Molecular Spectroscopy

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The purpose of this experiment is to measure and interpret the optical spectra of several diatomic molecules.

PREPARATORY QUESTIONS

1. Write the expression for the rotational energies of a rigid rotator with a moment of inertia I. Now consider transitions between two electronic states with different moments of inertia, I_1 and I_2 in which the vibrational quantum number does not change. Write an expression for the differences between the wave number of the absorption line corresponding to the $j = 0 \rightarrow 0$ transition and the various transitions corresponding to $\Delta j = 0, \pm 1$ that give rise to the fine structure of one of the spectrum bands. Estimate the difference in wave number between adjacent lines in the rotational fine structure of a typical diatomic molecule in which the two moments of inertia differ by 10%.

2. Write the expression for the vibrational energies of a diatomic molecule with two atoms of equal mass m in an electronic state in which the potential energy is $kr^2/2$. Now consider transitions between two electronic states with $j = 0$ and with different values of the "spring constant", k_1 and k_2. Write an expression for the difference between the wave number of the emission line corresponding to $v = 0 \rightarrow 0$ and the various allowed vibrational transitions.

3. Sketch the expected appearance of a typical band in the spectrum of CN, and estimate the spectral resolution $(\lambda/\Delta\lambda)$ that is required to resolve the rotational fine structure.

4. Suppose the echelle spectrometer is operated with an entrance slit width of 10μ and with the input optics arranged so that the collimated beam illuminates the grating to a width of 4 cm. What is the theoretical maximum possible resolution expressed as $\lambda/\Delta\lambda$? (Assume the collimator/camera mirror is a spherical mirror with a focal length of 3 m).

CAUTION: Parts of this experiment require the use of a carbon arc which is an intense source of ultraviolet light that can cause permanent eye damage. Wear the protective goggles provided, and never view the arc directly with naked eyes.

I. INTRODUCTION

Compared to the simplicity of the spectrum of atomic hydrogen or even a higher-Z atom the optical spectrum of the simplest diatomic molecule, H_2^+, is dauntingly complex. Like the spectra of other diatomic molecules, it is composed of "bands" which appear continuous at low resolution, but which are resolved at high resolution into many closely spaced narrow lines. Their structure reflects the dynamical properties of a system consisting of two nuclei and two electrons interacting by electromagnetic force with sixteen degrees of freedom - four particles each with three spatial plus one spin degrees of freedom. Such a system has many quantum states with different discrete energies, so it is no wonder that the spectrum of lines generated by transitions among these states is complex.

The key to understanding the spectrum of a diatomic molecule is the fact that its quantized energy levels are organized in a hierarchy corresponding to three kinds of motion of the particles of which it is composed. These motions, in order of decreasing magnitude of the energies of their quantum states, are: rapid motion of the electrons in the electric field of the nuclei and electrons, much slower "vibrational" motion of the nuclei with respect to one another, and rotation of the system as a whole. In an approximation, based in quantum theory on the "Born-Oppenheimer Principle", the energy of the molecule can be expressed as a sum of a term representing the energy of the electrons moving in the electrical field of two relatively slowly moving nuclei and the electrons themselves, a harmonic oscillator term representing the energy of the vibrational motion of the nuclei in the potential well that results from the balance of attractive and repulsive electrical interactions of the nuclei and electrons and the centrifugal force of the molecular rotation, and a term representing the rotational kinetic energy of the molecule as a whole.

Spectrum lines produced in transitions in which only the rotational motion of a molecule changes lie in the far infrared. According to the quantum theory of angular momentum, the rotational energy of a rigid body with moment of inertia I is $(h^2/8\pi^2 I)K(K+1)$ where K=0, 1, 2, ... Transitions are restricted by the dipole selection rule ΔK=±1. Thus the energies of the emitted (or absorbed) photons are proportional to 2(K+1) and are, in this approximation, evenly spaced. Actually, centrifugal force increases the internuclear separation as the rotational energy increases, thereby causing the moment of inertia to increase and the spacing to decrease.

Transitions between vibrational states without a change in the electronic state produce lines in the near infrared. Simultaneous changes of the rotational state can alter the vibration transition energy by small discrete amounts. Thus the pure vibration-rotation spectrum of a diatomic molecule consists of clusters of evenly spaced lines, each cluster corresponding to a particular pair of initial and final vibrational states, and each line within a cluster corresponding to a particular pair of initial and final rotational states.

Transitions between a particular pair of initial and final electronic states produce lines in a "band system" that may lie in the visible range of the spectrum. Each band within a band system corresponds to transitions between a particular pair of initial and final vibration states. Each line within a given band arises from transitions between a particular pair of rotational states.

The goals of this experiment are to measure the band spectra of CN, N_2, and I_2, and to interpret prominent features in terms of the quantum mechanics of diatomic molecules.

II. THEORY

In the Born-Oppenheimer approximation the wave function of a diatomic molecule is written as a product of three functions - an electronic wave function which represents the rapid motion of the electrons in the potential of the two nuclei with slowly changing internuclear separation, a vibrational wave function that represents the much slower periodic change in the internuclear separation, and a rotational wave function that represents the rotation of the molecule in the plane perpendicular to the internuclear axis. As the internuclear distances changes in the course of vibration, the electronic wave function changes adiabatically to adjust to the periodically changing potential.

The electronic state of a molecule is designated by a combination of symbols that specify its electronic orbital and spin angular momenta, its electronic configuration, its symmetry, and its parity.

Since the potential in which the electrons move has cylindrical symmetry about the internuclear axis (z axis), only the z components of the electronic orbital and spin angular momenta, $L_z = M_L(h/2\pi)$ and $S_z = M_s(h/2\pi)$ are constants of the motion. Electrical interaction separates the energies of states with the same principal quantum number but different M_L. Reversing the direction of motion of the electrons changes the sign of M_L but not the energy, so states with $\Lambda = \pm M_L$ are degenerate. Electronic wave functions can therefore generally be classified according to the value of $\Lambda = |M_L|$. States with $|M_L| = 0$, 1, 2, 3, ... are designated Z, Π, Δ, Φ, ... Spin-orbit interaction is magnetic and relatively much weaker. A state with total spin S and a given $\Lambda > 0$ splits into $2S+1$ different states labeled by $\Sigma = S_z = S, S-1, \ldots -S$.

Introductions to the theory of molecular spectra can be found in numerous texts. The bible of this field is Herzberg (1950 or 1989) which is on reserve in the science library. An excellent introduction is that of Leighton (1959).

III. INSTRUCTIONS

Instructions for this experiment are sparse. Use your own judgment about how to proceed. Ask for help if you get stuck.

There are two spectrometers available, a Bausch and Lomb reflection grating spectrograph, and a scanning echelle spectrophotometer. The B&L can provide a photographic record of a spectrum from 7000 to 4000 Å in first order and 4000 to 2500 Å in second order with a resolution of about 6000. The echelle provides a chart record of spectra from 6000 to about 3500 Å.

Here are a few experimental/theoretical goals toward which you may wish to aim:

1. Study the spectrum emitted by nitrogen discharge tube with both spectrometers. The orange-red light in the capillary portion of the discharge tube is due mostly to the so-called first and second positive systems of N_2^{14}, and the bluish light emanating from the region around the electrodes is dominated by the first negative system of N_2^{14+}. Specially interesting is the triplet grouping of the rotational lines in the 1/5 band of the second positive system ($C^3\Pi_u$-$B^3\Pi_g$) of N_2^{14} blueward from the band head at λ4270 Å, and the alternating intensities of the first negative system ($B^2\Sigma_u^+$ - $X^2\Sigma_g^+$) of N_2^{14+} which can be clearly seen in the blueish light from the electrodes in the 0/1 band that stretches blueward from λ4278 Å. Construct Fortrat parabolas. Identify the P and R branches and the location of the missing 0-0 transitions. Interpret the alternating intensity ratio in terms of the spin of the nitrogen nucleus.

2. Study the absorption spectrum of I_2 in the range from λ5500 to 5000 Å. A halogen lamp and an iodine absorption cell are available for this measurement. Photograph the broad band structure with the reflection grating spectrograph. From an analysis of the wave number dependence of the band heads estimate the dissociation energy of the molecule. Examine the details of the rotational structure of the bands with the scanning echelle spectrophotometer. Construct the Fortrat plot of one of the bands.

3. Study the broad UV band spectra of CN and the rotational fine structure of the 3883Å band of the CN emission spectrum. A carbon arc is available for generating the UV band spectra of CN. (Take care about protecting your eyes from the UV emission of the arc.)

IV. SUGGESTIONS

The mercury discharge tube provides a convenient calibration spectrum from UV to the yellow doublet. By manipulation of the slit control and decker on the B&L spectrograph you can superpose identifiable Hg calibration lines on your molecular spectra. In calibrating the echelle spectrometer you can determine which of the mercury lines is to be identified with a dial reading of a very bright line in the echelle spectrometer by viewing the return beam from the echelle grating with a hand-held mirror. With sufficient gain (HV<1000 v) you can detect and identify many faint lines of mercury *and argon* in the light of the mercury discharge tube.

35 mm UV-sensitive film is available for recording the UV band spectra of CN in second order of the reflection grating without interference from the visible portion of the spectrum.

V. THE SPECTROMETERS

V.1. THE REFLECTION GRATING SPECTROGRAPH

The grating spectrograph is illustrated in Figure 1. It has a slit assembly, a cylindrical correcting lens, a concave reflection grating with grooves blazed at 7° and a radius of curvature of about 1.5m, and a film holder. The spectrograph, a research instrument manufactured by Bausch and Lomb, Inc. was previously used in the MIT Spectroscopy Laboratory. It has been carefully aligned and focused so there is no need for you to make any adjustments except of the slit configuration. You can examine the interior of the instrument by sliding the light-tight lid back, but **please take care not to disturb any of the components inside the box.**

INSERT DIAGRAM OF JOBIN-YVON MONOCHROMATOR FROM HYDROGENIC LABGUIDE

Select the 60μ slit (the number should appear in the small circular hole) and adjust the vertical aperture slide control to full width. Mount the mercury discharge calibration lamp in a test tube holder on a ring stand and place it close to the slit so that the light admitted by the slit fully illuminates the grating. To check this condition remove the film carriage and search with your eye along the film plane for the green line of the mercury spectrum; look through the plate holder at the reflection grating with your eye about 30 cm from the film plane. Adjust the position of the lamp so that the image of the green line **seen against the background of the reflection grating** does not vary in brightness as you move your eye both horizontally and vertically. Narrow the slit to 10μ.

V.1.1. MERCURY CALIBRATION SPECTRUM

Make calibration exposures of the mercury spectrum, with and without the UV filter. Move the 10μ slit into position. Practice the operation of the slit length control and the shutter (the round disc that can be moved in front of the slit by its lever arm). Plan a sequence of manipulations that will give you three different exposures, say 10, 100, and 1000 seconds. In the darkroom, practice loading strips of exposed 35 mm film into the film holder and then inserting the dark slide, first in the light with your eyes open, then with your eyes closed, and then in the total darkness of the darkroom. Practice mounting the film holder on the spectrograph and withdrawing the dark slide **without pulling the film with it**. Again in the darkroom practice removing the film, attaching clips top and bottom, and "developing", first with the lights on, and then in total darkness. When you think you can do it with a reasonable chance of not wasting film, load the holder with fresh film (Kodak 5053 TMY) and take your series of exposures of the mercury spectrum. Develop the film according to the instructions posted on the darkroom wall. After thorough washing (30 minutes), squeegee the film and dry it completely.

The film of a long exposure (> 5 minutes) will probably show a profusion of lines - many more than the prominent yellow, green, blue and purple lines of the famous mercury spectrum. Many of the lines are, in fact, ultraviolet lines in the second-order spectrum, superimposed on the visible lines of the first-order spectrum, and all tabulated in the CRC Handbook. You may also find the lines of argon.

You can measure the spectra with high precision on the scanning microdensitometer in the next room. That device has two microscopes. The one in back is used in reverse as a projector to focus a demagnified fiducial image of the lamp filament onto the film mounted on the carriage which is moved by a motor-driven precision screw. The microscope in front is used in the normal way to focus a magnified image of the filament image onto an aperture slit in a metal slide just in front of a photocell housed in the cylindrical box on which a BNC connector is mounted. (Note that there is a large "field" lamp and a small fiducial lamp – use the small lamp for your measurements). The intensity of light passing through the film at the fiducial image and through the slide in front of the photocell is measured by the photocell and associated op amps inside the densitometer and registered directly on a chart recorder. As the carriage moves along, the chart shows a tracing of the film density as a function of position.

The quality of the densitometer record depends critically on proper adjustment of all the components of the system. First of all, inspect the fiducial image of the small lamp on the film with a magnifier and adjust the lamp housing (rotate) and projector microscope to achieve a sharply focused image on the film and parallel to the spectrum lines. Next, move the film to a clear spot, and adjust the second microscope and aperture slit position, alternately, to maximize the photocell signal (the final image of the filament must be focused precisely on the aperture slit in the metal slide). Test the setup by scanning over a narrow spectrum line and verifying that the signal shows an appropriately narrow minimum. In proper adjustment the densitometer should yield density peaks with a width of 1 Å or less when scanned over a well-focused and properly-exposed spectral line on a film from the spectrograph.

Read your mercury spectrum at a carriage speed and chart speed that yields a total scan of about 100 cm on the chart.

Please exercise care in changing the gears on the microdensitometer carriage drive. Never change gears while in motion. Rock the hand crank gently as you joggle the gears into the desired position.

V.1.2. ANALYSIS

Identify the lines by means of a bootstrap operation in which you first latch onto several of the most prominent lines, establish a tentative wavelength-position relation, and then see if the other fainter lines fall in place. The yellow doublet (5769.60 Å and 5789.66 Å) the green line (5460.74 Å) and the purple line (4358.33 Å) with two fainter nearby lines are specially useful landmarks in the mercury spectrum. It will help to make a plot of wavelength versus position. Look out for second order UV lines superposed on the first order visible spectrum (a 2500 Å line in second order is in exactly the same position as a 5000 Å line in first order). When you get it right, all the points should fall very close to a nearly straight line.

There is a program called ”spectrum.line.fitter Apl” available on the Junior Lab Macintosh computers with which you can fit a polynomial to a data set in a specified EDIT file in which wavelengths and positions and spectral order are listed in a three-column format, e.g.

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5460.74 23.85 1
2967.28 31.85 2
...     ...   .
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Turn on the Mac, insert the disk labeled “SPECTRUM ANALYSIS”, open “EDIT”, prepare your data file and save it with an identifying name, e.g. “hg3.smith.20oct90”, double click on the “spectrum.line.fitter Apl” icon, and follow the menu-driven instructions. Note that once you have made a tentative polynomial fit, you can use the fitted formula to find the expected position of a line of specified wavelength, or the wavelength of a line at a specified position. This makes identification of the fainter lines easy, once you have established an accurate overall calibration.

V.2. ECHELLE SPECTROPHOTOMETER

The echelle spectrophotometer is illustrated in Figure 2. The echelle grating itself is like a microscopic staircase, with the risers acting as mirrors, and the treads as spacers that keep the separations between adjacent mirrors precisely constant and equal. The unique feature of an echelle grating is that it is “blazed” for use at a very large angle of incidence (measured from the normal to the grating). As a result it provides a very high spectral dispersion, as explained in Appendix A. The manufacture of such gratings requires extremely high precision in the spacing of the grooves and became practical only with the development of interferometric servo-controlled ruling engines by Professor George Harrison at MIT in the 1940’s. Once a master grating is ruled it can serve as a mold for the production of replicas such as the one in the Junior Lab echelle scanning spectrophotometer which is available commercially for a price of about $3,000.

INSERT DIAGRAM OF JOBIN-YVON MONOCHROMATOR FROM HYDROGENIC LABGUIDE

The spectrophotometer has been painstakingly aligned. Please do not alter the arrangement of the optical components between the entrance and exit slits. You may adjust the other parts of the equipment, i.e. all the parts outside the wood cabinet. If you suspect misalignment of the internal parts of the spectrophotometer, ask for help. If you need to change the spacer bar on the grating control to shift the wavelength range, please ask for assistance.

Your first task is to prepare a calibration chart on mm graph paper of dial reading against wavelength to guide your subsequent work and reduce confusion as to where you are in the spectral range. The mercury spectrum you obtained with the Bausch and Lomb grating spectrograph and the CRC table of mercury wavelengths should be used to aid in your identification of the lines detected by the echelle spectrophotometer.

DO NOT MAKE CHART RECORDS OF WIDE RANGES OF THE SPECTRUM - CHART PAPER IS EXPENSIVE. ALL THE CALIBRATION DATA SHOULD BE RECORDED BY HAND. USE THE OSCILLOSCOPE AS YOUR DETECTOR. TABULATE THE DIAL READING OF EACH LINE TOGETHER WITH A COMMENT AS TO HOW STRONG IT IS. USE THE CHART RECORDER ONLY FOR THE SHORT RANGE SCANS (<2 FEET OF CHART) YOU NEED TO MEASURE: THE ISOTOPE SHIFT OF THE BALMER LINES OR ANY OTHER NARROW-RANGE FEATURES OF SPECIAL INTEREST.

Mount the mercury tube at a position such that the image cast by the field lens falls on the entrance slit of the spectrograph. Then, with the slit wide open (don’t force the micrometer control) and with a mirror held in the path between the entrance slit and the collimator mirror at the other end of the box, check that the light from the slit is illuminating the entire mirror. When this condition is achieved, dispersed images of the slit (i.e. the spectral lines) should be formed in the plane of the exit slit. As the echelle grating is rotated, the slit images will pass over the slit, causing the photomultiplier to register the presence of "spectral lines" at various angular orientations of the grating as indicated on the grating control dial.

While scanning back and forth over a very bright line, narrow the slit to about 0.1 on the micrometer control. Adjust the photomultiplier voltage (<1200 v), amplifier gain, and band pass controls to optimize the performance of the spectrometer. Turn the dial slowly by hand through its range, noting the readings and the relative peak intensities of the various lines. Since the dial reading-wavelength relation is nearly linear you should be able easily to match the pattern of the most prominent lines against that of the broad band spectrum you previously measured. The "spectrum.line.fitter apl" program on a Junior Lab Mac can assist you in the data reduction.

[1] R. Leighton, *Principles of Modern Physics*, McGraw-Hill, 1959.

[2] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. I - Spectra of DIatomic Molecules*, Krieger, 1989 (or Van Nostrand, 1950).

[3] F. K. Richtmeyer, E. H. Kennard, and C. Lauritson, *Introduction to Modern Physics*, McGraw-Hill.

[4] W. S. Struve, *Fundamentals of Molecular Spectroscopy*, Wiley, 1989.

[5] A. Lofthus, "The Molecular Spectrum of Nitrogen", *Spectroscopic Report #2*, Dept. of Physics, U. Oslo, Blindern, Norway (1960). (Xerox copy in the Junior Lab library)

VI. SUGGESTED THEORETICAL TOPICS

1. The Born-Oppenheimer Approximation.
2. Quantization of the harmonic oscillator.
3. Quantization of the rigid rotator.
4. THe effect of centrifugal distortion on the rotational fine structure.
5. The Franck-Condon principle.
6. Interpretation of the Fortrat parabolas.