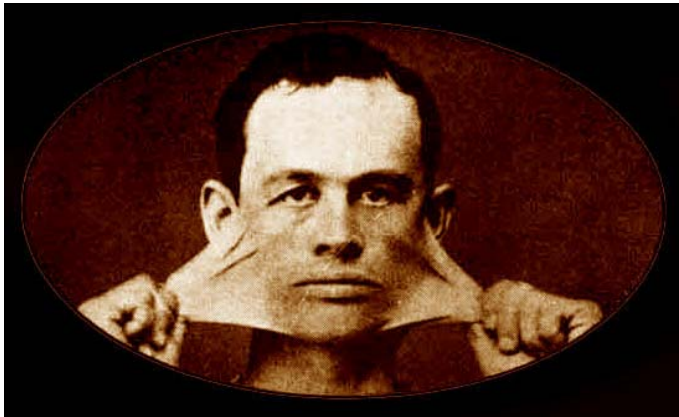
The University of Toledo
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**Chandrasekhra
Venkata Raman
1888-1970**

Elastic vs. Inelastic Light Scattering

Rayleigh Scattering: the scattered photon has the same energy as the incident photon.



<http://www.sideshowworld.com/blowofESman.html>

Raman Scattering: the scattered photon has a slightly lower or higher energy, shifted by one quanta of either vibrational or rotational energy.



http://en.wikipedia.org/wiki/Rayleigh_scattering

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:

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

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.

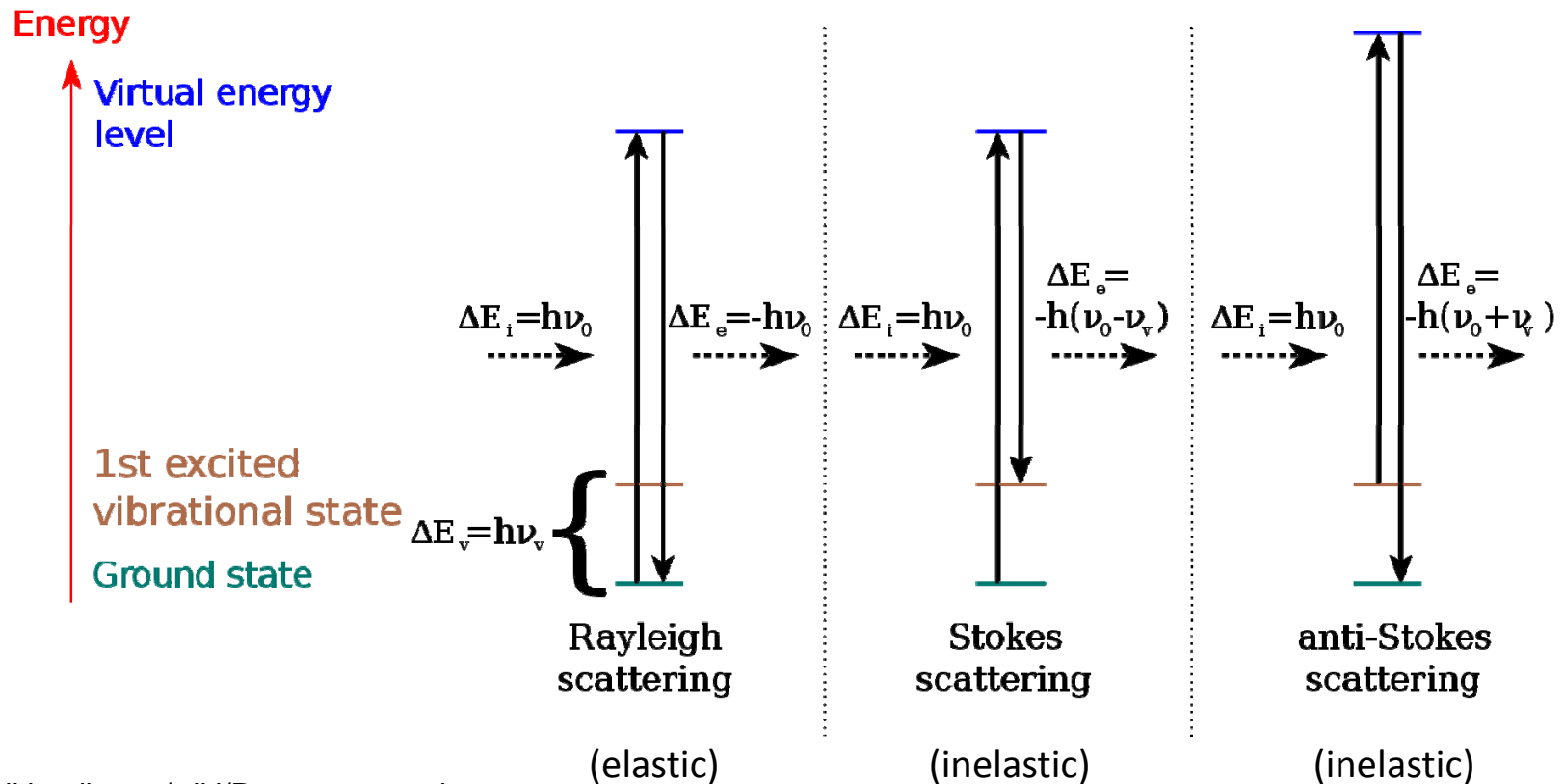
Inelastic light scattering (Raman scattering)

Although Rayleigh (elastic) scattering dominates, a small fraction of the light scatters inelastically. In a gas, Raman scattering (an inelastic scattering) can occur simultaneously with a change in vibrational, rotational or electronic energy of a molecule.

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 American Chemical Society (ACS) National Historical Chemical Landmark in recognition of its significance as a tool for analyzing the composition of liquids, gases, and solids.

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).



Rotational motion of a diatomic molecule

$$I = \mu R_0^2$$

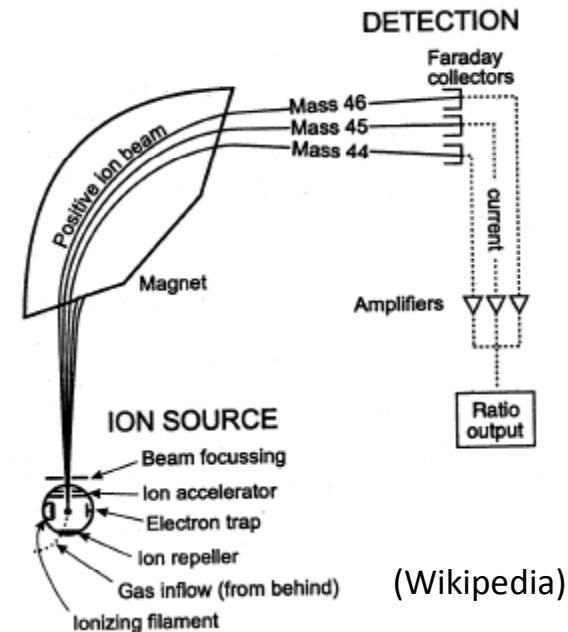
Moment of inertia, I , where R_0 is the equilibrium internuclear separation, and μ is the reduced mass.

What about the so-called “reduced mass”, and how does one determine the atom’s mass anyway?

“Given two bodies, one with mass m_1 and the other with mass m_2 , they will orbit the *barycenter* of the two bodies. The equivalent one-body problem, with the position of one body with respect to the other as the unknown, is that of a single body of mass.” (Wikipedia)

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

In the case of O_2 , the reduced mass is fairly simple since $m_1 = m_2$, so that $\mu = m_{\text{oxygen}}/2$.



Please note: we are talking about an O_2 molecule here, rotating about its center of mass. Therefore, the mass you’ll need to know is that of one oxygen atom (a very small number) – this is a critical piece of info for this lab’s analysis, so be sure you get it right! (Hint: m_{oxygen} is on the order of 10^{-23} g)

Quantum Mechanical Rotational Energies

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

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 .

This leads to the quantized form of the quantum-mechanically allowed rotational energies:

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

Changes in the rotational energy must follow the quantum-mechanical selection rule:

$$\Delta j = 0, \pm 2$$

$\Delta j = 0$ involves no change in rotational quantum number (j), and therefore no change in energy (i.e., this is *elastic* scattering, or *Rayleigh* scattering).

More essential details on rotational Raman scattering...

However, $\Delta j = \pm 2$ does involve a change in rotational quantum number j , and therefore a change in the quantized rotational energy, E_j :

$\Delta j = +2$: the scattered photon imparts (gives) energy to the O_2 molecule, and therefore the scattered photon loses some energy in the scattering process. Stokes scattering

$\Delta j = -2$: the scattered photon accepts (gets) energy from the O_2 molecule, and therefore the scattered photon gains some energy in the scattering process. anti-Stokes scattering

$$\Delta E = E_{j+2} - E_j = (\hbar^2/2I)(4j + 6), \text{ for Stokes Raman scattering } (\Delta j = +2), \text{ or}$$

$$\Delta E = E_j - E_{j-2} = (\hbar^2/2I)(4j - 2), \text{ for anti-Stokes Raman scattering } (\Delta j = -2)$$

(Note: j is the rotational quantum number of the initial state)

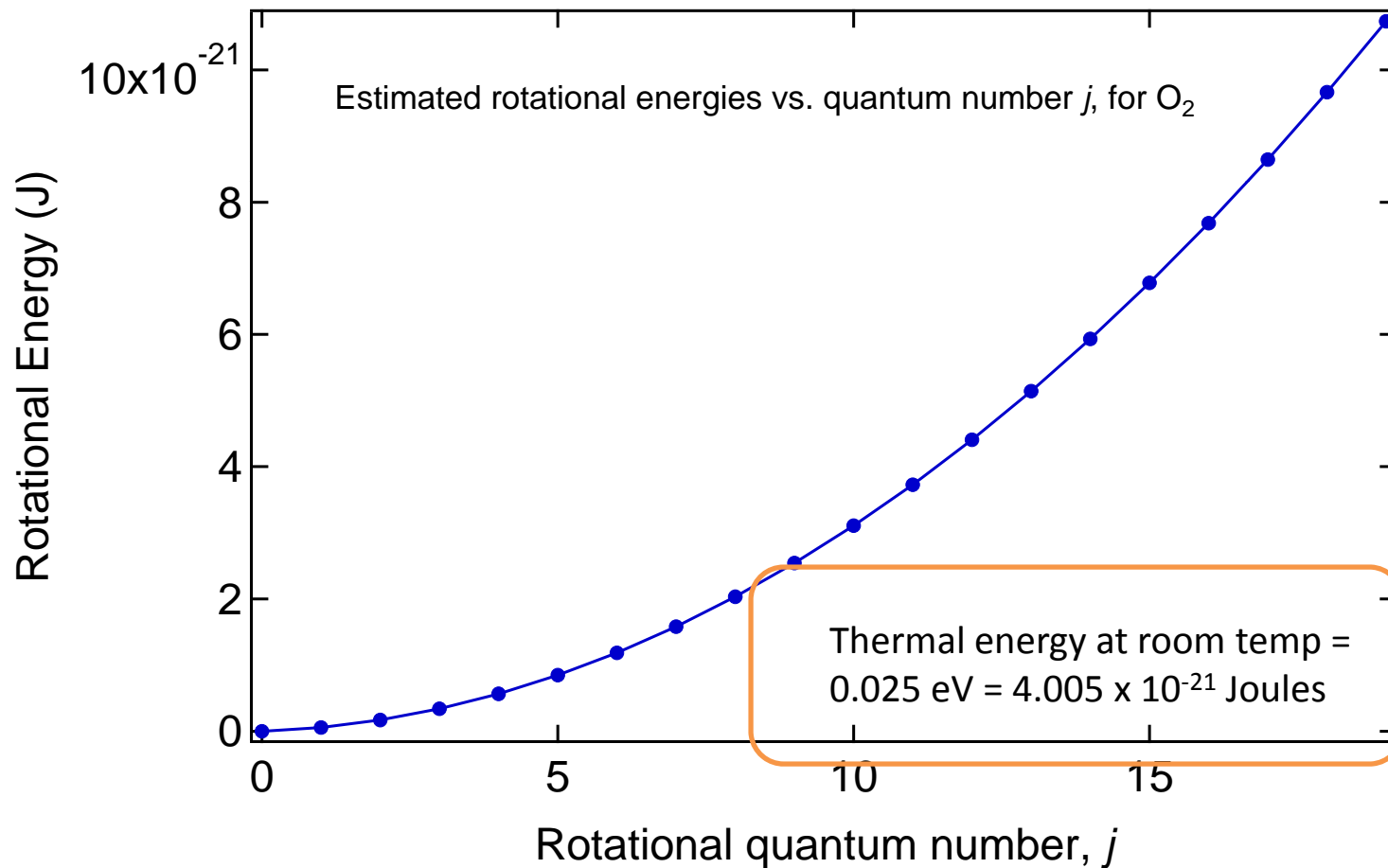
Finer details for O₂ molecules

- O₂ is a homonuclear molecule – what does this mean?
- ¹⁶O is “doubly-magic”, i.e., the number 8 of protons and neutrons in the nucleus is a magic number such that the nucleons are arranged in complete shells within the nucleus.
- In general, if the nuclei of a homonuclear diatomic (two atoms) molecule are *fermions*, then under exchange of the nuclei the overall wavefunction must be anti-symmetric; in contrast, if the nuclei are *bosons*, then the overall wavefunction must be symmetric under exchange of the two nuclei.
- ¹⁶O nuclei are indeed bosons, so the overall wavefunction of the O₂ molecule must be symmetric under exchange of the two nuclei.
- Following the (not so simple) discussion presented in the lab guide, it has been concluded that O₂ rotational states are only allowed to have odd values of j . This is a very important result, since knowing that j cannot be 0, 2, 4, 6, etc. makes all the difference when analyzing the data you’ll be acquiring!

Rotational energies of a diatomic molecule (not linear with j)

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

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



Experimental setup

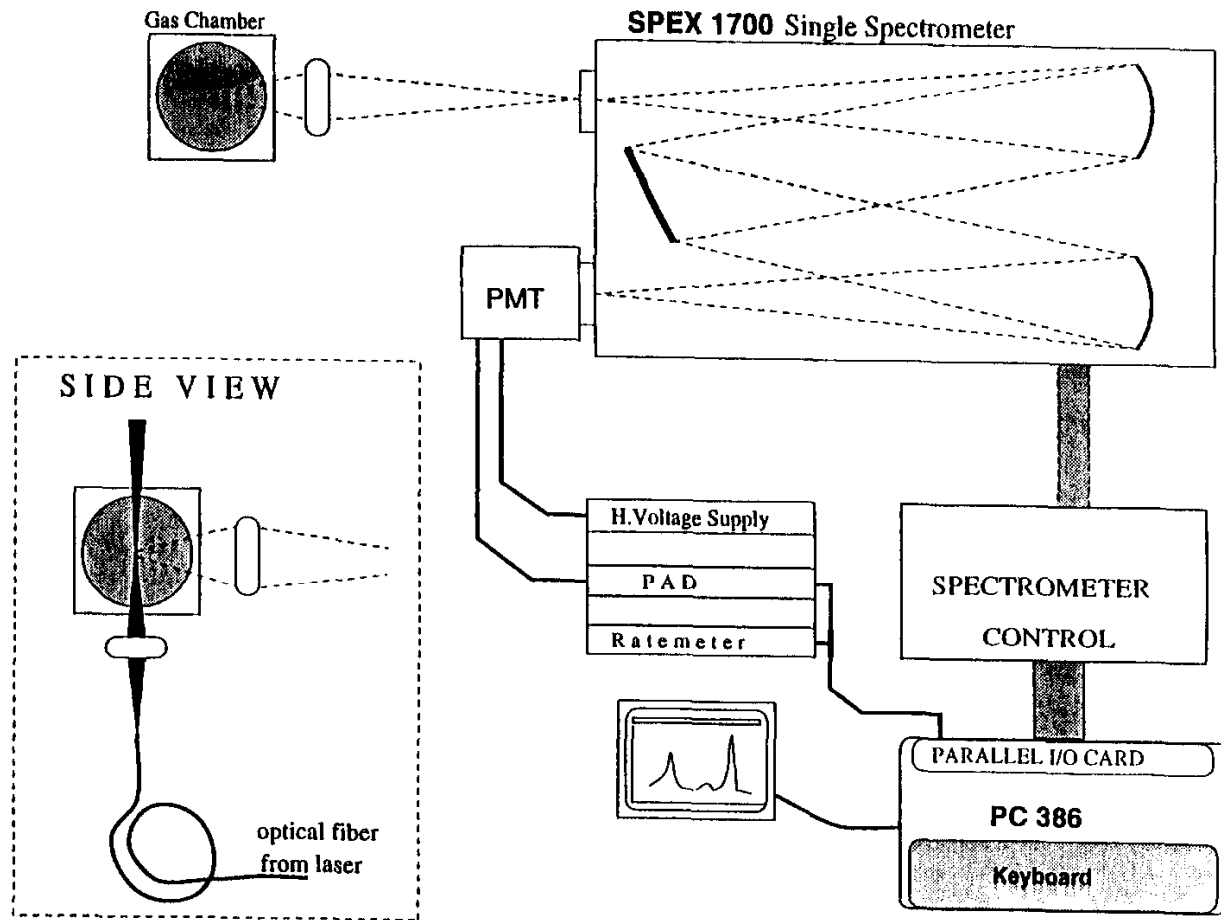
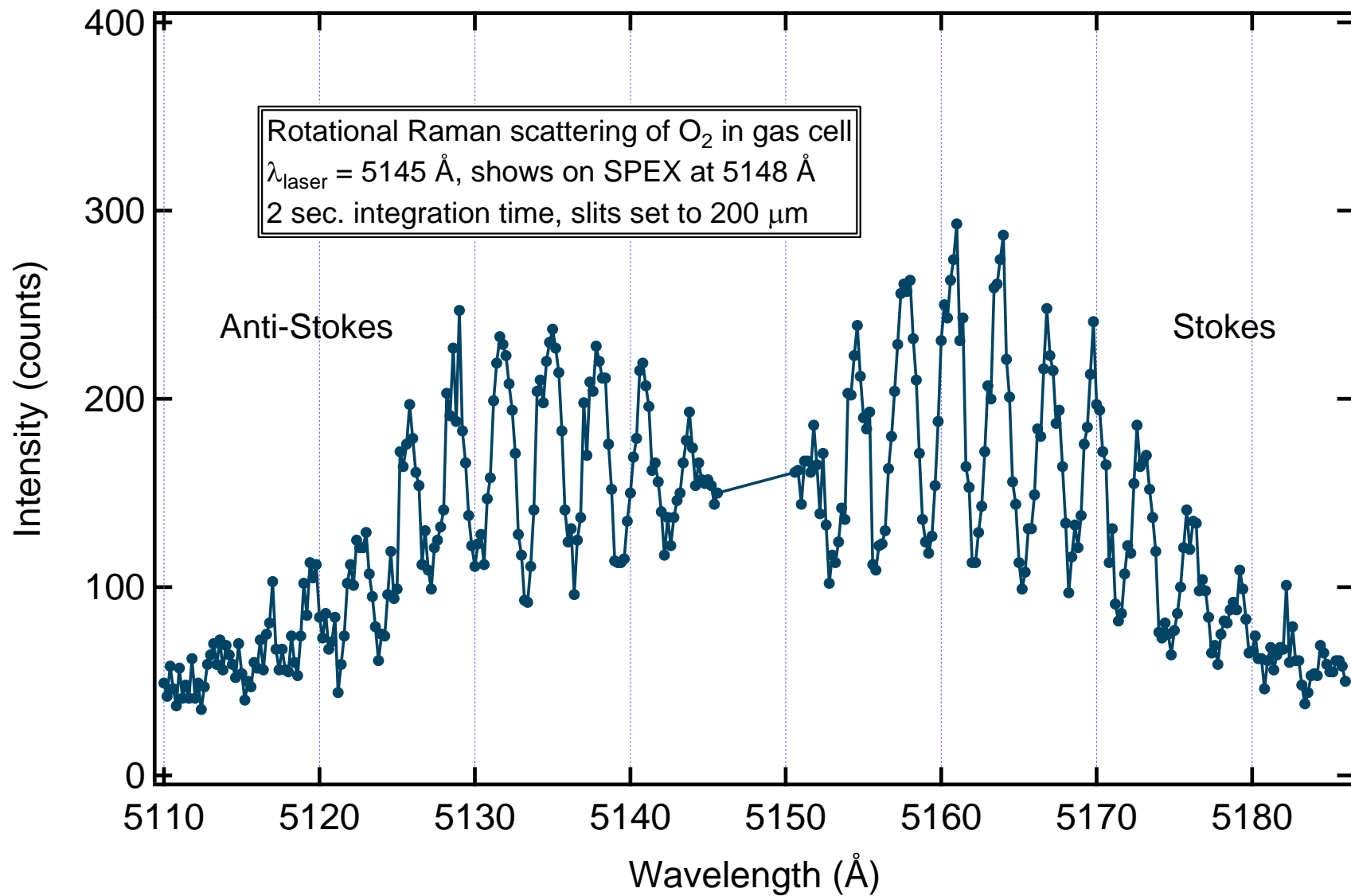


Fig. 1. Experimental arrangement for pure rotational Raman measurements using a single grating spectrometer.

Rotational Raman scattering data for O₂ molecules (raw data)

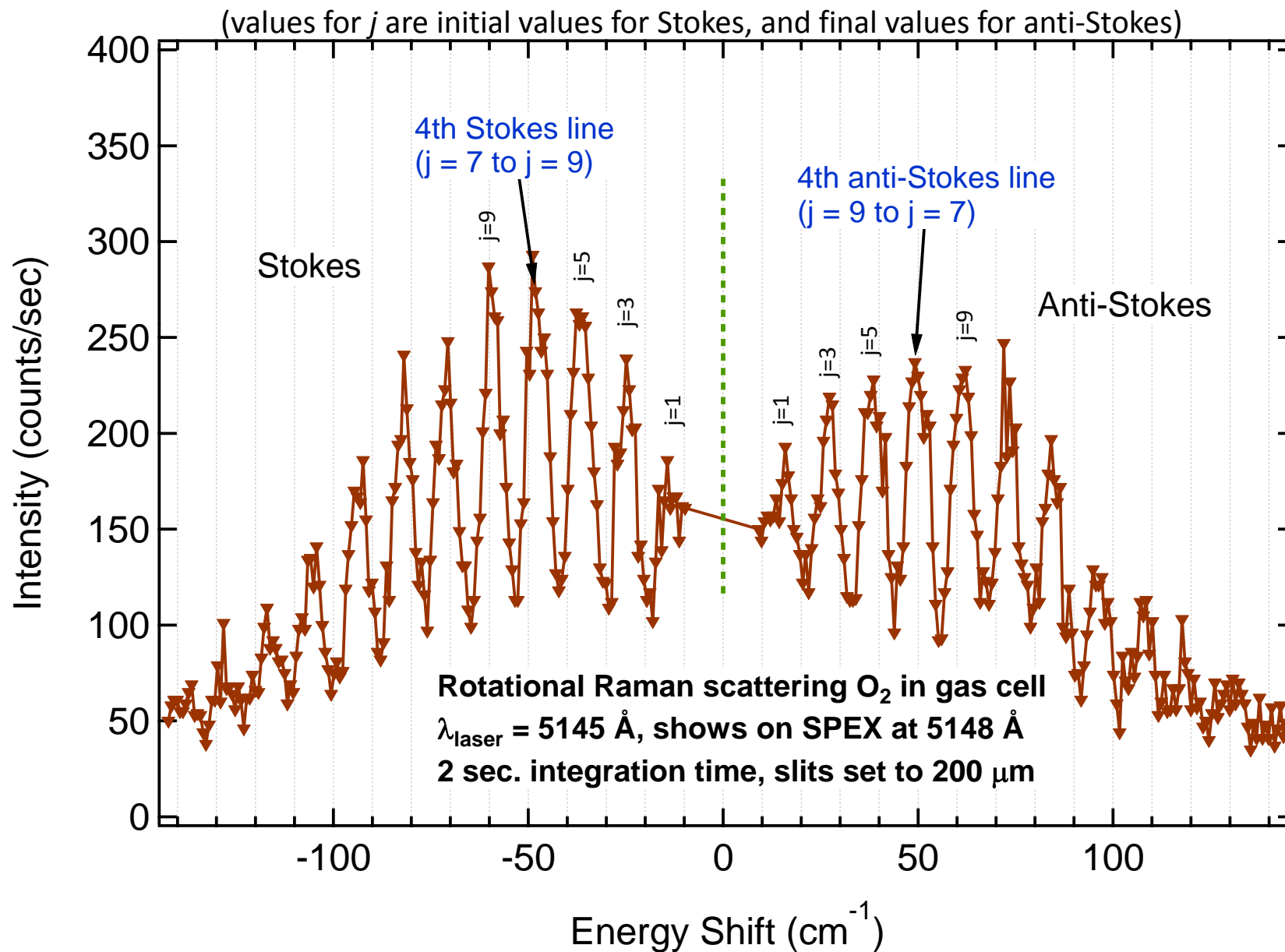


Rotational Raman scattering data: converting to wavenumber “shift”

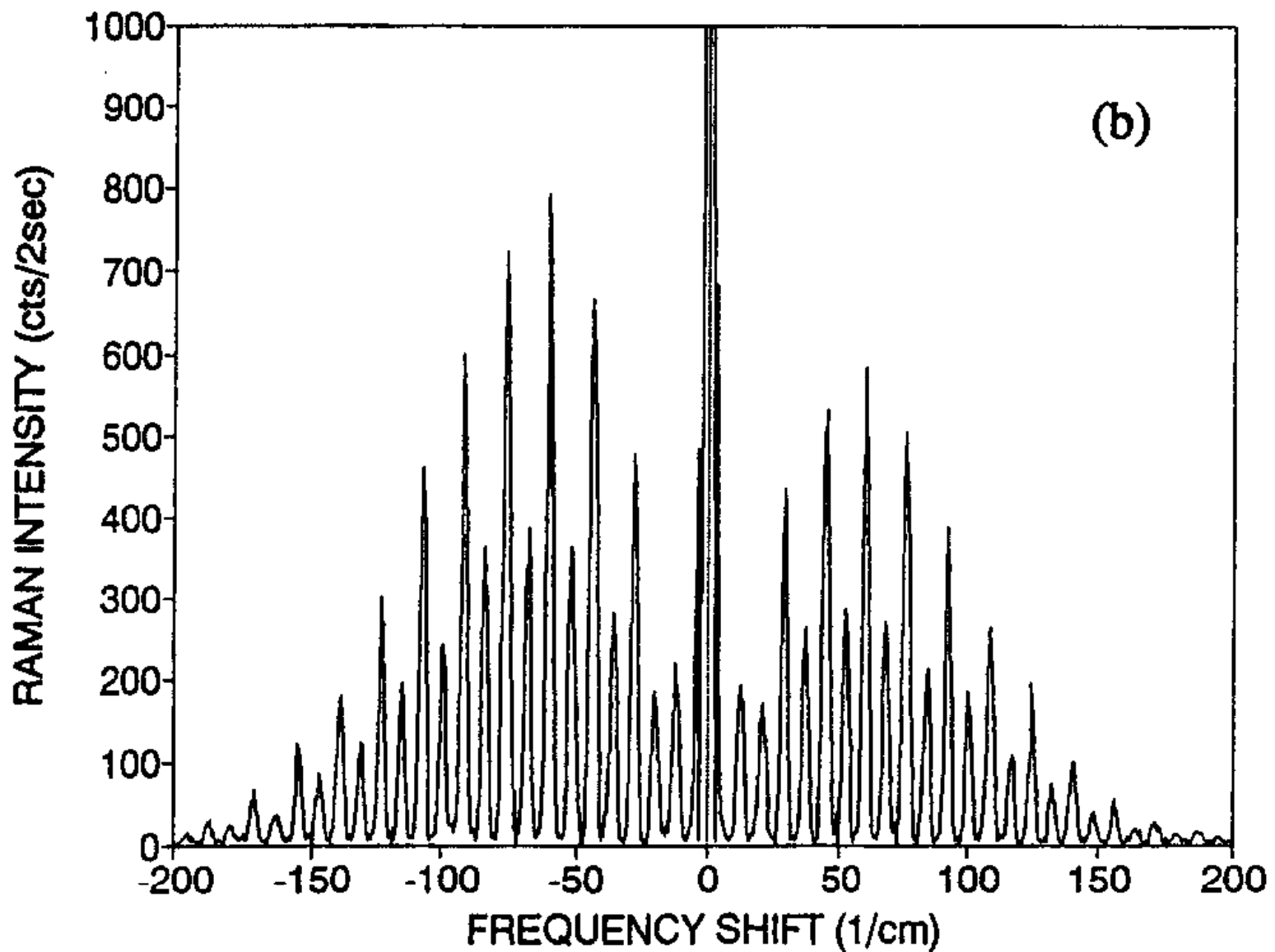
OK, so we have data in terms of the wavelength in Å, and we'd like to convert the data to wavenumber, expressed in terms of energy shift from the “central” laser (Rayleigh scattering) line. Not too difficult, as follows:

1. We can convert all of the data to wavenumbers, just by taking $1/\lambda$ with λ expressed in cm. So, take the Å data and multiple by $(10^2 \text{ cm})/(10^{10} \text{ Å})$, and then invert. So for an explicit example, 5145 Å becomes $(5.145 \times 10^{-5} \text{ cm})^{-1} = 1.943 \times 10^4 \text{ cm}^{-1}$.
2. Then take the wavenumber values for all of the data points and subtract the wavenumber value for the laser line. Example: if the laser line is at 5145 Å ($1.943 \times 10^4 \text{ cm}^{-1}$), then 5160 Å ($1.938 \times 10^4 \text{ cm}^{-1}$) yields an energy shift of $1.938 \times 10^4 - 1.943 \times 10^4 \text{ cm}^{-1}$, or $\sim 50 \text{ cm}^{-1}$. Note: you'll want to use one more significant figure in this case to determine your wavenumber shift (energy shift) values for analysis.
3. See next slide for a graph of sample data in terms of energy shift in wavenumbers!

Rotational Raman scattering data for O₂ molecules (wavenumber shift)



Rotational Raman scattering for N₂ gas

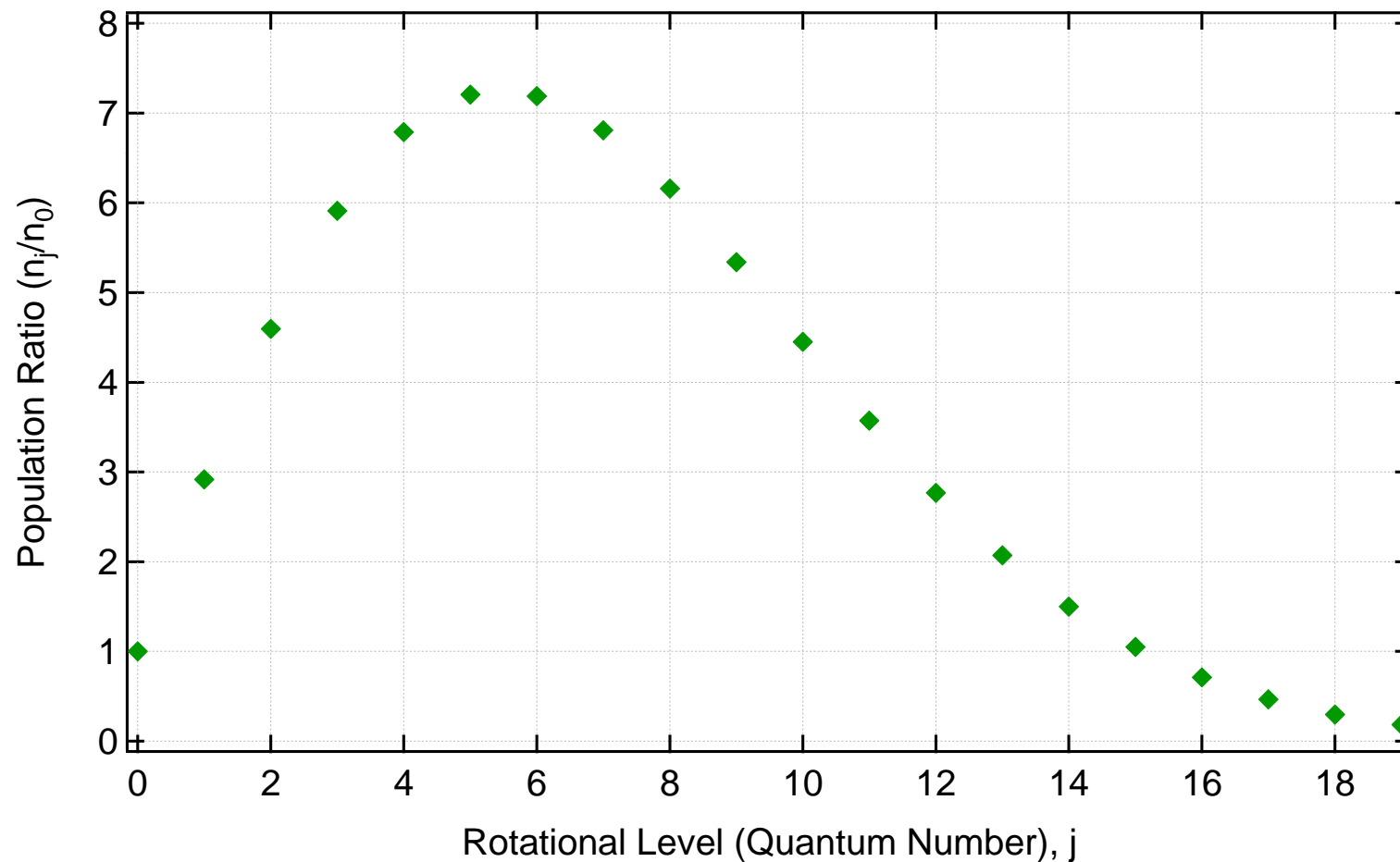


Rotational Raman scattering: intensity distribution of peaks at 300 K

$$\frac{n_j}{n_0} = \frac{\rho_j}{\rho_0} e^{-(E_j - E_0)/kT}$$

where the ρ 's are the degeneracy factors given by $\rho_j = 2j+1$ for the energy level E_j . One can see that $\rho_0 = 1$, and $E_0 = 0$, which simplifies the equation somewhat, to yield:

$$\frac{n_j}{n_0} = (2j+1)e^{-E_j/kT}$$



Extracting the equilibrium internuclear separation for O₂?

ΔE (from Rayleigh line) = $E_{j+2} - E_j = B(4j + 6)$, for *Stokes Raman scattering* ($\Delta j = +2$), or

ΔE (from Rayleigh line) = $E_j - E_{j-2} = B(4j - 2)$, for *anti-Stokes Raman scattering* ($\Delta j = -2$)

(Note: j is the rotational quantum number of the initial state)

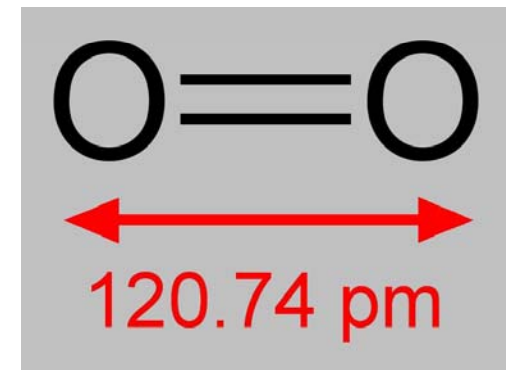
Note also that we've introduced a constant value, $B = \hbar^2/2I$.

OK, we can determine that the energy spacing between adjacent lines in our spectrum will be given by (Stokes example, for j to $j+2$) calculating ΔE : we get a difference of $B((4(j+2)+6) - (4j+6)) = B(4j+8+6-4j-6) = 8B$.

The first line will be spaced from E_0 , the laser or Rayleigh line, by taking (Stokes case) $j = 1$, so that $\Delta E = 10B$; or

The first line on the anti-Stokes side is for initial $j = 3$:
 $\Delta E = B(4j - 2) = 10B$.

So we'll use the data to fit for B , and use that to calculate I , from which we'll extract the value for R_0 .



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 $\sim 0.1 \text{ W} / 1000 \text{ W} = 0.02 \%$!

The Ar⁺ laser: photon flux

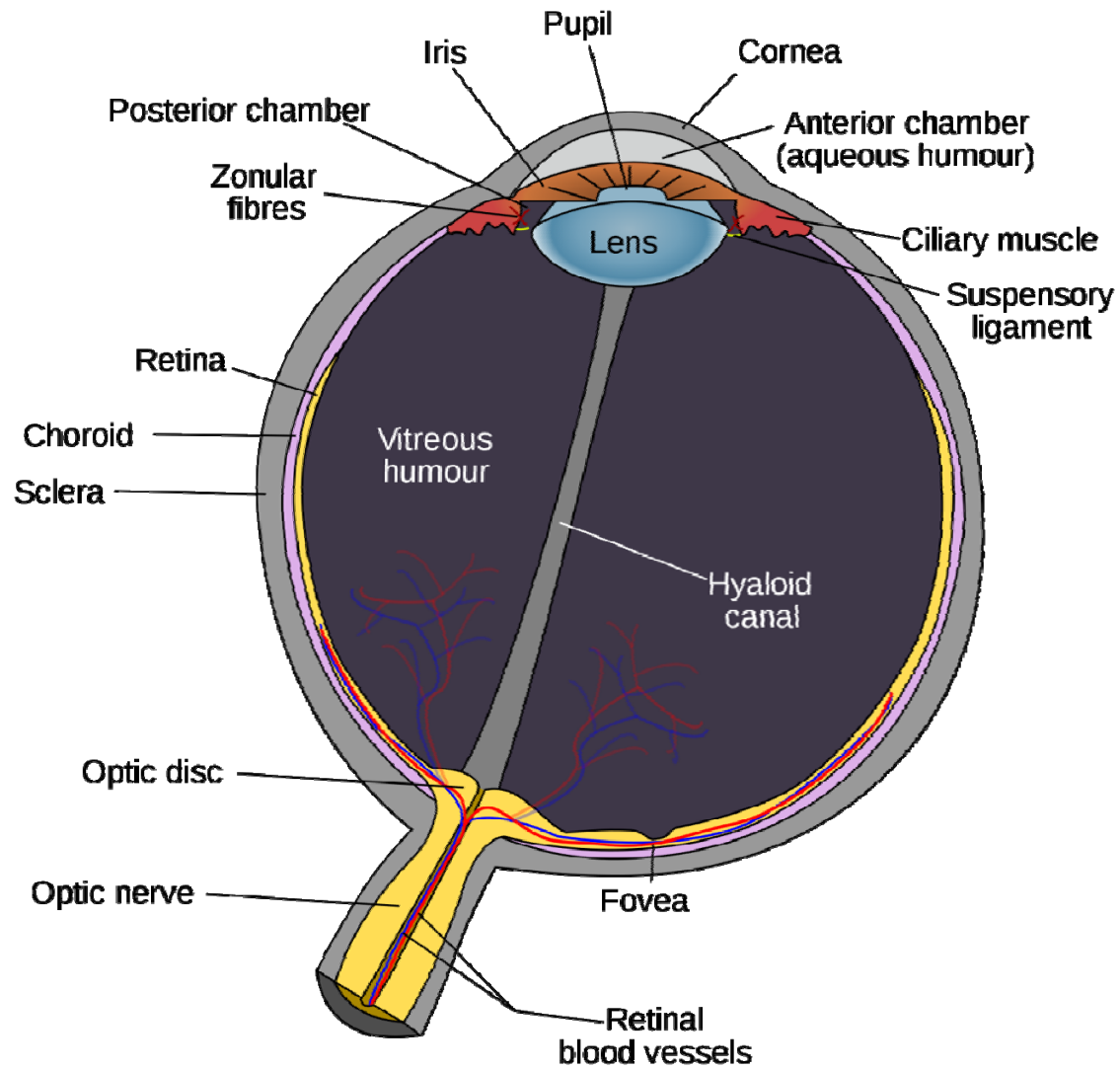
We can calculate the number of photons per second incident for a given area and average power. This laser puts out “continuous wave” light (i.e., it is not pulsed and is therefore “steady-state” with a constant power).

Let’s say we have 1 mW of power uniformly spread out over 10 cm² – that gives us an intensity of 1 mW/10 cm² = 0.1 mW/cm². How many photons per second, per cm² are incident on this area?

Well, 1 mW = 1 x 10⁻³ W = 1 x 10⁻³ J/s (energy per second, right??). So how many photons are there in all, per second? Just determine the energy in 1 photon, then compute the number of photons: (1 x 10⁻³ J) / (hc/λ). The divide by 10 cm², and you’ll have the answer.

Use this approach in your lab report when asked to estimate the number of laser photons incident in the experiment per mW of power, and then using your measurement of the amount of power in the beam, and your measurement of the actual Raman signal rate (photons detected per second), you can estimate the number of laser photons needed to generate (*and detect*) one Raman photon for O₂.

Laser Safety



Laser Safety

General precautions

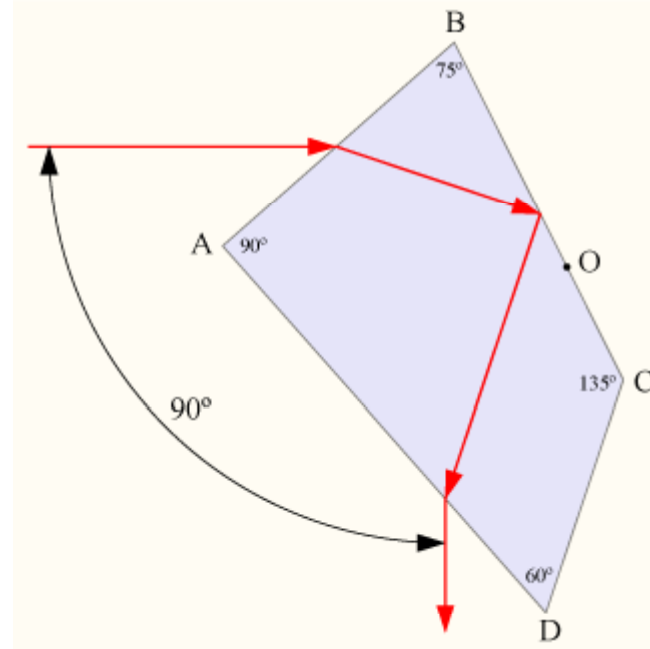
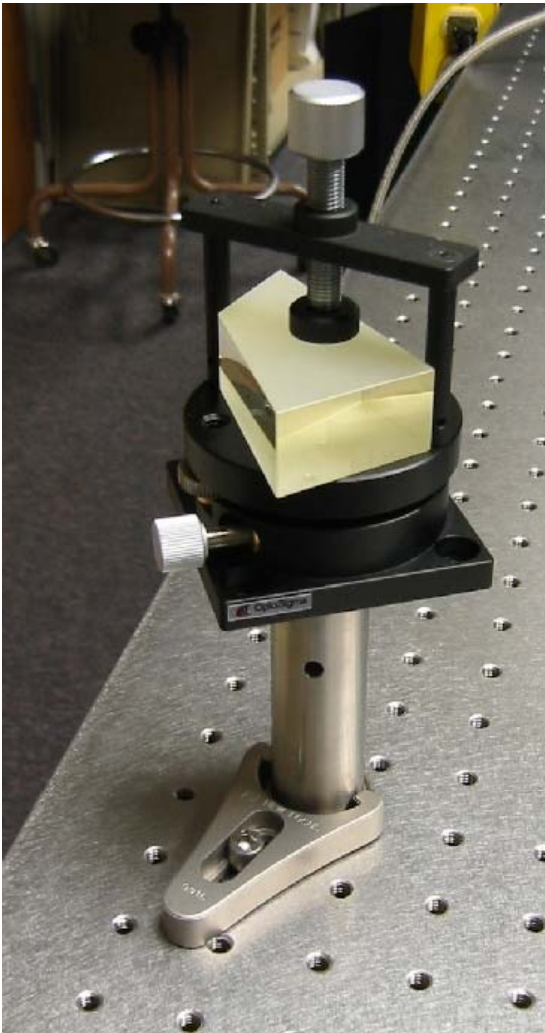
- Everyone who uses a laser should be aware of the risks. This awareness is not just a matter of time spent with lasers; to the contrary, long-term dealing with invisible risks (such as from infrared laser beams) tends to reduce risk awareness, rather than to sharpen it.
- Optical experiments should 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 beams at $0.38\ \mu\text{m}$ and $2.5\ \mu\text{m}$ by just 2° .