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"Investigations of Transition Probabilities in Molecular
Spectra: Transition Probabilities in the Spectra of
VO, CaH, MgO, and YO".

John G. Phillips

I. Introduction

The relative transition probabilities of bands in the spectra of
only a few diatomic molecules are known. Since such data are required, before
stellar atmospheric temperatures may be derived from studies of the intensities
of molecular bands in stellar spectra, it is worth while to attempt a system-
atic study of the intensities of bands in the spectra of as many molecules
of astrophysical interest as possible. This may be done most conveniently in
the laboratory, using as a source of radiation an electric furnace of the
carbon-resistance-tube type. In view of the fact that the photographic plate
introduces numerous uncertainties into the determination of the intensities
of the spectral features, greater photometric accuracy can be obtained if the
spectra can be scanned photoelectrically. Using modern techniques, an elec-
tronic system involving photoelectric cell, amplifier, and stripchart recorder
can be designed to be strictly linear over the entire useful range of inci-
dent intensities. The sensitivities of photoelectric cells are functions of
the wavelength of the incident light, but calibration may be readily made,
using a source of known spectral intensity distribution. Under given opera-
ting conditions, this calibration changes either very slightly with time or
not at all.

One difficulty connected with the use of photoelectric techniques
is that the intensity can be measured at only one wavelength at a time. Thus,
during a particular traversal of the spectral region of interest, both the
temperature and partial pressure of the molecules in the furnace must be kept
constant. After equilibrium conditions have been reached, the temperature
in the furnace is quite constant with time, but nevertheless slow changes of
the intensity of a particular feature are found. Apparently this is caused by
a change in the total number of molecules in the emitting column. Corrections
for this change can be applied by scanning the spectrum a number of times
in succession, and then plotting the intensity of a representative point in the
spectrum as a function of time. It is found that shape of the resulting curve
is, in general, independent of the particular representative point chosen.
Thus the curve may be used as a correction curve, and the results of successive
traversals of the spectrum may be combined to form a single mean intensity
record.

Various features in a band may be used to obtain the relative inten-
sities, $I_{v', v''}$, depending upon the particular situation, and the degree of
accuracy required. A few of these methods are listed below:

(1) The peak intensities at the band heads may be used, if it can
be shown that all the bands have the same structure, i.e., the lines in each
band contributing to the peak intensity lie within the same range of rotational

quantum number, J, and, furthermore, the relative orientations and separa-
tions of these lines are the same for each band. The method is accurate if
these conditions are fulfilled exactly, and the bands are unblended so that
the true location of the background continuum at each head is known. The
method is approximate to the degree that these conditions are not fulfilled.

(2) The total amount of radiation emitted in a band, integrating
over all wavelengths, provides the most accurate measure of its strength, if
it is completely unblended with any other spectral feature. In many cases
the bands of a system fall into close sequences, with the "tails" of each
band being blended with following bands of the sequence (see e.g., fig. 3).
In these cases the method may still be used, provided the rotational constants
are known, since in that case we may readily compute the contour that each
band would have exhibited if it had been unblended. In this way one may
determine the contributions of each band to the intensity in such a blend,
unless, of course, bands overlap completely.

(3) If the bands can be observed in absorption, with high enough
resolution to completely resolve the individual rotational lines, then the
relative transition probabilities of two bands will be equal to the ratio
of the combined intensities of all lines in one band arising from a common
initial state, to the combined intensities of those lines of the other band
arising from the same lower state. This ratio will be independent of the
number of molecules in the common lower state, provided all lines are weak.
Otherwise, there will not be a strict proportionality between the number of
molecules making the transition, and the integrated absorption in the corre-
sponding line.

Once the relative intensities of the bands in a system have been
found, the relative transition probabilities may be computed immediately,
since:

$$\frac{I_1}{I_2} = \left(\frac{\nu_1}{\nu_2}\right)^4 \left(\frac{|R_1|^2}{|R_2|^2}\right) e^{-\left[G_0(1) - G_0(2)\right]\frac{hc}{kt}} \qquad (1)$$

In this equation, subscripts 1 and 2 refer to any two bands of a system;
ν_1 and ν_2 are the frequencies of their respective band origins; $|R|^2$ is the
transition probability, $\left[G_0(1) - G_0(2)\right]$ is the difference of vibrational
energy of the respective initial states. This equation is valid for an
emission spectrum. In absorption, the frequencies ν, are taken to the first
power. Numerous investigations have found that conditions close to thermo-
dynamic equilibrium may be produced inside an electric furnace, if a partial
pressure of an inert gas in introduced, so that collisions between molecules
are frequent. Thus the Boltzmann exponential expression may be used to
compute the relative populations in the various initial vibrational levels.

It had been proposed that four of the following six molecules be
chosen for study: CaH, CH, SiO, YO, VO, and MgO. A survey showed that
while it was possible to produce CH, the furnace temperature required was
so high that the graphite heating tubes only lasted a very few minutes; not
long enough for careful photometry to be completed. SiO proved to have its
principal bands too far in the ultraviolet to be reached by the photoelectric
cell employed (1P21). The other four molecules (CaH, YO, VO and MgO) exhib-
ited none of these difficulties, and hence were chosen for study.

II. Equipment

As mentioned in the introduction, the source of radiation was a carbon-resistance-tube electric furnace of the King type. The particular installation employed has been described elsewhere. [1] The spectrum was produced by a three meter concave grating spectrograph with Eagle type mounting. The dispersion was 5 angstroms per millimeter in the first order. The optical system was designed to admit, to the spectrograph, only radiation from the gas in the furnace, and to exclude radiation from the walls of the heated graphite tube. This was accomplished by the use of a quartz lens between the furnace and spectrograph, of such a focal length, and in such a position, that the far end of the heater tube was imaged on the slit, magnified about three times. Imaging the far end of the tube on the slit ensured that the light from all other points in the tube would be out of focus on the plane of the slit, and outside a circular zone defined by this image. A diaphragm at the slit then readily shielded the slit from radiation from the walls of the tube. Since a strong spherical aberration was present in the particular lens employed, it was necessary to limit the aperture, by means of a second diaphragm about 18 inches in front of the furnace. A field lens was employed at the slit to increase the size of the beam at the grating. The receiver consisted of two parts: (1) a mechanical spectrum scanner and (2) an electronic amplifier and recorder. Each of these parts will be described in turn.

a. The spectrum scanner: This is illustrated in Figure 1. It consists of a carriage travelling on a curved track, which is concentric with the Rowland circle of the spectrograph. The carriage is pulled by a rectangular block, which slides on the flattened top of the thread of a long screw. A split nut fastened to the block engages the thread of the screw. The carriage is connected to the block by an arm, pivoted at the carriage. The arm slides in ways on the block, the direction of motion of the arm being perpendicular to the centre-line of the screw. The screw is turned by a synchronous motor through a reduction gear train. Change gears make possible a series of scanning rates, from 0.67 to 84.66 angstroms per minute.

The scanner carriage, in turn, supports a box-shaped probe, which carries the adjustable scanning slit at one end, and the photocell housing at the other. The probe is fastened to the carriage by means of a pivot concentric with the centre-line of the slit, which is held accurately on the focal plane of the spectrograph. The plate holder, on which the scanner is mounted, permits a travel of such a length that 2,000 angstroms of spectrum may be scanned at any particular spectrograph setting.

A complication is introduced in the design of the scanner, by the requirement that the axis of the probe be centered on the grating for all wavelengths. This requires an appreciable change in the orientation of the probe, relative to the carriage, as it is driven along the spectrum. An obvious way in which this movement of the probe could be accomplished would be to let an arm on the probe move along an appropriately shaped cam. The method that was finally adopted, however, is quite a bit neater, and is accurate enough for all practical purposes. It was planned to use the spectrograph primarily in the first order, in which case the grating is close to being across a diameter of the Rowland circle from the scanner probe.

Thus the change in direction of the probe's axis is close to being half the change in direction of the normal to the carriage as it moves along the spectrum. A simple linkage system is therefore all that is required to move the probe relative to the carriage. It is illustrated schematically in Figure 2. In the figure, point A represents the centre-line of the perpendicular slit, in the focal plane of the spectrograph. The probe pivots about this point. B is the point at which the carriage is pivoted to the arm which connects it to the block. As mentioned above, the arm slides in ways on the block. Now, if a pin is fastened to the arm at point C, such that the distance $C \rightarrow B$ is equal to the distance $A \rightarrow B$, then points A, B and C form an isosceles triangle and angle ψ will be half the angle θ for all positions of the carriage. Pin C slides in a slot in a sector plate, which is also pivoted at A. The probe is locked to the sector by a spring clip, so that angle ψ is constant for a given spectrograph setting, but may be changed if the setting is changed.

b. __Amplifier and Recorder__: The amplifier was built according to a design kindly furnished by Dr. Harold L. Johnson, now of the Lowell Observatory. While it was designed primarily for application to astronomical photometry, it has performed very satisfactorily as a laboratory instrument. It consists essentially of two parts: (1) a contact-modulated a.c. amplifier, (2) a d.c. power amplifier, which couples the a.c. amplifier to a Brown "Electronik" Strip Chart Recorder. While the amplifier was built to accept the output of various types of receiver (photomultipliers, photoelectric cells, photoconductive cells, and thermocouples) in the present application only a 1P21 photomultiplier cell has been used. The voltages on the various stages of the photomultipliers are provided by a radio-frequency oscillator. The voltage drop per stage could be varied from 75 to 135 volts. All the records used in study were made with 75 volts per stage.

No departure from linearity was observed over the useful amplification range of the amplifier. The linearity of the entire receiver, photocell plus amplifier plus recorder, was checked by observing the change, with temperature, of the intensity of the head of the (0-0) band of the Swan system of C_2 using the electric furnace as the source. The Swan system always appears whenever a carbon tube is heated above $2200^{\circ}C$. Previous investigations [1] have shown that one obtains a straight line, if one plots $1/T$ against a complicated expression which includes, among other quantities, the logarithm of the band intensity. The observation with photoelectric receiver also led to a straight line, over a range of intensity of 1:230.

It was necessary to determine the relative sensitivity of the apparatus as a function of wavelength. This was accomplished most conveniently by the furnace itself. A solid graphite plug was inserted into the heater tube, midway down its length. About three inches from the plug a baffle was introduced. Radiation from the cavity thus formed was allowed to pass through a small hole about 1/8 inch in diameter in the baffle. The furnace thus became a good black body, and the radiation from the hole in the baffle could be considered to have an intensity distribution given by the Planck radiation law.

The advantage to be gained by using the furnace as its own calibrating device is that the effects of scattering and absorption of

light in the optical system and spectrograph could be taken into account immediately. When the continuum produced by the black body was scanned, the spectrograph and optical system was in the same adjustment as it was later in scanning the molecular spectra. A wave-length scale was introduced into the continuum by interposing a mercury arc lamp into the optical path at appropriate times. The response curve of the photocell, as a function of wavelength, could then be correlated with the emitted intensity to give the over-all relative sensitivity curve of the apparatus.

Incidentally, it was found that the intensity of the black body continuum was at least ten times as great as the maximum intensities recorded for the molecular spectra at the same temperature and wavelength. Hence there was little likelihood that effects of self-absorption would cause errors in the final results.

III. The Observations and Results

a. VO.

The spectrum of vanadium oxide was produced by the decomposition of V_2O_5 powder in the furnace. The reduction of the pentoxide proved to be too complete if it was introduced directly into the graphite tube. The VO bands appeared weakly, and were soon replaced by emission lines of atomic vanadium. After some experimentation, it was found that a strong VO spectrum could be made to persist for over an hour with little reduction in intensity if the gas was shielded from the tube by a lining of tantalum foil and the powder placed in a tungsten boat. The required partial reduction of the pentoxide was accomplished by mixing the powder with equal amounts of powdered graphite, by molecular weight. The furnace was evacuated and 10 cms of argon introduced to reduce diffusion of VO molecules from the ends of the heated section. The VO spectrum was strong at a temperature of 1950°C. At higher temperatures the powder evaporated too rapidly. Several traversals were made in succession, covering the spectral region from 6150 A to 4950 A. The scanning rate was 84.66 per minute, with both slits 0.5 millimeters wide. With these wide slits the rotational structure of the bands did not appear on the records.

Slight changes in the intensity of the same feature on successive traversals indicated that there were changes in the number of emitting molecules with time. The method described in the introduction was used to correct for these changes. After further correcting for changes of the sensitivity of the apparatus with wavelength, the results of the successive traversals were combined into a single intensity curve.

Analysis: The spectrum of VO consists of a single system tentatively identified as being produced by a $(^2\triangle - ^2\triangle)$ transition. The bands fall in a series of close sequences. The $\triangle V = +2$ sequence is illustrated in Figure 3. The observed intensities in three successive traversals of the sequence are plotted in the figure.

The relative intensities of the individual bands were determined by computing the contribution that each band made to the intensity of its respective sequence. Since the rotational constants, B_v, appropriate to each band were known, it was possible to compute the profile of each band to be expected, at the observed temperature of the furnace, if it had been

unblended with any other band. This computation followed standard pro-
cedures, so that it is not necessary to describe it in detail here.
One simplification that was introduced was the neglect of the influence
of the finite slit widths. This was permissible, since only the tail of
each band was blended with higher members of its sequence, and the slope
of the band profile changes so slowly in the tail, that the effect of
reduced spectral purity, introduced by the wide slits, would be very low.
In the region of the head, this simplification introduces errors, and is
responsible for the departure of the computed profile (dotted lines) from
the observed profile. Of course, in determining the intensities, the ob-
served profiles were followed in the neighborhoods of the heads.

The contribution of each band to the intensity of its sequence
could then be determined immediately; starting with the first band of the
sequence, the computed tail was grafted into that part of its profile
that was unblended with any other band. The tail could then be grafted
onto the next band, and so on. The integrated areas on the graph, as de-
termined by a planimeter, were then proportional to the relative emissions
in the corresponding bands, and could be introduced into equation (1).
The results are listed below. All transition probabilities were determined
relative to the transition probability of the (0-0) band.

Band v', v''	λ (head)	Rel. Trans. Prob.
0-1	6087.1 A	1.205
1-2	6139.6	0.249
0-0	5736.7	1.000
1-1	5786.3	--
2-2	5837.7	0.605
1-0	5469.2	1.048
2-1	5517.8	0.256
2-0	5228.3	0.724
3-1	5275.7	0.674
4-2	5324.2	0.215
3-0	5010.6	0.287
4-1	5056.8	0.452
5-2	5104.2	0.342

It was not possible to compute probable errors, since the single mean intensity curve was used in the analysis. The general agreement of the results of successive traversals of the spectrum, as illustrated in Figure 3, is fairly good, so that accidental errors may be expected to be low. As far as systematic errors are concerned, the greatest possible source of error lies in the determination of the spectral sensitivity curve of the apparatus, i.e., in departures of the radiation from the furnace from a true black-body distribution. Such departures are believed to be small, but shortage of time did not permit an exhaustive study of this point.

The (1-1) band at 5786.3 A presents an anomaly. On all tracings, it was either so weak as to be barely detectable, or completely absent. Its weakness is probably associated with the fact that the relative transition probability of the (0-0) band is lower than the probabilities of either the (1-0) or the (0-1) bands. It may be a consequence of the manner in which the wave functions of the corresponding upper and lower vibrational states overlap.

b. $\underline{CaH}$:

The spectrum of CaH was produced in absorption, using a method described by Grundström [2]. The graphite heating tube was lined with a porcelain tube, and metallic calcium melted in the porcelain tube, in an atmosphere of hydrogen at 400 mm. pressure. The porcelain tube prevented the formation of calcium carbide. A tungsten ribbon filament lamp produced the continuum. At a temperature of $1000^{\circ}C.$, prominent absorption features were the (0-0) bands of the $(A^2\pi - X^2\Sigma)$ and $(B^2\Sigma - X^2\Sigma)$ systems, with band origins at 6908 - 46A and 6346 A, respectively. In the following these bands are called "A" and "B" respectively. Other bands of these systems were found to be too weak for study, so we were limited to these two bands. Slit widths were 0.15 mm. which gave individual rotational lines a triangular profile, with base width of 1.5 A. This was sufficient to completely resolve the rotational structures in all regions but the heads.

The determination of the relative transition probability of bands A and B was simplified by the fortunate circumstance that the lines, $P_1(18)$ and $P_2(18)$, of band A coincided almost exactly. Their respective wavelengths are 6991.9A and 6991.8A, according to the measurements of Hulthén (3). Furthermore, the lines $R_1(19)$ and $R_2(17)$ of band B at 6259.7A and 6259.6A also coincide almost exactly. The figures in parentheses are the K-values of the corresponding rotational levels in the lower state. Now the combined absorption of lines $R_1(19)$ plus $R_2(17)$ of band B will be very close to being equal to the combined absorption of $R_1(18)$ plus $R_2(18)$, and may, to a sufficiently good degree of accuracy, be taken as a measure of the combined absorption of these latter two lines. Thus we have the situation illustrated in Figure 4. In band A, two R lines and two Q lines arise from the K" = 18 state in addition to the observed P lines. These additional lines are too badly blended to be measured individually. However, their intensities may be readily computed from theoretical considerations [4]. Similarly, one may compute the strengths of the unobserved lines $P_1(18)$ and $P_2(18)$, which also arise from the K" = 18 level in the B band. Thus, from the observed absorptions in the two blends that could be observed, one can compute the relative numbers of molecules in the two bands which make transitions from the K" = 18 level, i.e., one can compute the relative transition probability.

If one now considers the transmission of radiation through an absorption tube at the frequency, ν, corresponding to the centre of an absorption line, the following equation holds for the residual intensity, I_ν, of the radiation, after an incident beam of intensity $I_{\nu,o}$ has suffered absorption by N molecules:

$$I_\nu = I_{\nu,o}\, e^{-Nk_\nu}$$

N is the number of molecules making the corresponding absorption transition, not the total number of molecules in the tube. The quantity k_ν is the absorption coefficient per molecule at the frequency ν; it may be considered to be the same for all rotational lines. Solving for N:

$$N = -\frac{1}{k_\nu}\, \log \frac{I_\nu}{I_{\nu,o}}$$

Since wide slits are used, the observed residual central intensities will not be equal to the true residual central intensities, but, in view of the fact that the two blends of interest were comparable in intensity, and were both quite weak, the errors made in each case will be approximately the same, so that one might write:

$$\frac{N_A}{N_B} = - \log\left(\frac{I_\nu}{I_{\nu,o}}\right)_A \Big/ \log\left(\frac{I_\nu}{I_{\nu,o}}\right)_B$$

Where N_A is the number of molecules producing the blend $\left[P_1(18) + P_2(18)\right]$ of band A, and N_B, the number producing the blend $\left[R_1(18) + R_2(18)\right]$ of band B. When the relative intensities of all lines in the two bands which arise from the level $K'' = 18$ are computed, it is found that:

$$\text{Rel. Trans. Prob.} = \frac{\text{Prob. A}}{\text{Prob. B}} = \frac{38}{17}\frac{N_A}{N_B}$$

Measurements were made on four successive tracings of the two bands, observed alternately. The strengths of the absorption lines decreased to 1/3 their initial amount by the end of the run, which took almost 3 hours. Corrections were applied, for this change in population, by comparing the intensities of representative absorption features on successive records, and drawing interpolation curves. No systematic change in the relative transition probability as a function of line strength was observed, which indicated that the effect of wide slits could be neglected. The combination of all measurements led to the result:

$$\text{Rel. Trans. Prob:} \left(A/B\right) = 3.74 \pm 0.08$$

c. **MgO:**

After considerable experimentation, the following conditions were found to be favorable for the production of a stable population of MgO molecules in the furnace. A sample of the purest MgO powder available was sintered in the form of a cylindrical tube that fit fairly closely into the graphite heater tube. This MgO tube was then split along a diameter and a piece about 3/4 of an inch long was inserted, concave side up, into a heater tube that had been completely lined with a double layer of metallic

foil. The outer layer, next to the graphite, was of tantalum foil, and the inner of tungsten. The lining prevented the reduction of the oxide by the carbon. The purpose of the sintering was to prevent a troublesome fuming that took place when MgO powder was heated. Solid particles were carried into the optical path and disturbed the records. The MgO was heated in an argon atmosphere at 15 cms. pressure.

The main sequence, at 5007 A, of the green system of MgO $(^1\Sigma - ^1\Sigma)$ appeared when the temperature was raised above 2200°C. The bands increased in intensity very rapidly with temperature. An upper limit to the useful temperature range was set at about 2400°C.; at this temperature the MgO evaporated so rapidly that only short runs could be made. Other bands of the green system were looked for, but were not found, nor were bands of the red system $(^1\Sigma - ^1\Pi)$. Emissions were observed in the region of the ultra-violet system, but they could not be positively identified as MgO bands; some coincidences with published wavelengths of heads were observed, but the system is so complex, with bands degrading in either direction, that further work is required before definite identification can be made. Hence the study was limited to the main sequence of the green system.

One difficulty that reduced the accuracy of the photometry of the green sequence was the persistent presence of the 5211 A bands of MgH. The tails of these bands extended through the spectral region covered by the MgO bands, and made it difficult to determine the location of the continuum. All attempts to eliminate the MgH bands failed. Apparently a minute trace of hydrogen is all that is required to produce the bands. The careful elimination of all water from the sintered MgO and argon reduced the intensity of MgH, but did not eliminate it. One suggestion that has been made, is that traces of hydrogen may be trapped in the carbon from which the heater tubes are manufactured.

Several traces of the green sequence were made at each of several temperatures, ranging from 2210°C. to 2325°C. Slit widths were 0.5 mm. The traces at 2325°C. were chosen for study in detail, because the bands were strong at that temperature, and successive traces indicated that conditions were the most stable. The combined profile, after correcting for receiver sensitivity, is shown in Figure 5. Observed points on two successive records are indicated by different symbols. The continuous line represents the best mean intensity profile.

As can be seen in Figure 5, successive heads in the sequence are close together, having an average separation of about 11 A. Thus, in order to determine the contribution of each band to the integrated intensity profile, it was necessary to compute, from theory, the expected contour of each band in detail, including the region of the head. In this computation it was assumed that each rotational line would exhibit a triangular profile, with base 5 A wide. The resultant contours of relative intensity versus distance from the band origins, in angstrom units, are shown in Figure 6. They were computed for a temperature of 2623°K, which is the observed pyrometer reading corrected for window absorption. The change in the contours, especially of the successive P heads, is produced by the difference in the rotational constants of successive bands.

The fitting of the successive band contours onto the observed profile of the sequence proceeded by trial and error. Since, as mentioned above, the presence of MgH emission made the determination of the background intensity quite uncertain, the fit with the observed profiles of the successive heads was taken as the criterion of agreement, and the intensity of the background was adjusted to make that fit as good as possible. The dotted lines in Figure 6 indicate the way in which the intensity of the sequence was finally divided up among the successive bands. The respective areas were then planimetered, and equation (1) was used to determine the relative transition probabilities. The pertinent data and final results are presented in the following table:

Band	λ_o (air)	Relative Area	Relative Transition Probability
(0-0)	4997.7A	1.212	1.000
(1-1)	4987.8	0.789	1.010
(2-2)	4977.7	0.518	1.023
(3-3)	4967.4	0.260	0.788
(4-4)	4957.0	0.138	0.638

One feature of the results that is difficult to understand, is the fact that the (1-1) and (2-2) bands have successively greater transition probabilities than the (0-0) band. This may be a consequence of the uncertainty in the intensity of the background. It is, indeed, possible for higher members of the main sequence to have greater transition probabilities than the (0-0) band, but in those cases, it is due to the fact that the equilibrium internuclear distances of the two electronic states are quite different; also, in those cases, additional off-diagonal sequences are observed which may be equal in intensity to the main sequence. These additional sequences are not observed in the furnace records of MgO. Therefore, in view of this anomaly, the foregoing results must be considered provisional. More conclusive data must await the careful study of the intensity distribution in the MgH bands.

d. **YO**:

The spectrum of YO was produced with good intensity in emission when a 1:1 mixture, by molecular weight, of Y_2O_3 powder and powdered graphite, was placed in a tungsten boat and heated to $2250^{\circ}C$. in a tube that had been lined with tantalum foil. At that temperature the spectrum persisted for several hours with no pronounced change in intensity. Bands of both the orange ($^2\Pi-^2\Sigma$) and blue-green ($^2\Sigma-^2\Sigma$) systems were observed. In the case of the orange system, the doublet Q branches of bands of the main sequence were strong. These formed two fairly close subsequences of heads, beginning with the Q heads of the (0-0) band at 5972.2 A, and 6132.1 A, respectively. These sequences were quite free of blends with atomic lines. The sequence at 6132.A is illustrated in Figure 7. The R heads of the main sequence, and heads of bands in off-diagonal sequences, were either so weak that positive identification was impossible,

or were too badly blended with atomic emission lines. This is interesting in view of the fact that their intensities on arc plates are reported to be quite high [6] It sheds some doubt on the correctness of the currently accepted analysis.

As far as the blue-green system is concerned, only the (0-0) band at 4817.4 A could be positively identified. Other weaker bands were probably present, but the presence of great numbers of strong atomic lines throughout the blue-green region of the spectrum made positive identification impossible, and even made it impossible to be certain of the profile of the (0-0) band; hence, no quantitative measure of its intensity could be made. Thus the study was limited to the observeed features of the orange system.

If the analysis of the orange system is correct, then the relative transition probabilities of the bands of the main sequence of the system could be derived from a determination of relative intensities of the Q branches in either the 5972.2 A or the .2.1 A subsequences. The latter sequence was chosen for study, because it appeared to be less affected by irregularities, produced, presumably, by atomic lines.

Since no rotational analysis of the YO spectrum has, as yet, been carried out, it was not possible to compute profiles of the Q branches. Instead, the assumption had to be made that the relative intensities of the successive Q branches were proportional to the relative intensities of their heads. It is probable that this assumption is not too bad. It was pointed out in the introduction, that the relative intensities of band heads may be used, if it can be shown that all bands so treated have the same structure. This will be essentially the case, for bands in a narrow wavelength interval, if the separation of head and origin, in wave number units, is the same for all bands. Now, this separation depends upon the rotational constants, according to the equation:

$$\nu_{head} - \nu_o = -\frac{(B'_v + B''_v)^2}{4(B'_v - B''_v)}$$

where B'_v and B''_v are the rotational constants of the upper and lower vibrational levels, respectively. Since, in general, B'_v and B''_v do not differ very much, it is evident that changes in the interval $(\nu_{head} - \nu_o)$, as one goes from one band to the next in the sequence, will depend primarily upon changes in the denominator, $(B'_v - B''_v)$. Now, the rotational constants are unknown but one may make use of the empirical fact that there is an approximate proportionality between the rotational constants and the corresponding vibrational quanta for all bands pertaining to a particular molecule, i.e.:

$$B_v \propto (\Delta G_{v+\frac{1}{2}} = W_e - 2W_e X_e - 2W_e X_e V)$$

The proportionality constant is usually of the order 1:1000. Thus:

$$(B'_v - B''_v) \propto [(W_e' - W_e' X_e') - (W_e'' - W_e'' X_e'') -$$
$$- (2W_e' X_e' V' - 2W_e'' X_e'' V'')]$$

and changes in $(B'_v - B''_v)$ with increasing V' and V" will be proportional to changes in the last term. Since $W_e' X_e'$ is 2.80 cm $^{-1}$, and $W_e'' X_e''$ is

2.45 cm^{-1}, changes in this term will be small. Thus it might be expected that the structures of the successive Q branches in the subsequences will not be very different.

The principle source of uncertainty in the measurement of the relative intensities of the Q heads, lies in the determination of the intensities of the corresponding backgrounds. The best that could be done, was to assume that the intensity profiles immediately in front of the successive heads could be extrapolated linearly, as is shown by the dotted lines in Figure 7.

The measured intensities, relative to that of the (0-0) band, in eight successive traversals of the sequence were combined, after correcting for the sensitivity of the receiver. The results as listed below, together with the resulting relative transition probabilities, computed according to equation (1). The temperatures, corrected for the window absorption, was 2540°K.

Band	λ of Q_2 head	Relative Intensity of Q_2 head	Relative Transition Probability
(0-0)	6132.1 A	100.0	1.00
(1-1)	6148.4	60.6	1.07 ± 0.03
(2-2)	6165.1	39.7	1.21 ± 0.05
(3-3)	6182.3	26.7	1.40 ± 0.08
(4-4)	6139.9	15.9	1.40 ± 0.09
(5-5)	6218.0	8.7	1.36 ± 0.09

Here, just as in the case of the MgO bands, the resulting relative transition probabilities increase with increasing vibrational quantum number. The results must, therefore, again be accepted with reservations, for the same reasons. The uncertainties in the respective backgrounds introduce large systematic uncertainties in the results. The probable errors quoted above merely represent the accidental errors, and do not include possible systematic errors. A more definite determination of the relative transition probabilities must await a rotational analysis of the YO spectrum.

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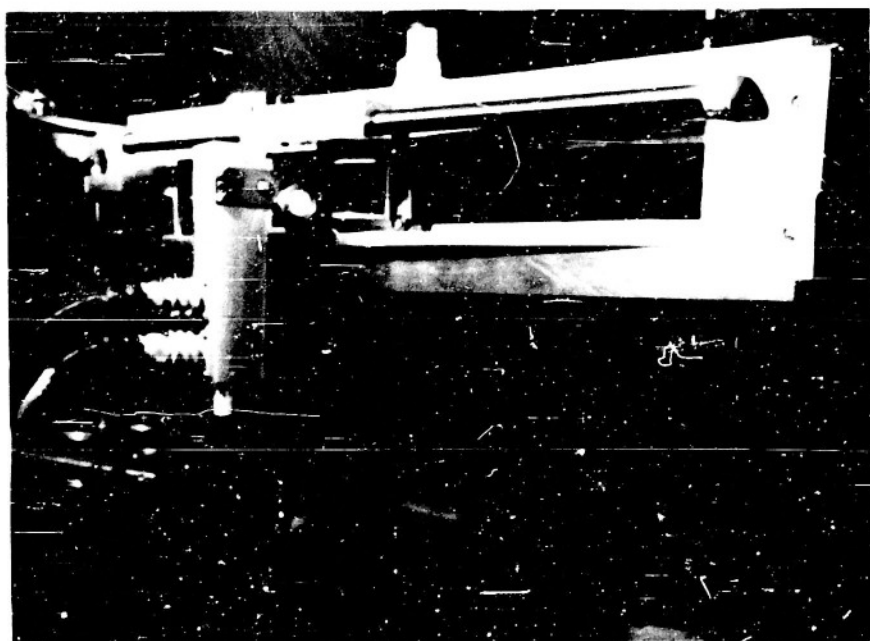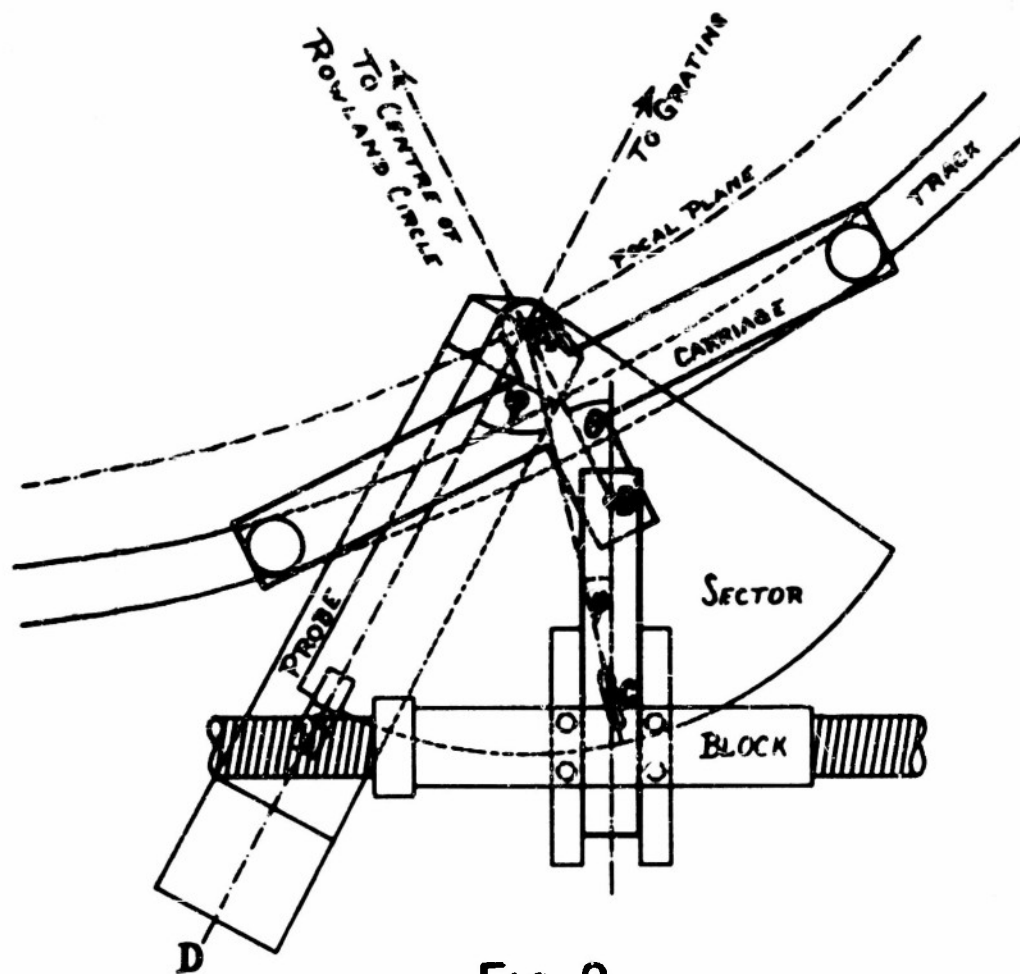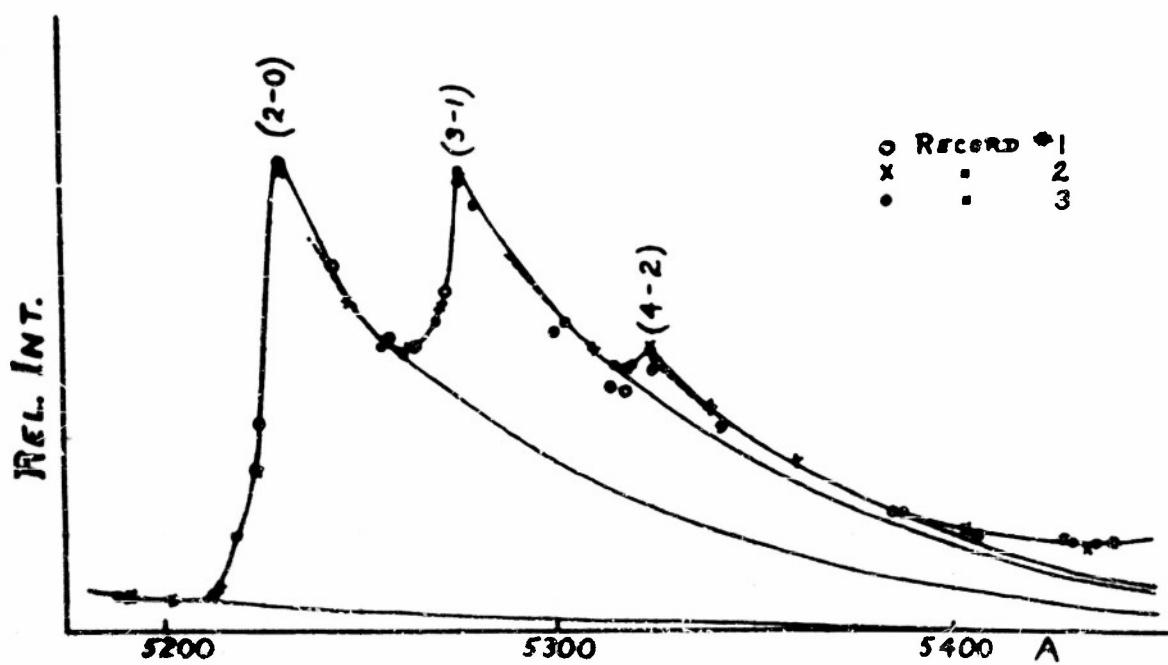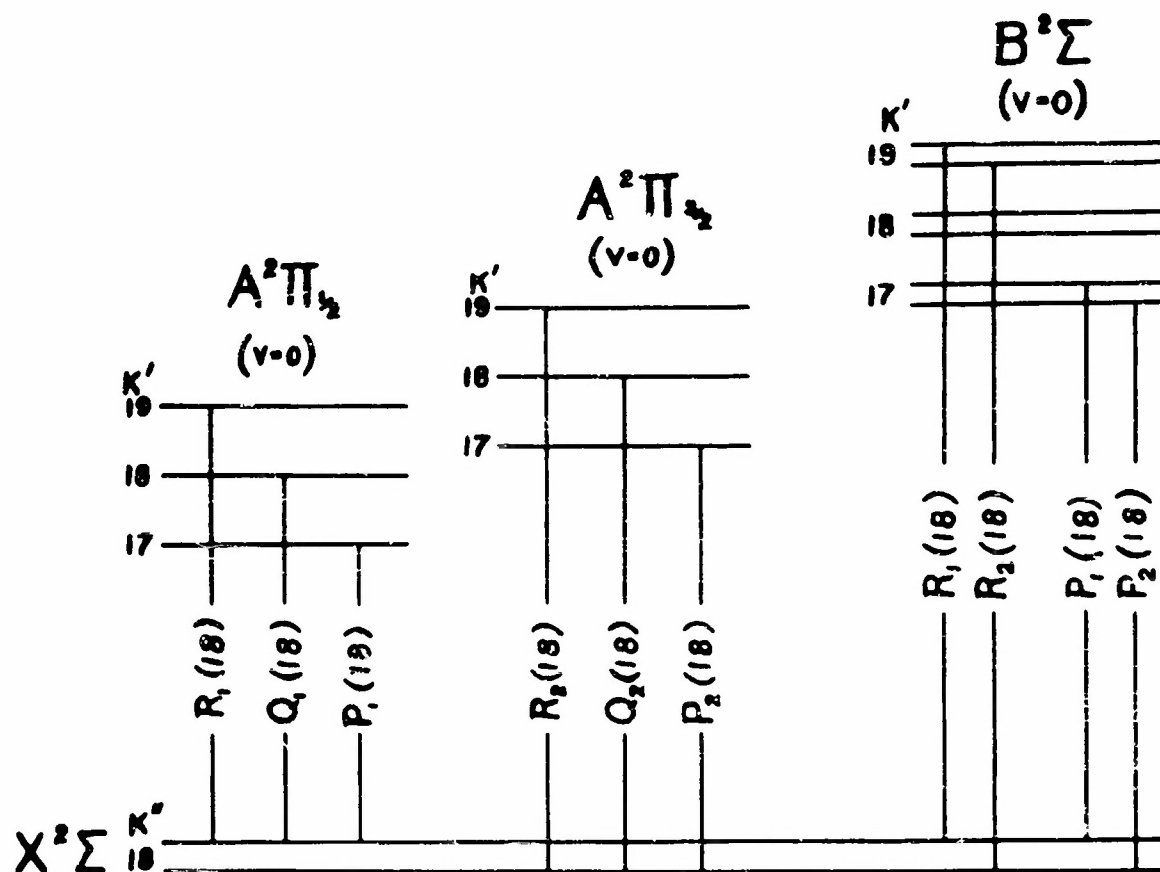
FIG 1

FIG. 2

FIG. 3

FIG. 4

MgO

FIG. 5

MgO

REL. INT.

(0-0)
(1-1)
(2-2)
(3-3)
(4-4)
(5-5)

-10   0   +10   20   30   40   Δλ

FIG 6

YO
HEADS OF Q₂ BRANCHES

(0-0) 6132.1A
(1-1) 6148.4A
(2-2) 6165.1A
(3-3) 6182.3A
(4-4) 6199.9A
(5-5) 6218.0A
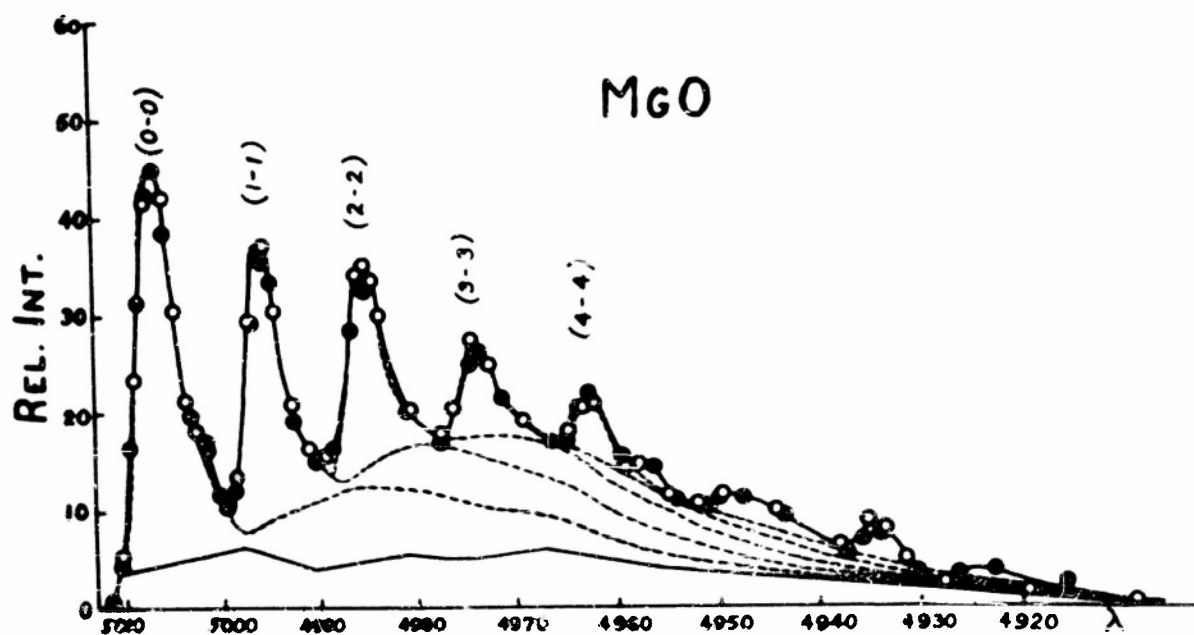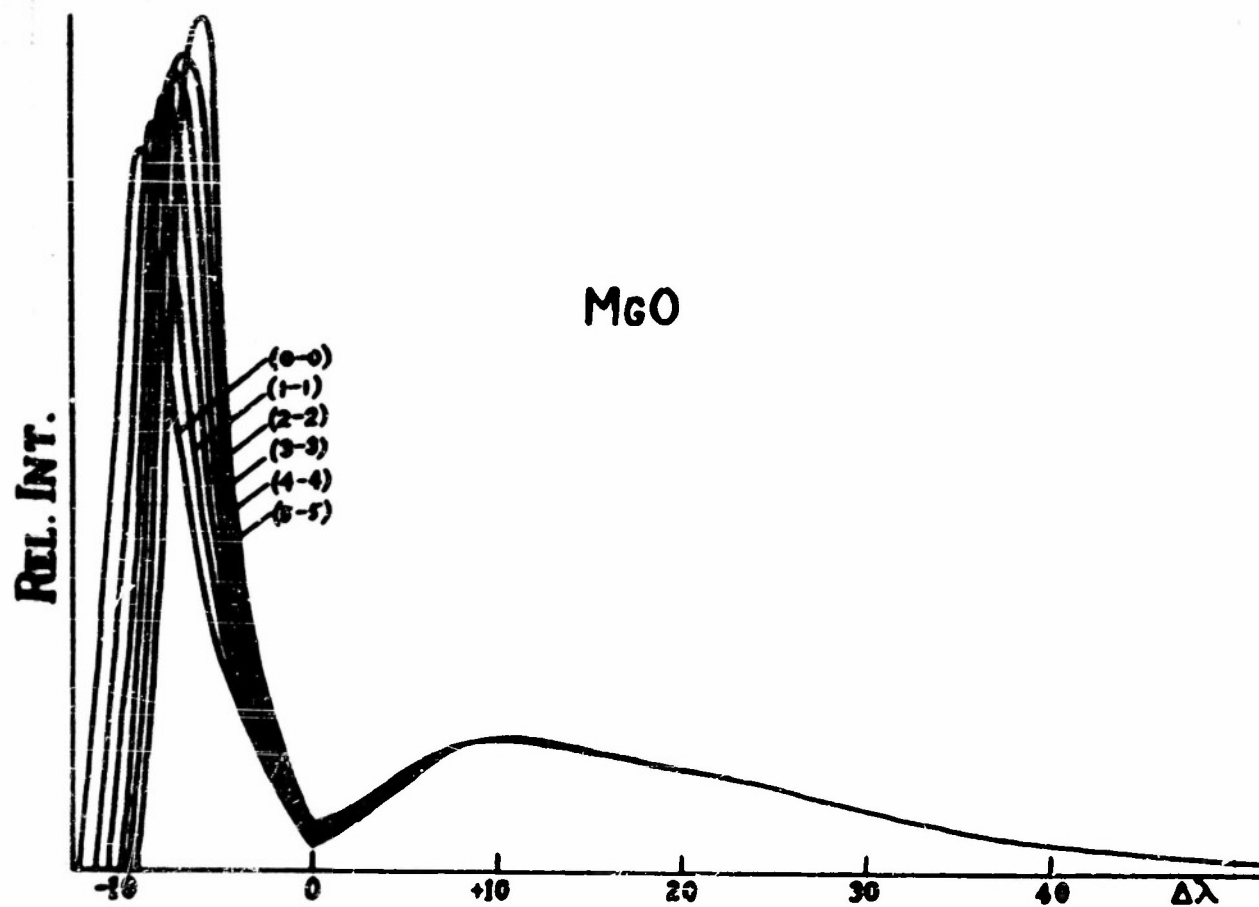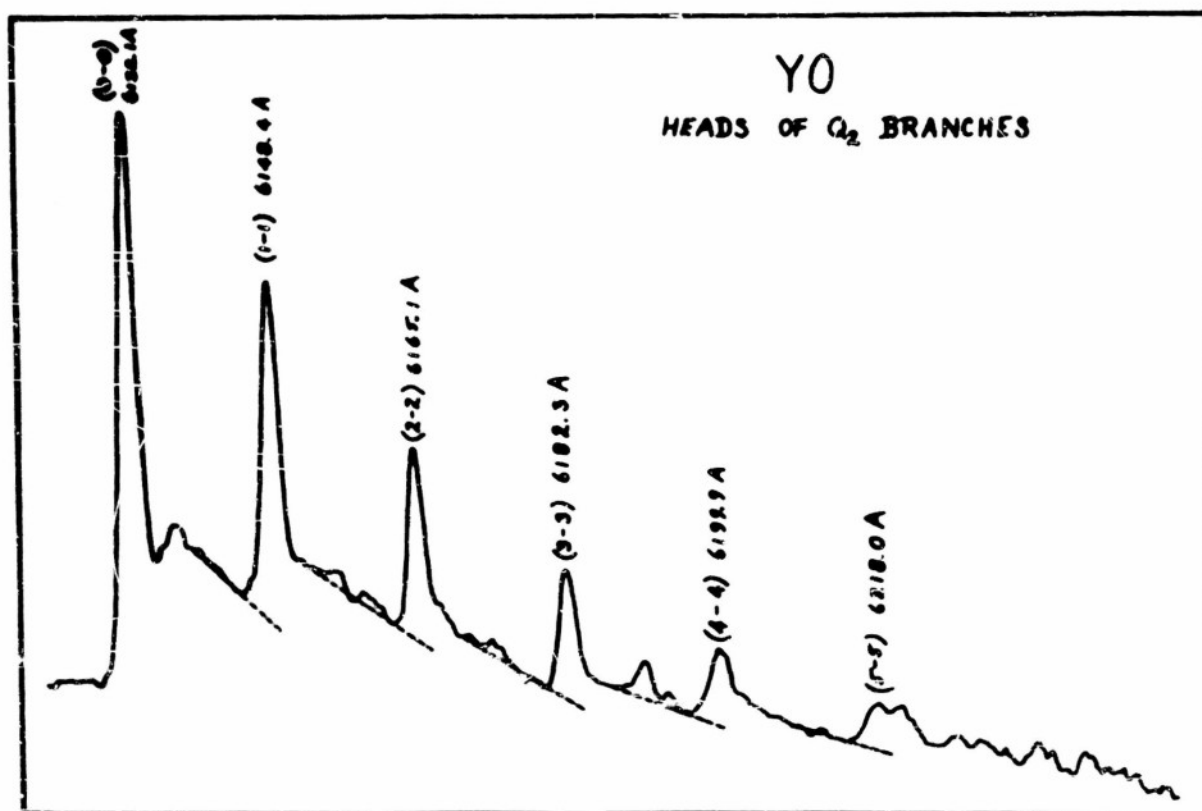
FIG. 7

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