**Title**

CALCULATED VIOLET BAND HEADS OF MAGNESIUM OXIDE

**Permalink**

https://escholarship.org/uc/item/0f1493c4

**Author**

Green, David W..

**Publication Date**

1967-10-01

# University of California

# Ernest O. Lawrence Radiation Laboratory

CALCULATED VIOLET BAND HEADS OF MAGNESIUM OXIDE

David W. Green

October 1967

# DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

CALCULATED VIOLET BAND HEADS OF MAGNESIUM OXIDE

David W. Green

October 1967

# CALCULATED VIOLET BAND HEADS OF MAGNESIUM OXIDE

David W. Green

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
Department of Chemistry, University of California
Berkeley, California

## ABSTRACT

A computer program has been written to calculate band heads from
known spectroscopic constants. Many of the observed, but unassigned,
band heads in the region from 3600 Å to 4000 Å in the spectrum of MgO
have now been assigned.

## I.  INTRODUCTION

The MgO molecule has a red spectrum[1,2,3] attributed to $B^1\Sigma^+-A^1\Pi$, a green spectrum[1-7] attributed to $B^1\Sigma^+-X^1\Sigma^+$ and a complex violet system. At least two emitters give band heads in the region 3600 Å to 4000 Å, namely MgO and MgOH.  Extensive overlap has made early analyses difficult and only band heads have been reported.[5,8-14]  Recently high resolution studies[15,16] have assigned two MgO electronic transitions within the violet region.  The lower state is $A^1\Pi$ and the upper states have been assigned as $C^1\Sigma^-$ and $D^1\Delta$.[16]

The only band heads assigned in the violet region are those analyzed in high resolution,[15,16] and those attributed to MgOH.[11]  With the spectroscopic constants of the three states of MgO involved in the violet transitions, it was felt that additional features could be assigned to other bands of these electronic transitions.

## II.  COMPUTER PROGRAM

Program "Heads" was written for the CDC 6600 computer to calculate band heads from the spectroscopic rotational and vibrational constants. The program requires as input data $\omega_e$, $\omega_e x_e$, $\omega_e y_e$, $B_e$, $\alpha_e$, $D_e$ and $\beta_e$ for both electronic states as well as $\nu_e$ for the transition. A flow diagram of the program is shown in Fig. 1.

The vibrational energies and rotational constants for that vibrational level are calculated for both states.

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3$$

$$B_v = B_e - \alpha_e(v + 1/2) \tag{1}$$

$$D_v = D_e + \beta_e(v + 1/2)$$

The Q-head occurs at the origin and may be calculated immediately. There is one Q-head for every band in this program.

$$\text{Origin} = \nu_e + G'(v) - G''(v) \tag{2}$$

The primes refer to the upper state and the double primes to the lower state. The computer then calculates either a P or an R head for each band. Normally an R-head occurs when $B_v'' > B_v'$ and a P-head when $B_v'' < B_v'$. If the $B_v$ values are identical in both states, the $D_v$ values will determine the head.

The rotational energy, $F_v(J)$, of a vibronic state used in this program contained both a $B_v$ term and a $D_v$ term. The neglect of higher terms could affect the J value of calculated heads if J is large.
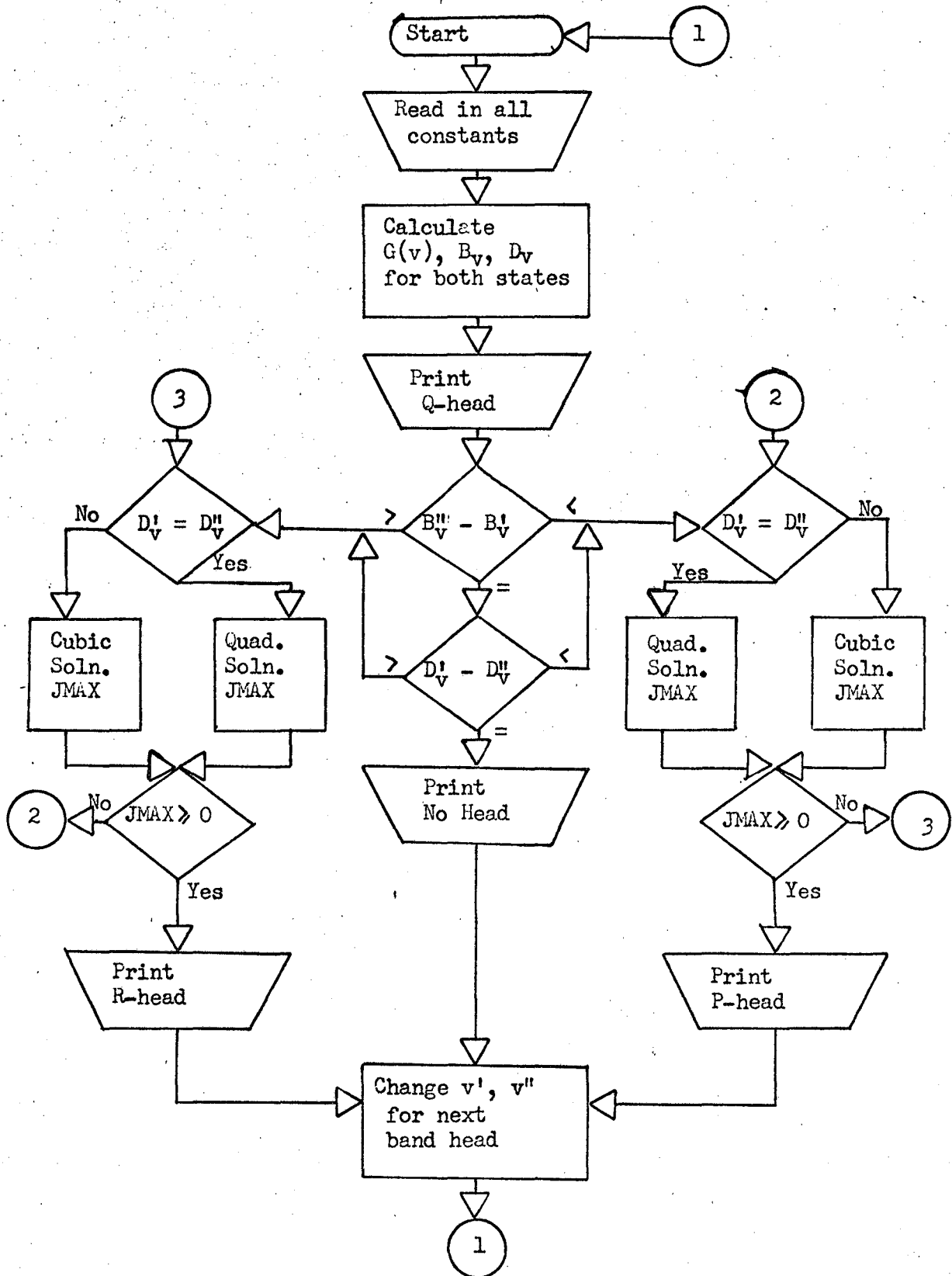
$$F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 \tag{3}$$

Figure 1. Flow diagram for program "Heads."

R and P lines may be represented in terms of $F_v(J)$.

$$R(J) = \text{Origin} + F_v'(J + 1) - F_v''(J)$$

$$(4)$$

$$P(J) = \text{Origin} + F_v'(J - 1) - F_v''(J)$$

The value of J at which a P-head is formed is found by solving the equation of $\partial P(J)/\partial J = 0$.

$$J^3 + J^2 \frac{3(D_v'' + d_v')}{2(D_v'' - D_v')} + J \frac{(B_v' - B_v'' - D_v' + D_v'')}{2(D_v'' - D_v')} + \frac{(B_v' + B_v'')}{4(D_v' - D_v'')} = 0 \quad (5)$$

If $D_v'$ and $D_v''$ are equal the equation becomes quadratic and is treated separately in the computer. An analogous equation is solved for an R-head. Care must be taken to distinguish the physically real root or roots from the mathematical ones.

It should be noted that the $D_v$ terms are very important in determining the heads in MgO. Estimates of the J of heads obtained by solving the linear equations (only $B_v$ values) are greatly in error. In addition, for some MgO bands the $B_v$ values are so close that an R-head is formed even though $B_v' > B_v''$. This is shown in the flow diagram by testing the J of the head (JMAX) to see if it is positive.

The program begins with $v' = 0$ and $v'' = 0$ and increases $v'$ by one until it reaches some chosen limit. Then it sets $v'' = 1$ and calculates the same number of bands for this $v''$, etc. In this work the computer calculated bands from (0,0) to (10,10).

## III. RESULTS

The spectroscopic constants for the $^1\Sigma^-$, $^1\Delta$ and $^1\Pi$ states were taken from the paper of Trajmar and Ewing.[16] Calculations were made for all 121 bands with v' and v" less than 10. Comparison is made in Tables I and II with the unassigned observations of Pesic,[6] Verhaeghe,[8] Barrow and Crawford,[5] and Pesic and Gaydon[11] for the two electronic transitions $C^1\Sigma^-$-$A^1\Pi$ and $D^1\Delta$-$A^1\Pi$. No head occuring at a J greater than 100 is listed and only a few of the bands calculated by the program are listed. All heads are given as Qv'v" etc. and the J at which the P or R-heads occur is given. The calculated wavelengths listed are corrected to air by interpolation of the formula given by Edlén.[17] The data of Pesic and Gaydon were corrected to obtain vacuum wave-numbers from wave length in air. All comparisons are then made in terms of vacuum wave-numbers.

It should be noted that a systematic error in the work of Verhaeghe shows up in the (0,0) sequence of the $^1\Delta$-$^1\Pi$ transition as a constant difference of 6 $cm^{-1}$.

Tables III and IV compare similar data for the isotopic $MgO^{18}$ molecule to unassigned heads observed by Pesic.[6] The Q01 head of the $^1\Sigma^-$-$^1\Pi$ transition can be assigned in the $MgO^{18}$ molecule, but has not been seen in the $MgO^{16}$ molecule. In view of the expected Franck-Condon factors,[18] this assignment is tentative.

Naturally occurring magnesium has three stable isotopes. $Mg^{25}$ and $Mg^{26}$ constitute little more than 10% each and might be expected to contribute weak features to the violet spectrum. Tables V and VI show the expected positions of these isotopic band heads as well as the calculated isotopic shift.

The error caused by the neglect of higher terms in J has been evaluated by means of a program which calculates rotational lines including an $H_v$ term in the rotational energy. In the (0,0) sequence of the $C^1\Sigma^- - A^1\Pi$ of MgO, the error caused by this neglect of higher terms is less than 0.1 $cm^{-1}$. Furthermore errors of this sort would appear systematically as a function of J in comparing observed heads to calculated heads. No such systematic error is observed.

Table I.   MgO$^{16}$  $^1\Sigma$-$^1\Pi$ band heads.

| Head | J | Calculated Å | Calculated cm$^{-1}$ | Pesic | Verhaeghe | Barrow and Crawford | Pesic and Gaydon |
|------|---|--------------|----------------------|-------|-----------|---------------------|------------------|
| R00 | 77 | 3768.3 | 26 545.0 | 26 545.1 | 26 543 | 26 545.9 | 26 545.2 |
| R11 | 68 | 74.0 | 504.7 | 505.0 | 502 | 505.1 | 505.0 |
| Q00 | | 74.6 | 500.8 | 501.3 | | 500.9 | 501.3 |
| Q11 | | 79.5 | 466.2 | 465.7 | 459 | 466.0 | 465.8 |
| R22 | 62 | 80.0 | 463.0 | 462.9 | 459 | 462.7 | 462.9 |
| Q22 | | 84.8 | 429.1 | 428.9 | | 431.8 | 429.0 |
| R33 | 56 | 86.2 | 419.4 | 418.2 | 415 | 419.9 | 418.2 |
| Q33 | | 90.5 | 389.2 | 388.4 | | | 388.4 |
| R44 | 51 | 92.7 | 374.0 | 371.0 | 368 | 373.2 | 371.0 |
| Q44 | | 96.6 | 346.8 | | | | |
| R55 | 47 | 99.6 | 326.3 | | | | |
| Q55 | | 3803.1 | 301.8 | | | | |
| R10 | 47 | 3684.5 | 27 147.8 | | | | |
| Q10 | | 87.9 | 122.8 | | | | |
| R21 | 43 | 91.0 | 100.6 | | | | |
| Q2$\bar{1}$ | | 94.1 | 77.8 | | | | |
| R23 | 93 | 3870.1 | 25 846.4 | | | | |
| Q01 | | 70.4 | 844.2 | | | | |
| Q12 | | 74.5 | 817.4 | | | | |
| R34 | 83 | 76.2 | 805.9 | | | | |
| Q23 | | 78.9 | 788.1 | | | | |
| R20 | 32 | 3604.4 | 27 751.3 | | | | |
| Q20 | | 6.6 | 734.4 | | | | |
| R31 | 30 | 3611.8 | 27 694.8 | | | | |
| Q31 | | 13.8 | 679.0 | | | | |
| Q02 | | 3970.1 | 25 195.4 | | | | |
| Q13 | | 73.1 | 176.4 | | | | |
| Q24 | | 76.5 | 154.8 | | | | |

Table II.  MgO$^{16}$  $^1\Delta$-$^1\Pi$ band heads.

| Head | J | Calculated Å | Calculated cm$^{-1}$ | Pesic | Verhaeghe | Barrow and Crawford | Pesic and Gaydon |
|------|------|------|------|------|------|------|------|
| R00 | 83 | 3800.4 | 26 320.6 | 26 320 | 26 314. | 26 320.2 | 26 320.5 |
| R11 | 74 | 6.4 | 279.3 | 279.6 | 273 | 279.1 | 279.6 |
| Q00 | | 7.4 | 272.0 | 271.8 | | 271.8 | 271.9 |
| Q11 | | 12.5 | 237.3 | 237.2 | 231 | 237.4 | 237.3 |
| R22 | 66 | 12.6 | 236.5 | 237.2 | | 237.4 | 237.3 |
| Q22 | | 17.9 | 199.8 | 200.1 | | 200.8 | 200.1 |
| R33 | 60 | 19.1 | 192.0 | | 186 | 195 | |
| Q33 | | 23.8 | 159.5 | | | | 160.3 |
| R44 | 54 | 25.9 | 145.4 | | 139 | 145 | |
| Q44 | | 30.1 | 116.4 | | | | |
| R55 | 50 | 33.0 | 96.6 | | | | |
| Q55 | | 36.8 | 70.5 | | | | |
| R10 | 49 | 3715.8 | 26 920.4 | | | | |
| Q10 | | 19.4 | 893.9 | | | | |
| R21 | 45 | 22.4 | 872.7 | | | | |
| Q21 | | 25.7 | 848.6 | | | | |
| Q01 | | 3905.0 | 25 615.4 | 25 616.7 | 25 600 | | 25 616.7 |
| Q12 | | 9.1 | 588.5 | 589.0 | | 591 | 589.1 |
| R34 | 89 | 10.2 | 581.4 | | | | |
| Q23 | | 13.6 | 558.8 | 559.2 | 561 | | 559.2 |
| R45 | 80 | 16.8 | 538.4 | | | | |
| Q34 | | 18.6 | 526.3 | 526.5 | 519 | | 526.5 |
| R56 | 72 | 23.6 | 494.1 | | | 494.9 | |
| Q45 | | 24.0 | 491.0 | 490.3 | 480 | | 490.3 |
| Q56 | | 29.9 | 452.9 | | | 454 | |
| R67 | 65 | 3930.7 | 25 448.2 | | | | |
| Q67 | | 36.2 | 412.0 | | | | |
| R20 | 33 | 3634.3 | 27 522.9 | | | | |
| Q20 | | 36.7 | 505.2 | | | | |
| R31 | 31 | 41.9 | 465.7 | | | | |
| Q31 | | 44.1 | 449.3 | | | | |
| Q02 | | 4006.4 | 24 966.6 | | | | |
| Q13 | | 9.5 | 947.5 | | | | |

Table III. $MgO^{18}$ $^1\Delta-^1\Pi$ band heads.

| Head | J | Calculated Å | Calculated cm$^{-1}$ | Pesic | Calculated Isotope Shift | Observed Isotope Shift |
|---|---|---|---|---|---|---|
| R00 | 85 | 3800.7 | 26 318.6 | 26 318 | - 2.0 | -2 |
| R11 | 75 | 6.4 | 278.9 | 278.1 | - .4 | -1.5 |
| Q00 | | 7.3 | 272.6 | 271.8 | .6 | 0.0 |
| Q11 | | 12.2 | 239.2 | 238.1 | .7 | .9 |
| R22 | 67 | 12.4 | 238.0 | 238.1 | 1.5 | .9 |
| Q22 | | 17.4 | 203.1 | 202.0 | 3.3 | 1.9 |
| R33 | 61 | 18.6 | 195.4 | 195.3 | .3.4 | 6.8 |
| Q33 | | 23.1 | 164.5 | | 5.0 | |
| R44 | 55 | 25.1 | 150.9 | | 4.5 | |
| Q44 | | 29.1 | 123.2 | | 6.8 | |
| R55 | 51 | 31.9 | 104.3 | | 7.7 | |
| Q55 | | 35.6 | 79.3 | | 8.8 | |
| R10 | 51 | 3718.7 | 26 899.0 | | -21.4 | |
| Q10 | | 22.2 | 873.7 | | -20.2 | |
| R21 | 46 | 25.0 | 853.4 | | -19.3 | |
| Q21 | | 28.2 | 830.4 | | -18.2 | |
| Q01 | | 3901.6 | 25 638.1 | 25 638.3 | 22.7 | 21.6 |
| Q12 | | 5.5 | 611.9 | 611.6 | 23.4 | 22.6 |
| R34 | 91 | 6.7 | 603.9 | | 22.5 | |
| Q23 | | 9.9 | 583.2 | 582.6 | 24.4 | 23.4 |
| R45 | 81 | 12.0 | 562.7 | | 24.3 | |
| Q34 | | 13.7 | 551.8 | 551.3 | 25.5 | 24.8 |
| R56 | 73 | 19.5 | 520.3 | | 26.2 | |
| Q45 | | 19.9 | 517.8 | 516.5 | 26.8 | 26.2 |
| Q56 | | 3925.6 | 25 481.2 | | 28.3 | |
| R67 | 67 | 26.3 | 476.4 | | 28.2 | |
| R20 | 34 | 3639.8 | 27 481.8 | | -41.1 | |
| Q20 | | 42.1 | 465.0 | | -40.2 | |
| R31 | 32 | 47.0 | 427.5 | | -38.2 | |
| Q31 | | 49.1 | 411.7 | | -37.6 | |
| Q02 | | 399.4 | 25 010.8 | | 44.2 | |
| Q13 | | 4002.4 | 24 991.9 | | 44.4 | |

Table IV.  $MgO^{18}$  $^1\Sigma - ^1\Pi$ band heads.

| Head | J | Calculated Å | Calculated cm$^{-1}$ | Pesic | Calculated Isotope Shift | Observed Isotope Shift |
|------|---|--------------|----------------------|-------|--------------------------|------------------------|
| R00 | 78 | 3768.6 | 26 543.1 | 26 543.1 | - 1.9 | -2.0 |
| R11 | 70 | 74.0 | 504.5 | 504.4 | - .2 | -.6 |
| Q00 |  | 74.5 | 501.4 | 501.0 | .6 | -.3 |
| Q11 |  | 79.2 | 468.1 | 468.5 | 1.9 | 3.2 |
| R22 | 63 | 79.7 | 464.5 | 464.0 | 1.5 | 1.1 |
| Q22 |  | 84.3 | 432.3 | 428.1 | 3.2 | -.8 |
| R33 | 57 | 85.7 | 422.8 | 421.1 | 3.4 | 2.9 |
| Q33 |  | 89.8 | 394.1 | 392.4 | 4.9 | 4.0 |
| R44 | 52 | 91.9 | 379.3 | 376.8 | 5.3 | 5.8 |
| Q44 |  | 95.7 | 353.5 |  | 6.7 |  |
| R55 | 48 | 98.5 | 333.9 |  | 7.6 |  |
| Q55 |  | 3801.9 | 310.5 |  | 8.7 |  |
| R10 | 48 | 3687.5 | 27 126.4 |  | -21.4 |  |
| Q10 |  | 90.9 | 102.6 |  | -20.2 |  |
| R21 | 44 | 93.8 | 81.3 |  | -19.3 |  |
| Q21 |  | 96.8 | 59.6 |  | -18.2 |  |
| R23 | 94 | 3867.0 | 25 867.3 |  | 20.9 |  |
| Q01 |  | 67.1 | 866.9 | 25 866.6 | 22.7 |  |
| Q12 |  | 70.9 | 840.8 |  | 23.4 |  |
| R34 | 84 | 72.8 | 828.6 |  | 22.7 |  |
| Q23 |  | 75.2 | 812.3 |  | 24.2 |  |
| R45 | 76 | 78.7 | 789.0 |  | 24.3 |  |
| R20 | 33 | 3609.8 | 27 710.3 |  | -41.0 |  |
| Q20 |  | 3611.9 | 27 694.1 |  | -40.3 |  |
| R31 | 31 | 16.8 | 656.5 |  | -38.3 |  |
| Q31 |  | 18.8 | 641.4 |  | -37.6 |  |
| Q02 |  | 3963.1 | 25 239.6 |  | 44.2 |  |
| Q13 |  | 66.1 | 220.8 |  | 44.4 |  |

Table V.  Mg$^{25}$O band heads.

| Head | Upper State | J | Calculated Å | Calculated cm$^{-1}$ | Calculated Isotope Shift |
|------|-------------|---|--------------|----------------------|--------------------------|
| R00 | Δ | 84 | 3800.5 | 26 320.1 | -.5 |
| R11 | Δ | 74 | 6.4 | 279.2 | -.1 |
| Q00 | Δ | | 7.4 | 272.2 | .2 |
| Q11 | Δ | | 12.4 | 237.8 | .5 |
| R10 | Δ | 50 | 3716.4 | 26 915.4 | -5.0 |
| Q10 | Δ | | 20.1 | 889.2 | -4.7 |
| Q01 | Δ | | 3904.2 | 25 620.8 | 5.4 |
| R20 | Δ | 34 | 3635.6 | 27 513.2 | -9.7 |
| Q20 | Δ | | 38.0 | 495.7 | -9.5 |
| Q02 | Δ | | 4004.8 | 24 977.1 | 10.5 |
| R00 | Σ | 77 | 3768.4 | 26 544.5 | -.5 |
| R11 | Σ | 69 | 74.0 | 504.6 | -.1 |
| Q00 | Σ | | 74.5 | 501.0 | .2 |
| Q11 | Σ | | 79.4 | 466.7 | .5 |
| R10 | Σ | 47 | 3685.3 | 27 142.7 | -5.1 |
| Q10 | Σ | | 88.7 | 118.1 | -4.7 |
| Q01 | Σ | | 3869.6 | 25 849.6 | 5.4 |
| R20 | Σ | 32 | 3605.7 | 27 741.6 | 9.7 |
| Q20 | Σ | | 7.9 | 724.9 | 9.5 |
| Q02 | Σ | | 3968.4 | 25 205.9 | 10.5 |

Table VI. $Mg^{26}O$ band heads.

| Head | Upper State | J | Calculated Å | Calculated cm$^{-1}$ | Calculated Isotope Shift |
|------|-------------|---|--------------|---------------------|--------------------------|
| R00 | Δ | 84. | 3800.5 | 26 319.7 | -.9 |
| R11 | Δ | 74 | 6.4 | 279.1 | -.2 |
| Q00 | Δ | | 7.4 | 272.3 | .3 |
| Q11 | Δ | | 12.3 | 238.2 | .9 |
| R10 | Δ | 50 | 3716.0 | 26 910.7 | -9.7 |
| Q10 | Δ | | 20.7 | 884.7 | -9.2 |
| Q01 | Δ | | 3903.4 | 25 625.8 | 10.4 |
| R20 | Δ | 34 | 3636.8 | 27 504.2 | -18.7 |
| Q20 | Δ | | 39.1 | 486.9 | -18.3 |
| Q02 | Δ | | 4003.2 | 24 986.8 | 20.2 |
| R00 | Σ | 77 | 3768.4 | 26 544.1 | -.9 |
| R11 | Σ | 69 | 74.0 | 504.6 | -.1 |
| Q00 | Σ | | 74.5 | 501.1 | .3 |
| Q11 | Σ | | 79.4 | 476.1 | .9 |
| R10 | Σ | 47 | 3685.9 | 27 138.0 | -9.8 |
| Q10 | Σ | | 89.2 | 113.6 | -9.2 |
| Q01 | Σ | | 3868.9 | 25 854.6 | 10.4 |
| R20 | Σ | 32 | 3606.9 | 27 732.6 | -18.7 |
| Q20 | Σ | | 9.0 | 716.1 | -18.3 |
| Q02 | Σ | | 3966.9 | 25 215.6 | 20.2 |

## IV. CONCLUSIONS

Agreement between calculated band heads and the unassigned ob-
servations is excellent. Further proof of the correctness of these
assignments comes from the agreement of the calculated isotopic shifts
and those observed by Pesic.[6] The observed band heads in Tables I and
II may be considered assigned. The calculated heads which have not
been observed are expected to be quite accurate and could possibly be
observed. Only small Franck-Condon factors hinder their observation.
Nearly all of the intensity of the $D^1\Delta$-$A^1\Pi$ is in the (0,0) sequence[18]
and, by analogy, the $C^1\Sigma^-$-$A^1\Pi$ is expected to be strong only in the
(0,0) sequence.

With these assignments it is expected that the complex violet
system of MgO and MgOH may be greatly simplified. Furthermore, pro-
gram "Heads" has proven to be a valuable tool in assigning low resolu-
tion spectra and can be expected to work equally well for other diatomic
molecules.

## ACKNOWLEDGMENTS

## REFERENCES

1.  P. C. Mahanti, Phys. Rev. 42, 609 (1932).

2.  P. C. Mahanti, Indian J. Phys. 9, 517 (1935).

3.  A. Lagerqvist and U. Uhler, Arkiv för Fysik 1, 459 (1949).

4.  P. N. Ghosh, P. C. Mahanti and B. C. Mukkerjee, Phys. Rev. 35, 1491
    (1930).

5.  R. F. Barrow and D. V. Crawford, Proc. Phys. Soc. A57, 12 (1945).

6.  D. S. Pesic, Proc. Phys. Soc. A76, 844 (1960).

7.  D. S. Pesic, Proc. Phys. Soc. 83, 885 (1964).

8.  J. Verhaeghe, Wis-en Natuurk. Tijdsche 7, 224 (1935).

9.  L. Brewer and R. Porter, J. Chem. Phys. 22, 1867 (1954).

10. L. Brewer and S. Trajmar, J. Chem. Phys. 36, 1585 (1962).

11. D. S. Pesic and A. G. Gaydon, Proc. Phys. Soc. A73, 244 (1959).

12. D. S. Pesic and M. Kliska, Glasnik Hem. Drustva Beograd 28 (7), 347
    (1963) Chem. Abstract 63:3786A.

13. S. Trajmar, UCRL-9773 (1961).

14. S. Trajmar and G. E. Ewing, J. Chem. Phys. 40, 1170 (1964).

15. L. Brewer, S. Trajmar and R. Berg, Astrophys. J. 135, 955 (1962).

16. S. Trajmar and G. E. Ewing, Astrophys. J. 142, 77 (1965).

17. B. Edlén, J. Opt. Soc. Am. 43, 339 (1953).

18. Y. P. Srivastava and R. C. Maheshwari, Proc. Phys. Soc. 90, 117 (1967).