Experiment S-8

Vibrational Structure of a Band System in the Molecular Structure N₂

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The purpose of this lab is to investigate the vibrational properties of a prototypical diatomic molecule, N₂, using optical spectroscopy. In particular, you are to look at the second positive system of transitions (see references). Determine the wavenumbers of the band heads, look for sequences and progressions, and determine the vibrational quantum numbers of the initial and final states. Fit the spectra using an anharmonic theoretical model of the vibrational states, infer the relevant parameters, and compare to previous results. Discuss the intensities of the observed spectral features in light of the Franck-Condon principle.

Apparatus:

Sources: There are two light sources. First a mercury lamp is used for calibration and for familiarizing yourself with all the aspects of the measurement. Then a capillary discharge tube is used to excite the nitrogen (in air) inside the capillary using a 2-3 kV transformer. A pump is used to partially evacuate the tube. The pressure is set by adjusting the leak rate of air into the tube. A pinkish glow should be obtained. Lenses are used to focus the emission on the inlet slit of the spectrometer. An optical chopper is used to periodically modulate the light for lock-in detection.

Spectrometer: The spectrometer is a Czerny-Turner scanning double monochromator. A photomultiplier tube set at ~ 0.8 kV is used to detect the light emerging from the monochromator. The output is fed into a PAR 122 lock-in amplifier. The output of the lock-in is recorded using a chart recorder.

Hint: If you see a peak at a given wavenumber, it may not be a first order peak!

References:

Included in folder:
Thompson, A Converse in Chemical Spectroscopy, Chapters IXV, V (1838)

Others:
G. Herzberg, Molecular Spectra and Molecular Structure: Diatomic Molecules.
Vibrational Structure of a Band System in
A Molecular Spectrum

In the 1st order of the Rowland Grating Spectrograph (slit set at 20) photograph (1 1/2 to 2 hrs) a position (roughly 3000Å - 5000Å with plate holder centered on (4000Å) of the 2nd positive band system of Nitrogen. Put on an iron comparison spectrum (about 15 secs through diffuser screen) superimposed on a direct mercury spectrum (10 minutes) for line identification. Use type II-G plates.

Determine the band head's wave numbers, assign rough intensity values and analyze the system as far as possible into sequences and progressions. Interpret in light of Frank Condon principle.

References:

*Thompson, Chemical Spectroscopy, Chaps. IV, V. 1
*Johnson, Molecular Spectra, pp. 1-27. 2
for Rowland Grating, sec: CANDLER, "Modern Interferometers" Chapter VII. (In main library)

Jevons, Band Spectra of Diatomic Molecules,
Herzberg, Molecular Structure: Diatomic Molecules.
Mecke and Landau, Phys. Zs. 25, 299 (1924)
Sawyer-Exp. spect.
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These two experiments are so similar they may be explained in some detail together. They use the same apparatus and really only differ in the operation of the source. The analysis is of course quite different.

In S-8, the molecular spectrum of N₂ is obtained and a vibrational analysis made; in S-9, a single band of CO is obtained and the rotational analysis is carried out. Both spectra are obtained in 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. Wavelength determination is made by comparison with the spectrum of an iron arc, the usual standard.

The source in each case is a capillary discharge tube run at a not-so-low pressure, energized by a 2 or 3 KV gas lighting transformer. The tube is evacuated by a small forepump and proper pressure is obtained by adjusting a leak into the tube. For S-8 (N₂ experiment) one simply leaks air into the tube at a rate given by adjustment of a pinch clamp on a rubber hose. One adjusts the leak rate until the maximum vinkish brilliance is obtained. At that, it is none too bright so that careful positioning of the source on the axis of the imaging lens and the axis of slit-grating of the spectrograph is necessary. The back of the discharge capillary is covered with an aluminum foil to increase the forward light intensity somewhat to reduce somewhat the exposure time needed in the photography. For S-9 (the CO spectrum) the only source difference is in the gas which is leaked into and the leak arrangement. One leaks in CO₂; the CO is what appears in the spectrum photographed. CO₂ is obtained by pumping slowly on dry ice contained in a small thermos flask. One wants to insure that he is not pulling air into the discharge; thus, the evolution of CO₂ by sublimation wants to be greater than the rate at which it is pumped off into the discharge tube; the excess goes off into the atmosphere. One can be sure that there is an excess going off by bubbling it through water. Adjustment of the pump rate with a pinch clamp on a rubber hose or a series of partially opened stopcocks will take care of this. Again one adjusts for maximum brightness in the discharge— this time a nearly white discharge. Again, the brightness is not brilliant so that a long exposure is required.

Proper illumination of the slit is important. An image of the source is located on the slit, this with a lens exterior to the spectrograph room. The lens is of rather larger aperture than necessary, simply because it was available. It is not achromatic so that the image in all wavelengths is not of constant intensity; no great consequence in these experiments, but should be recognized in instances where accurate photometry of the spectrum might be required. The important thing, however, is that the axis of the lens more or less coincides with that of the spectrograph slit-grating axis. It is all very well to have the source image on the slit but if coming through a lens offset to one side, the light may never get to the grating. Presumably the alignment of lens and spectrograph is OK but it may not be. It is possible, with the weak illumination from the source, to see the illumination on the grating by placing the eye behind a spectral band and close to the spectrograph image plane. It sometimes takes some doing— getting dark adapted, finding a spectral band in the dark, etc. It can help by widening the slit way open and looking. If things are really out, but don't take this on unless it is obviously so— one can remove the imaging lens, position the iron arc and fire it up and simply look for the patch of bright light allowed through the wide slit. The arc is moved around until the patch is centered or less on the grating. Then the lens is put in and positioned until the arc image is on the slit. At least then the lens and spectrograph are in the right juxtaposition and it only remains to put the various sources in the right place so that they are imaged on the slit.

One thing the glass lens prevents, which may or may not be an advantage, no ultraviolet light is transmitted. The iron spectrum will be pretty cleanly only visible light; no UV lines will be mixed in as second order lines along with visible wavelengths, 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 line image because of the astigmatic light almost to 3000 A comes from Pyrex. For other lines a second order appears at all order levels.
tigmatism 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 overlapping exactly with every other line image from other points in the slit. This will be the situation if slits is parallel to grating rulings. If it is not the case, the 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 rectangles which they will be if the slit is wide. As the slit is narrowed, the rectangular image will be narrower but just as bright per unit area. It is difficult to say just how narrow one should make the slit. Clearly, if it is infinitely narrow, the line image is not; aberrations, grating resolution combine to keep it finite in width. One narrow the slit down until the line image ceases to narrow and the brightness (energy per unit area) starts dropping off. That's not easy to ascertain but that is what one should try to attain. Using a hand lens to view the spectrum with iron arc illumination of the slit or a mercury source, one can arrive at a reasonable slit width just by visual inspection. The best thing is not to play around with the adjustments here until it is obvious that all is not well, either visually or in the photograph.

Because of the astigmatic nature of the optical arrangement, it is not feasible to use a so called Hartmann diaphragm to get the iron spectrum alongside the unknown. Rather a shadowing device in front of the photographic plate. The unknown spectrum is made through a slot in an obstacle immediately in front of the plate. The obstacle is turned about an axis through the length of the slot so that the exposure made through it is now shadowed from any radiation from the grating. The iron exposure is then made; the two spectra are each separately distinguished but overlap slightly to allow measurements to be made in the overlap region.

The photographic plates are thin 1" x 10" plates bent to the Rowland circle by a curved clamping plate pressing the plate against the similarly curved plate support. We never used to specify plate thickness in ordering; they just came thin and nice and flexible, seldom breaking in bending them to the circle. The last batch came much thicker and can barely take any bending at all. They frequently crack. This mostly doesn't make the measurement impossible unless it breaks and shifts in between the iron spectrum and that of the unknown (that is, between the taking of the exposures). The moral is: just barely tighten the clamping screw in securing the plate in position. If it is heard to crack while putting it in, we say go ahead and "save the pieces", developing and fixing each. They are likely to be quite usable.

Plates are brought from the "refrigerator" dark room in a transport box and loaded in the dark on the spectrograph plate support and lightly clamped. The emulsion side is forward, of course; touched against a slightly moist lip, the emulsion side sticks— it is gelatine, after all. Don't forget to separate the known (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 is not moved during operations; the flipper should be free and not bind in turning.

After processing and drying, the plate is measured. In the vibrational 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 it way off and come up to it again. There is a fair amount of backlash. For precise work, the plate would be reversed and the whole business repeated from the other end. Not here, sorry. Orientation of cross hairs is somewhat optional; either vertical or symmetrically oriented relative to the line. Some psychological optics enters here. In any event, at least on a typical line, a dozen or so measurements should be made to give one some idea of the experimental reproducibility and error. For most lines, three or four
settings and a mental average should suffice, assuming the spread in the readings is reasonable, judged from the spread observed in the dozen or so settings made on the typical line. The iron lines are identified with the aid of the various charts of the iron spectrum lying around at the comparators. For the rotational spectrum, since it 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, linear interpolation is adequate. For a long spectrum, such as the \( N_2 \) spectrum in S-8 iron lines are identified over the whole plate and a correction curve should be made. From linear interpolation between the iron lines at either end, the wavelengths of those in between are calculated from the measurements. These won't quite agree with tabulated wavelengths, so a correction curve is plotted and then used on the unknown lines. In principle, the curve should be a sine curve, zero at the ends and in the middle and arises in the fact that 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.)