CH Flame Spectroscopy

Advised Prerequisite:
Though not required, this lab is much easier if students have already completed the "HD Isotope Shift" lab. This will provide the necessary background required to operate the spectrometer effectively. It would also be beneficial if students print out directions from this previous lab in order to operate the machine. Questions about the spectrometer and its operation should be directed to the TA.

Purpose:
To record and analyze the $^2\Sigma \rightarrow {}^2\Pi$ vibrational-rotational band of the CH molecule.

I. Introduction:
When a hydrocarbon such as butane, propane or methane is burned in air, excited CH molecules are formed in the blue inner core of the flame. CH is a simple heteronuclear diatomic molecule whose spectrum in the region 3000-5000 Å is especially interesting. The transitions from the first two excited states $^2\Delta$ and $^2\Sigma^-$ to the $^2\Pi$ ground state are easily seen and studied. (See Herzberg for an explanation of molecular state nomenclature.) Both vibrational and rotational fine structure can be seen in the $A^2\Delta \rightarrow X^2\Delta$ and $X^2\Pi^- \rightarrow B^2\Sigma$ transitions and analyzed to identify the R, P, and Q branches and determine the corresponding rotational constants ($B_v' \; B_v''$) and the rotational temperature for the flame. The CH spectrum displays the two interesting effects of "lambda type doubling" and "spin splitting". Lambda type doubling is produced by the interaction of the rotation of the nuclei and the electronic orbital angular momentum and results in a doublet splitting of all levels whose component of orbital angular momentum along the internuclear axis is nonzero, *i.e.*, $\Lambda \neq 0$ states. The splitting increases with the rotational quantum number J. Spin splitting arises in some molecules (CH included) when the nuclear rotation is large enough to uncouple the resultant spin $\vec{s}$ from the orbital angular momentum $\vec{\Lambda}$. When this occurs (at large rotations), the net spin $\vec{s}$ couples with the same of the orbital, $\vec{\Lambda}$, and rotational, $\vec{N}$, angular momenta to form a total angular momentum $\vec{j}$. The net results for a $^2\Pi$ state is a doublet splitting of the rotational lines.

II. Equipment:

A. The Spectrometer
Refer to the lab "HD Isotope Shift" for details. Information about the spectrometer, gratings, and detectors is available there. Figure 1 shows a diagram of the spectrometer we are using with all the parts labeled.

Do <u>not</u> take the cover off the spectrometer to look inside. Also remember that the counter displays only the approximate wavelength of the light entering the PMT.

B. The PMT, Picoammeter, Spectra Recorder, etc.
The power supply to the PMT should be left on at all times to make sure that it is always warmed up. Again, the operation of these pieces of equipment are explained in the "HD Isotope Shift" lab. Further questions should be directed to the TA.

C. The Butane Flame
See your TA for a demonstration <u>before</u> attempting to light this yourself!
    (a) Open the valve on the methane tank.
    (b) Open the appropriate valve on your burner and light the methane gas. This should be a yellow flame. Adjust flame till you see that color flame.
    (c) Open the valve on the oxygen tank.
    (d) Slowly open the valve on the burner. This will add the oxygen to the already burning methane flame. Adjust the input of both gases such that the flame isn't jumping too high.
    (e) Slowly adjust the oxygen burner valve until the flame makes a noticeable noise.
    (f) Keep opening the valve of the oxygen until you see a small blue flame forming. This blue flame is what you will be analyzing.
    (g) When you are finished with the flame close off the oxygen valve on the burner first, then close off the methane valve on the burner. After, close both valves on the tanks.

Remember: <u>THE FLAME IS HOT!</u> Please be careful when working around or adjusting the burner.

III. Experimental Procedure:

1. Set the size of the slit that the light is incident on. 30μm is the recommended setting out of the four possible. The PMT slit should be set to the same size. The mirrors are already set in place and should not be moved.

2. You will be using the 3131 Å Hg doublet to calibrate the spectrometer. This calibration is exactly the same as you would have done in the "HD Isotope Shift" lab. Do not reuse your previous calibration spectra and data!!

Remember, that you will be using the second order lines. In other words, look for the doublet at 6262 Å. The resolution will be better but there will be some loss of intensity.

3. Measure the Hg spectrum over the range 3600 to 4200 Å. You may want to use a sweep rate of 20 Å/min. Compare your lines with the attached list of the Hg emission lines. This spectrum will provide your calibration (Å/box on the chart).

4. Focus the edge of the image of the cone in the butane flame on the, and parallel to, the spectrometer slit using the concave mirror. Find the C-H lines near 3900 Å and maximize the intensity by moving the flame.

5. Superimpose the Hg light onto the butane flame image at the spectrometer slit.

6. Measure the emission spectrum in the region from 3600 to 4200 Å in the second order. The $^2\Sigma^- \to {}^2\Pi(0,0)$ band of the C-H extending from 3700 Å to about 4075 Å is shown in the attached spectrum.

7. Though it should be fairly easy to get a good spectrum, the analysis is difficult. The theory presented in Herzberg is really needed. Chapter II of Herzberg introduces the nomenclature, the basic systematics of molecular spectra, and the Fortrat parabola. Chapter IV discusses vibrational-rotational spectra and analysis of the R,P, and Q branches. Chapter V covers the remaining theory needed for the analysis of the C-H spectrum. The theory for determining the rotational temperature is given below.

IV. Rotational Temperature Determination:

A diatomic molecule acts like a rigid rotator of moment of inertia, I, about an axis perpendicular to the molecular axis. In a flame, the molecules will be distributed among the rotational states according to the Boltzmann distribution. The intensities of the rotational lines corresponding to a given vibrational transition are thus determined by the temperature of the flame. The "rotational temperature" of the flame is the value of T obtained by analyzing this intensity distribution assuming the flame is in thermodynamic equilibrium. (It isn't but the results still serve as a good characterization of the flame). Somewhat different values of the "effective temperature" would be obtained by other measuring techniques.

The rotational energy levels of a rotator are given by $E = (\hbar^2 / 2I) J(J+1)$ where J is the rotational quantum number. Thus for a transition between levels E′ and E′′ the wave number of the line is given by :

$$hc\,\bar{\nu} = E' - E''$$

(The double prime refers to the lower state). It is customary in molecular spectroscopy to define the rotational constant :

$$B_\nu = E / hc$$

Therefore, $B_\nu = \dfrac{h}{8\pi^2 cI}$ and $\nu = B'J'(J'+1) - B''J''(J''+1)$

Since the intensity of a given rotational line is proportional to the population of the excited state and the population of the excited state E′ is :

$$n(E') = (2J'+1)\exp\left[-B'_\nu hcJ'(J'+1)/kT\right]$$

we find (Herzberg, pg. 203) :

$$I_{cm} = c(2J'+1)\exp\left[-B'_\nu hcJ'(J'+1)/kT\right]$$

and

$$\log\left(\frac{I_{cm}}{2J'+1}\right) = A - \frac{B'_\nu hcJ'(J'+1)}{kT}$$

By measuring the intensities of several rotational lines of known J′ and B_ν′ (as determined in the spectral analysis) and plotting $I_{cm}/(2J'+1)$ vs. J′ (J′+1) on semi-log paper a value for the rotational temperature may be found.

V. Calculations:

- o The Herzberg book and papers should <u>NOT</u> be removed from the main lab at any time! Doing so can result in a lower lab grade.
- o The additional document posted with this lab is also extremely useful in doing the below calculations.

1. Analyze the 3900 Å, $^2\Sigma^- \to {}^2\Pi$, band of CH as discussed in Herzberg, pages 3, 42-50, 113-171, 177, 203-205. For accurate results you need to convert to vacuum wave numbers using the index of refraction of air. Construct a Fortrat parabola from your data and identify the R, P, and Q branches. Check your results in: H.P. Broida, *Spectrophotometric Atlas of the Spectrum of CH from 3000 – 5000* Å, published by USDC-NBS.

2. Determine the molecular constants (B_v' B_v'') from your data (compare to those in Herzberg). Determine the internuclear spacing, (γ_e). See Herzberg 177-183.

3. Find evidence for spin splitting and Λ-doubling in your data. Discuss these effects.

4. Determine the rotational temperature for CH in your flame.

Include the following in your lab book:

- All questions from the 'Calculations' section
- Calibration Calculations
- Print Out of your Calibration Spectrum and Flame Spectrum
- Procedure and Conclusion

References :

1. Gaydon, A.G., *The Spectroscopy of Flames*, **QC 454 GE**.

2. Mavrodineau and Boiteaux, *Flame Spectroscopy*, **QD 95 M36** (6th floor)
   - more information, theory, and references

3. Herzberg, G., *Spectra of Diatomic Molecules*, **QC 451 H4**, Vol. 1
   - this is the bible for theory; CH constants are given

4. Broida, H.P., *Rotational and Vibrational Temperature of CH Flames at Atmospheric Pressure*, J. Chem. Phys. **21**, 340 (1953).

5. *Elements of Diatomic Molecular Spectra*, H. Brian Dunford, (Addison-Wesley), 1968.
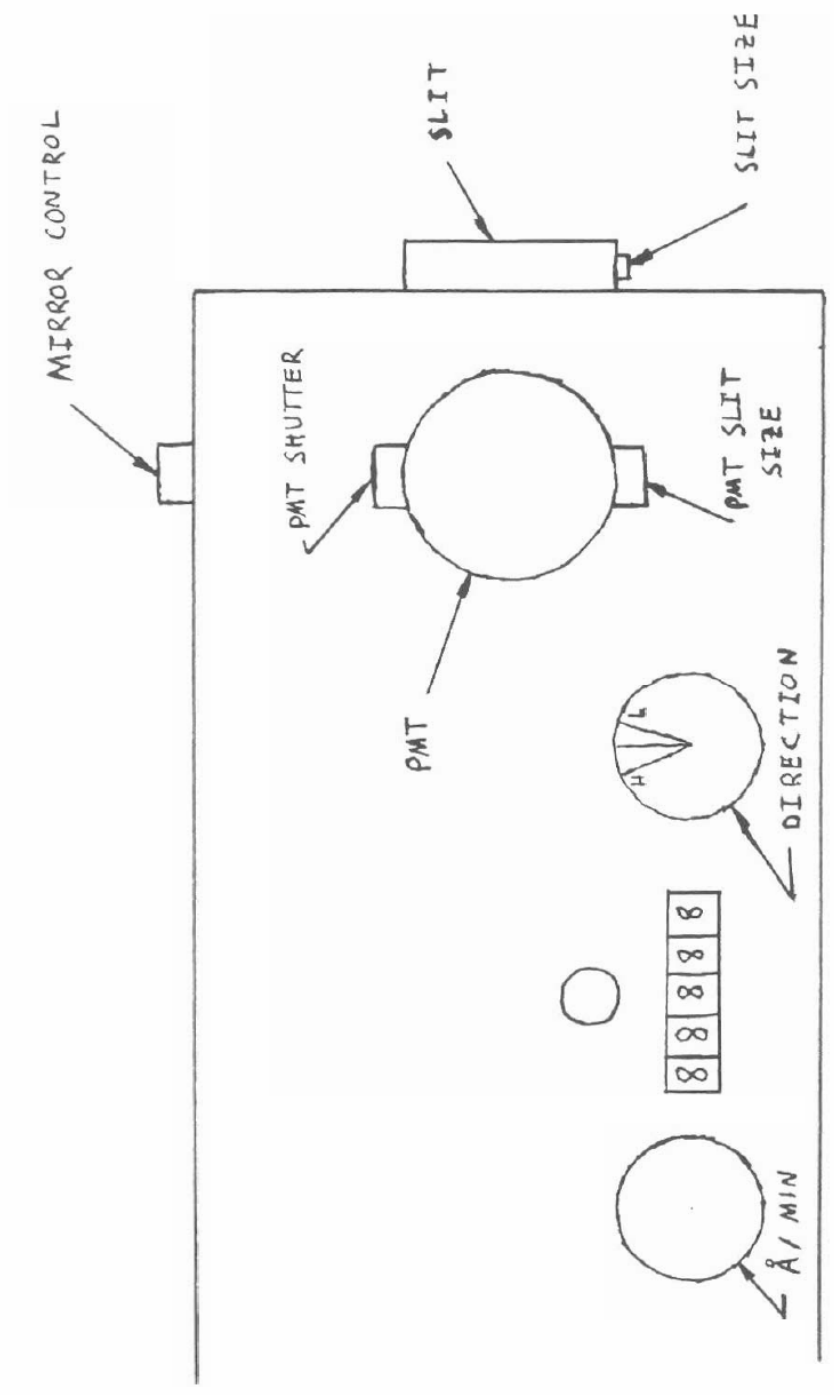
FIGURE 1 THE SPECTROMETER

University of California, Santa Barbara
Senior Lab Physics Department

The $^2\Sigma^- \to ^2\Pi$ (0,0) spectrum of CH
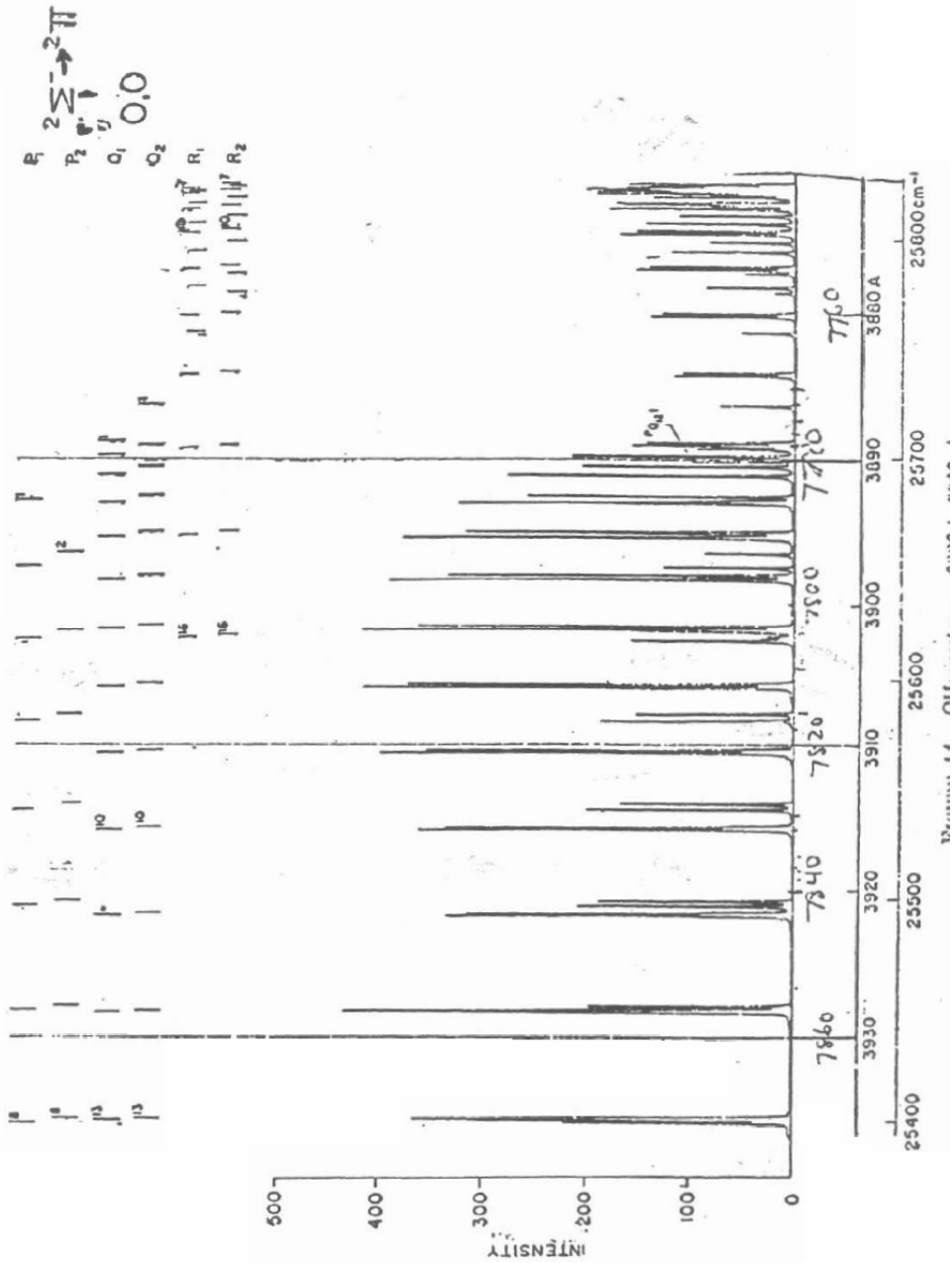
Table 1: List of Hg Lines Suitable for Use in Adjusting the Spectrometer

1st Order	2nd Order	3rd Order
1849.52	3699.04	-
2536.52	5973.04	7609.56
3125.67*	6251.34*	9377.01*
3131.55*	6263.10*	9394.65*
3131.84*	6263.68*	9395.52*
3650.15†	7300.30	-
4046.56	8093.12	-
4077.83	8155.66	-
4358.32	8716.64	-
5460.73	-	-
5769.60	-	-
5790.66	-	-

* The spacing of these lines should be used to determine which one is being used

† This line has three near neighbors, 3654.3 (weak), 3662.9 (medium), and 3663.2 (strong) which can be used to aid in identification