Experiment 8-9

Rotational Structure of a Band in a Molecular Spectrum

In the 2nd order of the Rowland Grating spectrograph (slit set at 20') photograph (exposure about 1 1/2 to 2 hours) some of the CO bands with the plate are centered near A4850A (2nd order). The plate will cover roughly from A5300A to A4300A. Put in an iron comparison spectrum using a diffi.1ser screen before the slit (30-40 sec.) It may be of some aid in identification to include, superposed on the comparison, a 15 minute direct exposure to mercury. Use type II-G plates.

Measure one of the bands obtained and analyze it into its three branches and make a Fortrat diagram for the band. Determine moments of inertia for the molecular vibrational states and the iteratomic distances.

References:

1. Thompson, *Chemical Spectroscopy,* Chapters 4 and 5. 2. Johnson, *Molecular Spectra,* pp. 1-21.
3. Jevons, *Band Spectra of Diatomic Molecules.*
4. Herzberg, *Molecular Structure- Diatomic Molecules.*

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Notes on Experiment S-8 &

S-9

These two experiments are so similar they may be explained in some detail together. They use the same apparatus and really only differ in operation and vibration analysis; in 8-9, a single band of CO is obtained and the rotational analysis is carried out. Both spectra are obtained in the photography using an old, antiquated Rowland mounting of a concave grating; the N2 spectrum is taken in first order and the CO, in second order. Determining the wavelength is accomplished by comparison with the spectrum of an iron arc, a usual standard.

The source in each case is a capillary discharge tube run at a mid-sized pressure, energized by a 2 or 3 k V sign lighting transformer. The tube is evacuated by a small fore pump and proper pressure is obtained by adjusting a leak into the tube. For 8-8, (the N2 experiment) one simply leaks air into the tube at a rate controlled by the adjustment of a pinch clamp on the rubber hose. The leak rate should be adjusted until the maximum pinkish brilliance is obtained. Even at maximum brilliance, it will still not be too bright. Careful positioning of the source on the axis of the imaging lens and the axis ofsplit- grating of the spectrograph is required. The back of the discharge capillary is covered with an aluminum foil to increase the forward light intensity to slightly reduce the exposure time needed in the photography. For S-9 (the CO spectrum) the only source difference is the gas leaked in and the in the leak arrangement. The gas initially leaked in is CO2 while CO appears in the photographed spectrum. CO2 is obtained by slowly pumping on dry ice contained in the small thermos flasks. Avoid pulling air into the discharge. The evolution of CO2 by sublimation is greater than the rate at which it is pumped off into the discharge tube; the excess escaping into the atmosphere. To ensure that the excess is dissipated into the atmosphere, bubble it through water by adjusting the pump rate with the pinch clamp on a rubber hose or a series, partially opened stopcock. Adjust for maximum brightness in the discharge -this time, a pearly white discharge. Again, the brightness is not brilliant and requires a long exposure.

Proper illumination of the slit is important. An image of the source is located on the slit, with a lens exterior to the spectrograph room. The lens has a larger aperture than necessary .It is not an achromat, so the image in all wavelengths is not of constant intensity .This is of no great consequence in these experiments, but should be accounted for when seeking accurate photometry of the spectrum. The important thing, however, is that the lenses more or less coincide with the spectrograph slit-grating axis. It's acceptable to have the source image on the slit, but, if the light is coming through the lens off to one side, it may never reach the grating. Alignment of the lens and spectrograph mayor may not be okay. It is possible with the weak illumination from the source and a properly narrow slit to see the illumination on the grating by placing the eye behind a spectral band and close to the spectrograph image plane. Getting accustomed to the dark and finding a spectrum band will take some effort. It may help to widen the slit for
viewing. If you are not having any success, (do not attempt this unless you really must), remove the imaging lens and position the iron arc and fire it, imply looking for the patch of bright light coming through the wide slit. Move the arc about until the patch is centered on the grating, attach the lens and adjust it until the arc image is on the slit. The lens and the spectrograph will be in the right juxtaposition, leaving only the adjustment of the various sources so that their image also appears on the slit.

Whether or not it's advantageous~ the glass lens does not transmit ultraviolet light. (Light almost to 3,000 A comes through the pyrex third order lines -3,000 A appears at the second order 4500 A) The iron spectrum will be predominantly visible ligh4 no UV lines will mix in as second order lines along with the visible wavelength, as is the situation in the iron comparison spectrum charts used to identify iron lines.

Slit adjustment makes considerable difference in the sharpness of the photographed lines. The slit should be parallel to the grating rulings. A point source at the slit gives a lii1e image because of the astigmatism inherent in the off-axis illumination of the spherical mirror on which the grating is ruled. Every point in the slit should make its line image overlap exactly with every other line image from other points in the slit. This will only occur if the slits are parallel to the grating rulings. If it is not the case, the slit image is widened and the ends of the line will appear "chisel" profile. The actual slit width is also important. The spectral lines should be lines rather than the rectangles characteristic of wide slit widths. The slit image will become more linear as the slit width becomes narrower without affecting the brightness per unit area. It is difficult to say just how narrow to make the slit. Even if the slit is infinitely narrow, the line image won't disappear: aberrations and grating resolution combine to keep it finitely wide. Shorten the slit until the line image ceases to contract and the brightness (energy per unit area) starts to decrease. The fine tuning is difficult but necessary. Use a hand lens to view the spectrum by either the iron arc illumination of the slit or a mercury source. Simple visual inspection will detennine the appropriate slit width. The best recourse is not to adjust anything unless the photograph or visuals are u!1~m~nageablybad.

Because of the stigmatic nature of the optical arrangement, it is not feasible to use the Hartman diaphragm to get the iron spectrum alongside the unknown. Inst~ use a shadowing device in front of the photographic plate. The unknown spectrum is made through a slot in the obstacle immediately in front of the plate. Turn the obstacle about an axis through the length of the slot so that the exposure is shadowed from the radiation emanating from the grating, and take the iron exposure. The two spectra are easily distinguished though they overlap slightly to allow for measurements in the overlap region.

The photographic plates are thin 1" x 1 0" plates bent towards the Rowland circle by a curved clamping plate support. We never used to specify plate thickness when ordering -they always came thin and flexible, seldom breaking when bent into circles. The last batch was different in that the plates were thicker and resisted bending. The new plates often break, which doesn't interfere with the measurements unless the broken plate shifts in between the iron spectrum and unknown spectrum (between the tacking and the exposures). To avoid this failure, just barely tighten the clamping screw of the securing plate into position. If it cracks in the process, save the pieces, developings, and fixings, chances being that they are salvageable.

Obtain plates from the "refrigerator" dark room using a transport box by loading them in the dark onto the spectrograph plate support and lightly clamping them. The emulsion side should face forward and touch a moist lip. (The emulsion side is gelatin and sticks!) Don't forget to separate the iron from the unknown spectrum by flipping the slotted mask in front of the plate. Keep the external illumination low to minimize plate fogging. After loading the plate, drop a black cloth over the back of the housing. Make sure the wheel is locked so that the plate remains stationary during the operations. The flipper should be free and not bind when turning.

After processing and drying, measure the plate. In the vibration spectrum, a long travel is necessary so the long comparator is used. Always move the carriage so as to raise the weight when taking a line measurement. If it is overshot, back way off and come up to it again. There will be a fair amount ofbacklash. For precision, the plate would be reversed and the work repeated from the other end. However, orientation of the cross hairs is optio~ either vertically or symmetrically orient them relative to the line. On the typical line, at least a dozen measurements should be made to determine error and to obtain reproducible results. For most lines, three or four settings and a mental average should suffice, assuming the spread in the readings is reasonable, judging from the spread observed in a dozen settings made on the typical line. The iron lines are identified with comparators. Since the rotational spectrum is short, either of the projection comparators can be used, (their travel is one inch). For comparison of an unknown line against a nearby iron line, use linear interpolation. For a long spectrum, such as the N2 spectrum in S-8, iron lines are identified across the whole plate and a correction curve should be made. From linear interpolation between the iron lines at either end, the wavelengths of the lines in between can be calculated. Because these won't agree with the tabulated wavelengths, a correction curve needs to be plotted and used on the unknown lines. In principle, this should be a sine curve with zero crossings at both ends and in the middle because the sine of the angle of diffraction is not equal to the angle of diffraction. (Note that at the plate center, this angle is zero; the center lies on the grating normal).