Experiment S-8

Vibrational Structure of a Band System in the Molecular Structure N_2

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The purpose of this lab is to investigate the vibrational properties of a prototypical diatomic molecule, N_2, 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 Frank-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)
Johnson, An Introduction to Molecular Spectra, pp. 1-27 (1949).

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, Chapts. 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. <u>25</u>, 299 (1924)

Sawyer-Exp. spect.

1985

Experiment S-8,9

These two experiments are so similar they may be explained in some detail together. They use the same apparatus and really only differ in the operation of the source. The analysis is of course quite different.

In S-8, the molecular spectrum of N_2 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 N_2 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 (s gn) 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 (N_2 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 pinkish 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 in and the leak arrangement. One leaks in CO_2; the CO is what appears in the spectrum photographed. CO_2 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 CO_2 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, partially opened stopcock will take care of this. Again one adjusts for maximum brightness in the discharge---this time a pearly 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 XXXXXX 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 an achromat 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 coincide 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 off 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 and 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. It sometimes takes some doing---getting dark adapted, finding a spectrum 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 by the wide slit. The arc is moved around until the patch is centered more 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 as-

Overstated- light almost to 3000Å comes thru Pyrex—
2nd order lines ~3000Å appear at 2nd order 6000Å.

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 infintely 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 ar-
rive at a reasonble slit width just by visusl inspection. The best
thing is not to play around with the adjustments here until it is obvious
that all is not well, either cisually or in the photograph.

Because of the astigmatic nature of the optical arrangement, it is
not feasible to use a so called Hartmann diaphram to get the iron spectrum
alongside the unknown. Rather a shadowing device in front of the photo-
graphic plate. The unknown spectrum is made through a slot in an ob-
stacle immediately in front obf 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 over-
lap 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 simil-
arly 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 XXX take any bending at all. They frequently break. 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 fix-
ing each. They are likely to be quite useable.

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 vibrat-
ional 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 psycholog-
ical 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 inter-
polation 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 prin-
ciple, 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.)