Physics 4780: Atomic and Nuclear Physics Laboratory

Experiment A1: Rotational Raman Spectra of Diatomic Molecules

References: Preston and Dietz pp 219-221

A. Compaan, A. Wagoner, and A. Aydinli, "Raman Scattering in the Instructional Laboratory," Am. J. Phys. 62, 639 (1994)

G. Herzberg, **Spectra of Diatomic Molecules** (Van Nostrand Co., Princeton, N.J. 2nd ed) [This is one of the authoritative sources on molecular spectra with very valuable tables at the end of the book covering rotational, vibrational and electronic states of the diatomic molecules.]

R. Eisberg and R. Resnick, **Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles**, (Wiley, New York, 2nd Ed., 1985). See pp. 423-437, pp 534-545, and p. 599.

Objectives: *To learn the essentials of inelastic light scattering, particularly Raman scattering in molecules. In the simple linear (diatomic and triatomic) molecules, the high degree of symmetry allows one to measure, by Raman scattering, the rotational inertia of the molecule and thus the internuclear separation. In addition, we can observe directly and dramatically the effects of the nuclear spin on the symmetry of the overall wavefunction and thus on the permitted populations of states of different rotational angular momenta. The difference between* O^{16} *nuclei (bosons) and the* N^{14} *nuclei (fermions) are directly seen.*

Overview--In this experiment we shall use the grating spectrometer and a low power, air cooled argon laser to try to examine the rotational Raman spectra of the diatomic molecules, N_2 and O_2, and the linear triatomic molecule, CO_2. Raman scattering is convenient for analysis because we do not have to worry (to first order anyway) about any stretching of the molecule as it rotates (or vibrates). [For Raman scattering the molecule remains in the ground electronic state; in contrast with optical transitions in which the electronic state changes as well as (possibly) the rotational and vibrational states. Thus the molecule may be treated as a rigid rotator. However, the spectra of these homonuclear diatomic molecules do illustrate in a very pretty way the influence of nuclear spin statistics on the symmetry of the molecule and its permitted rotational states. You will be using the SPEX 1-meter grating spectrometer for the Raman analysis. Normally, with Raman scattering one uses a double or a triple spectrometer because the *elastic* light scattering is very much stronger than the *inelastic* Raman scattering and when the frequency shifts are small it is difficult to "see" the weak Raman lines in the vicinity of the very strong "Rayleigh" peak. Therefore you will have to use great care to avoid any unnecessary elastically scattered laser light entering the spectrometer. *Elastic* refers essentially to a scattering process in which the scattered entity (a photon in this case) does not change energy; *inelastic* referes to a scattering process in which energy is lost (or perhaps gained, as we'll see).

The amount of Raman scattered light may be only $\sim 10^{-14}$ times a strong as the original laser beam

and therefore it is necessary to be extremely careful to collect as much light as possible. Whereas in some experiments you can just plop down a discharge lamp somewhere in front of the spectrometer, now you will have to use a very carefully aligned high quality collecting lens to observe any kind of signal. Small misadjustments will prevent you from seeing any signal!! As described in Paragaph 2 under Set-up, you will use the camera lens to collect the Raman light over as large a solid angle as possible and image the track of the laser beam carefully into the entrance slit of the spectrometer. You must also be certain that all of the light which enters the spectrometer also falls on the first (collimating) spherical mirror of the spectrometer. There are many ways to fail to see a signal, but if you exercise some care you should be able to collect state-of-the-art data comparable to that shown in the reprint by Compaan, Wagoner, and Aydinli (Appendix XXV) for the single monochrometer.

[For the record, efforts to collect data like that in the paper have resulted in relatively successful spectra only for O_2 in the recent past (i.e., Spring 2010); we'll see whether we can improve on that in these Fall 2010 lab sessions.]

Background:

The classical rigid rotator has a kinetic energy given by

$$E = (1/2)I\omega^2 = J^2/(2I)$$

where I is the rotational inertia and J is the rotational angular momentum. For a diatomic molecule $I = \mu R^2$, where R is the internuclear separation and μ is the reduced mass

$$1/\mu = 1/m_1 + 1/m_2.$$

The quantization condition can be introduced via Bohr's angular momentum postulate

$$J^2 = \hbar^2 j(j+1),$$

so that in quantized form

$$E_j = (\hbar^2/2I)j(j+1).$$

[Note that rotational states are <u>un</u>equally spaced in energy, unlike vibrational states.]

For (pure rotational) Raman scattering, there are <u>two</u> electric dipole transitions (normally) involved so that the total angular momentum change is

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

The $\Delta j = 0$ term will be elastic scattering and just adds to other processes contributing to *Rayleigh scattering*, but the magnitudes of the energy shifts for rotational Raman scattering are just

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

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

In both cases above, j = the rotational quantum of the *initial* state. Note that for *Stokes* scattering, the molecule *receives* (or *absorbs)* two quanta of rotational energy so that the scattered photon has *lower* energy or longer wavelength. The opposite is of course true for *anti-Stokes* scattering, for

which the molecule *provides* (or *emits*) two quanta of rotational energy resulting in a scattered photon with *higher* energy than the incident photon.

You may think of the Raman process as a temporary electric dipole absorption (to a virtual excited electronic state) followed by re-radiation back to the ground electronic state. This ground electronic state may, however, be associated with a different rotational quantum number. There generally is no excited electronic state which is resonant in energy with the photon energy and thus this "absorption" is a virtual process -- or equivalently occurs to a "virtual" state. Note that in second order perturbation theory such a two-photon scattering process would have a matrix element with the form

$$M_{i'i} = M_{i'k} M_{ki} / [(E_k - E_i) - h\nu + ih\Gamma_k].$$

The matrix elements $M_{i'k}$ and M_{ki} are just the usual electric dipole transitions (examined in atomic spectroscopy experiments). For all of the gas molecules we will be studying, the photon energy $h\nu$ is 2 - 4 eV away from resonance with the lowest lying electronic excited state E_k. This is one reason that Raman scattering is so weak!

The intensity of any particular Raman line will depend, naturally, on the square of this matrix element. (We shall not ask you to calculate these for your write-up!) In addition, however, the Raman intensity of a particular line will be proportional to the population in the initial rotational state j. Since the gas is very low density, one need not worry whether the molecule is a fermion or a boson since the low density limit will be Maxwellian anyway. Thus we can use a Maxwell-Boltzmann distribution with the rotational energies given above by $E_j = (\hbar^2/2I)j(j+1)$. *In addition*, however, you *must* properly include the multiplicity of the state, namely, 2j+1 in front of the Maxwell distribution! Then the distribution of intensities of the lines ought to enable calculation of the gas temperature. Why is the Stokes intensity for a given Raman shift (say the fourth line from the origin) larger than the anti-Stokes intensity?

From Eisberg and Resnick, the Boltzmann factor gives us the ratio of n_j, the number of molecules in the rotational level j, to n_0, the number in the j = 0 level, for a sample at equilibrium temperature T:

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

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:

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

Symmetry of the rotational states:

Now for the finer details!

For homonuclear diatomic molecules, the overall wavefunction must have a definite symmetry under exchange of the nuclei. If the nuclei are *fermions*, the overall wavefunction must be antisymmetric under exchange of the nuclei and if the nuclei are *bosons*, then the wavefunction must be symmetric under the exchange operation.

Consider a diatomic molecule such as H_2, O_2, or N_2:
The overall wavefunction may be written to a good approximation as a product wavefunction (under certain assumptions not specified here). Thus

$$\psi_{tot}(R_1R_2r_ar_bI_1I_2s_as_b) = \psi_e(r_ar_b)\chi_e(s_as_b)\psi_n(R_1R_2)\chi_n(I_1I_2),$$

where the subscripts 1 and 2 refer to the nuclei and the subscripts a and b refer to the electrons (just two in the case of the H_2 molecule, or properly summed and symmetrized in the case of larger molecules).

For H_2 with normal, light hydrogen (protons for nuclei), the ψ_{tot} must be antisymmetric under the operation which exchanges $R_1 \leftrightarrow R_2$ to satisfy the Pauli exclusion principle (a proton is a fermion, as is also true for a neutron). For ${}_8O^{16}$, the nucleus is doubly "magic" and I = 0 so that the nuclei are bosons. (See Eisberg and Resnick figure 15-18.) Thus in the case of the O_2 molecule, the ψ_{tot} will have to be symmetric under the operation $R_1 \leftrightarrow R_2$. [You can figure out the case of ${}_7N^{14}$ for yourself!]

Now how does this relate to the rotational states with quantum numbers j??

-The space part of the rotational state wavefunction, $\psi_n^j(R_1R_2)$ has the symmetry $(-1)^j$ under the operation $R_1 \leftrightarrow R_2$.

-The space part of the electronic state wavefunction, $\psi_e(r_ar_b)$ will normally be symmetric under exchange of nuclei for the ground state of the molecule. [However, the case of O_2 is an exception since it is antisymmetric (according to Herzberg).]

-The spin part of the electronic state wavefunction may usually be assumed symmetric under the exchange $R_1 \leftrightarrow R_2$.

-Finally, the nuclear spin part of the molecular wavefunction will depend on the individual nuclear spins. Thus, if you start from the state of maximum spin projection, i.e., both m_I maximum, this state will be symmetric under exchange. [I.e., for H_2, the $I_{tot} = 1$ will be symmetric, whereas I = 0 will be antisymmetric. For O_2, since the individual I = 0, then the state $I_{tot} = 0$ will be symmetric. For a molecule with individual I = 1, on the other hand, the state $I_{tot} = 2$ will be symmetric, I = 1 will be antisymmetric, and I = 0 will be symmetric again.]

Now here comes the interesting part: there will often be some restrictions on the possible values of rotational quantum j which are allowed since the overall wavefunction must satisfy the appropriate

symmetry property. [Note that this is entirely a quantum statistics effect. There is no classical analog!] Thus for H_2, since the space and spin parts of the electronic wavefunction are symmetric (in the ground state), and since the total nuclear spin may be either $I_{tot} = 0$ or 1, there are two possibilities: Since the individual nuclear spin is 1/2 (protons are fermions), the overall wavefunction must be antisymmetric, and thus

if $I_{tot} = 0$, (nuclear spin wavefunction is antisymmetric) then only states of even j are permitted, [This para-hydrogen is not permitted by Q.M. to exist in odd j rotational states!!]

OR

if $I_{tot} = 1$, (nuclear spin wavefunction is symmetric) then only states of odd j are permitted. [This ortho-hydrogen is not permitted by Q.M. to exist in even j rotational states!!]

The energy difference between ortho- and para-hydrogen is exceedingly small so that the populations will be in the ratio of the spin degeneracy -- ortho ($2I_{tot}+1 = 3$) to para ($2I_{tot}+1 = 1$) is 3.

You should be able to make the argument now for showing that the O_2 molecular rotational states will only be allowed to have odd j. Also you should be able to argue from a little understanding of nuclear physics that if ${}_8O^{16}$ has I = 0 then ${}_7N^{14}$ must have I = 1, (the N nucleus is therefore a boson) hence I_{tot} has the possibilities 0, 1, 2. This should lead to the prediction of alternating intensities in the rotational Raman spectrum. What is the intensity ratio you predict?? Which Raman lines correspond to which rotational states and which values of I_{tot}?

What happens to all of these arguments for the molecule ${}_7N^{14}$-${}_7N^{15}$??

Set-up:

WARNING!!! The laser beam used in this experiment is sufficiently powerful to cause immediate and permanent retinal damage if you look directly into the beam. Use extreme care at all times! Always know where the beam is going when you make adjustments, and ensure that your lab-mates are aware of your actions and are wearing proper laser safety eyewear. Also, be very careful to remove any reflective jewelry (watches, badges, etc.), and to avoid bringing any shiny objects into the beam.

1. Since the entrance slit is vertical, we need to arrange the laser beam to pass vertically at some distance in front of the spectrometer. Assuming the collecting lens has 50 mm focal length and an f/number of 1.7 [f/1.7], we may calculate the optimum position for the laser beam in front of the spectrometer. [The definition of f number is f/# = F/D, where F is the lens focal length and D is the lens diameter. For a spectrometer, the f/# is just the distance from the entrance slit to the first spherical, collimating mirror -- divided by the mirror diameter.] The beam geometry is shown by the sketch in Fig. A1-1 below.

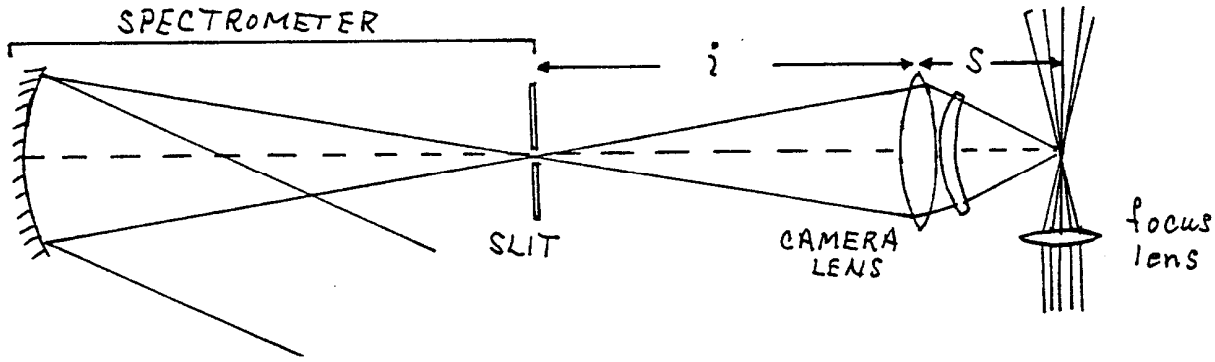

Fig. A1-1. Sketch of f/# matching condition or solid angle matching.

A primer on light gathering power--You should be able to verify that for a spectrometer f/# of 9 and the lens f/# of 1.7, the image to source distance for the collecting lens should be in the ratio of 9/1.7 = 5.3. Hence if our lens has a focal length of F = 50 mm, then the optimum distance (object + image) of the laser beam from the spectrometer slit is ~40 cm. **[Please check this calculation by treating the camera lens as a thin lens and using the 1/s + 1/i = 1/F formula with i = 5.3 s, and F = 5.0 cm.]** Thus it is possible to collect the light over a large solid angle and bring it into the spectrometer with a much smaller solid angle. The ratio of solid angles is $(9/1.7)^2 = 28$. This advantage in light-gathering power comes, of course, at some price! The price you pay is that the image area is magnified by the same ratio. However, if you take care to focus the laser beam very tightly, say to 25 μm in diameter, then it should be possible to get all of the laser beam waist into a spectrometer slit of 150 μm (since the magnification is 5.3) and you lose only in one dimension -- parallel to the slit. One final note--good camera lenses are corrected very well for spherical aberrations and chromatic aberrations for a wide range of conditions. However, designers have assumed that the film plane is always close to the lens and the objects (to be photographed) are a meter or more distant. The lens is obviously not symmetric! Time reversal invariance holds and the light propagation direction doesn't matter, but the geometry does! Always use the lens with the intended film side toward the near focus--i.e., toward the source of the scattering. All of these considerations are important to be able to detect the weak Raman scattered light.

Focussing the laser beam--Achieving as small a beam waist as possible means using a short focal length lens to focus the laser beam (probably a 2.7 cm focal length). Diffraction theory predicts that the beam waist (diameter), w, will be given by

$w = 2.44\ f\lambda/d$, for a circular aperture of diameter, d, uniformly illuminated, or
$w = 1.27\ f\Delta\theta$, for a gaussian beam with angular divergence, $\Delta\theta$.

Carefully position the mirror and the lens to achieve a vertical beam with a beam waist at the height of the slit of the spectrometer.

2. With the beam in air you should be able to see enough Rayleigh scattering to follow its path. Use a piece of paper or metal to intercept the beam at its waist to provide a very bright source for

aligning the collecting lens. This is a standard camera lens (50 mm focal length, f#/1.7). Adjust the lens to bring the image into the entrance slit of the spectrometer. Be sure to "fill" the monochromator optics.

3. You should now be ready to mount the Raman scattering cell into position so that the beam waist passes through the middle of the cell. **Be careful to block the laser beam while you are adjusting the cell into position to avoid any reflections hitting your eyes!!**

4. Before you turn on the PMT, be aware that the strong elastic scattering at the laser line can destroy the PMT photocathode. Therefore you must **never** scan the spectrometer through the laser wavelength without having at least 10^3 - 10^4 attenuation in front of the spectrometer.

5. You should now be ready to turn on the spectrometer, the PMT voltage, and the electronics. The recommended settings for the EMI 9658B tube are: PMT cathode voltage -1200 V (absolute maximum for this tube is -1500 V), coarse gain 16, fine gain ~0.6, threshold 3 V, and time constant 0.5 sec. If the settings are correct, you should see a dark count (in the dark!) of about 10 - 20 counts per second. Slit settings of 100-200 μm are recommended. Start by placing a 10^3 (O.D. = 3) filter in front of the SPEX and scanning through the laser line so that you will know exactly its position. (All frequency shifts are to be measured from this line.) **Consult Appendices II and III for more details!**

Experiments:

A. Fill the gas cell with one atmosphere of O_2 gas. Do not try to pressurize the cell! Just open both valves and allow gas to flow through for 30 seconds or so to flush out the residual air. Acquire a spectrum. You may have to use a very slow scan to achieve good counting statistics since the Raman scattering is very weak. Take a spectrum which covers the anti-Stokes as well as the Stokes scattering region. (Stokes = lower frequency or longer wavelength region.) You should be able to acquire both anti-Stokes and Stokes lines on one continuous scan. Just block the input to the SPEX as it passes through the laser line. Your final data should be analyzed in terms of frequency shift, not wavelength shift. (The traditional spectroscopy unit is $\nu = \nu/c(\text{cm/sec}) = 1/\lambda(\text{cm})$ and is called "wavenumbers" with the units of cm^{-1}.)

B. Refill the gas cell with pure N_2 and redo the experiment.

Choose one of the next two:

C. Refill the cell with CO_2 and repeat. Note, because the rotational inertia of the O-C-O molecule is much larger than for O-O, the rotational Raman lines are much closer spaced. This will require the use of very small slits; perhaps ~30 μm.

OR:

D. Refill the cell with H_2 and repeat. Here it is necessary to calculate the expected rotational shifts first so that you will know where to look! I suggest that, rather than making a long scan with mostly emptiness, just do several short scans over the regions where the Raman lines are expected.

Analysis and Write-up:

I. For the O_2 gas studies, plot your data as a function of intensity vs. wavenumber shift (cm^{-1}). Analyze the frequency shifts to obtain the rotational inertia and the internuclear separation of the molecule. Include a detailed explanation of your analysis, including error analysis. Express the values of the rotational inertia and internuclear separation in SI units (kg-m^2, and m). What is the value of the constant B described and defined in Appendix XXV (in units of cm^{-1}). Annotate your graph to include information on the locations of Stokes, Rayleigh, and anti-Stokes lines.

II. Analyze the intensities of the O_2 lines to obtain an estimate of the gas temperature. Start by generating the ratios of n_j/n_0. Show that the population of rotational levels first increases with j, and then decreases as j continues to increase. (Because the data are weak and possibly noisy, this estimate may be poor. However, by estimating the errors in this measurement, you should be able to show that the intensities are consistent with T = 300K.) As queried above, answer the question as to why the Stokes intensity for a given Raman shift (say the fourth line from the origin) is larger than the anti-Stokes intensity.

III. Calculate the estimated flux of laser photons (at 514.5 nm, the green line) in terms of photons per second, per mW of incident green beam power. For the strongest O_2 rotational Raman line you measured, what is the approximate fraction of Raman photons detected per incident laser photon? List as many sources of inefficiency as you can, giving them order-of-magnitude estimated values.

IV. Write a short analysis of the Raman spectrum describing either:

a) why every second line is missing in the O_2 spectrum, or

b) why the adjacent lines alternate in intensity in the N_2 spectrum.