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THE VIOLET BAWD SYSTEMS AND ELECTRONIC STATES OF GASEOUS MAGNESIUM OXIDE

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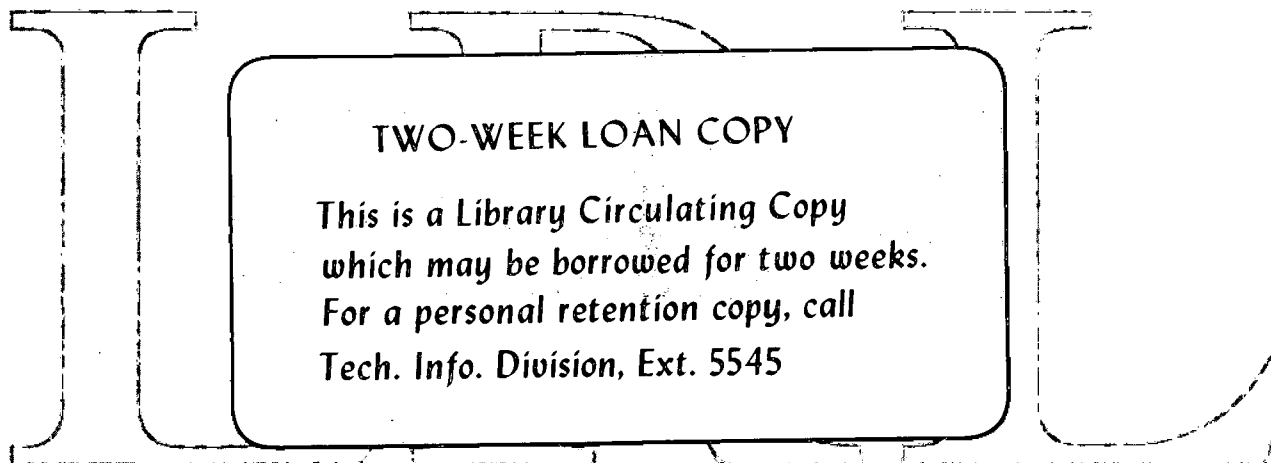
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The Violet Band Systems and Electronic States of Gaseous Magnesium Oxide

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## ABSTRACT

The nature of the known electronic states of gaseous magnesium oxide is discussed. Predictions are made of unobserved electronic states and their possible effect on the MgO spectrum. Dissociation products of the known states are suggested and the discrepancy between the spectroscopic extrapolation and the presently accepted dissociation energy of MgO is discussed. Assignments are made to a number of previously unassigned band heads in the violet spectrum of MgO. Two additional band systems in the violet region are assigned to the MgO molecule. The possible assignment of the  $C^1\Sigma^-$  and  $D^1\Delta$  states of MgO to triplets is considered.

## INTRODUCTION

The gaseous MgO molecule has a red band system<sup>1-4</sup> assigned to  $B^1\Sigma^+ - A^1\Pi$ , a green band system<sup>1-8</sup> attributed to  $B^1\Sigma^+ - X^1\Sigma^+$  and a complex violet spectrum. At least two emitters give band heads in the region from 3600 to 4000 Å, namely MgO and MgOH. Extensive overlap of bands has made early analyses difficult and only unassigned band heads have been reported.<sup>6,9-16</sup> Recently high resolution studies<sup>17,18</sup> have assigned two MgO electronic transitions within the violet region. The medium resolution arc spectrum of MgO has been re-examined in the violet region from a source in which the contamination from MgOH has been reduced in order to determine which bands could be attributed to transitions between known electron states and which to new transitions. A consideration of the known electronic states has been undertaken in order to assign molecular orbital configurations and to predict which other electronic states may be important in the MgO molecule.

## THEORY

Table I summarizes the experimental data for the states of the violet bands<sup>18</sup>, the green and red bands.<sup>3</sup> The spectroscopic constants of the C and D states are of special interest. The small energy separation ( $229 \text{ cm}^{-1}$ ) reported between these states and the extreme similarity of the spectroscopic constants leads to speculation that the C and D states could actually be components of a triplet state. This point will be discussed later in connection with calculations and experimental results.

One of the most striking results of a consideration of the molecular states arising from various atomic states of magnesium and oxygen is that only triplet molecular states arise from ground state atoms as shown in Fig. 1. The atomic energy levels have been taken from Moore.<sup>19</sup> The lowest atomic configuration which gives singlet electronic molecular states is  $15\,868\text{ cm}^{-1}$  above the ground-state atoms. A singlet molecular ground-state from neutral atoms would be expected only if the bonding energy between magnesium  $^1S$  and oxygen  $^1D$  is at least  $15\,868\text{ cm}^{-1}$  greater than the bonding between magnesium  $^1S$  and oxygen  $^3P$ .

Using an ionization potential of  $61\,669\text{ cm}^{-1}$  for magnesium<sup>19</sup> and an electron affinity of  $11\,857\text{ cm}^{-1}$  for oxygen<sup>20</sup>, the ground-state ions lie about  $49\,800\text{ cm}^{-1}$  above the ground-state of the neutral atoms. This is low enough to have a considerable effect on the character of the low-lying electronic states if it does not in fact give rise to the molecular ground-state.

Since five electronic states have now been characterized for MgO, a thorough consideration of the molecular orbitals and assignment of the known states to particular configurations seems useful. Of particular interest is the estimation of the number and possible energies of triplet electronic states and the prediction of which electronic transitions should be available for analysis of the MgO spectrum. The "Third-Law" determination of the dissociation energy of the MgO molecule depends on the energies of low-lying electronic states, especially triplet states whose large degeneracy can appreciably affect the internal partition function.



Table II presents the molecular orbital configurations and corresponding electronic states which may be expected to be low in energy. Estimation of which orbitals are low-lying is based on the calculated orbital energies of McLean and Yoshimine<sup>21</sup> for the molecular orbital configuration I of Table II. Eight configurations are considered involving single and double excitations from the calculated<sup>22</sup> electronic ground-state (configuration I).

Table III shows the term energies of a limited basis set ICAO MO SCF calculation of configurations I, II, and III.<sup>22</sup> A semi-empirical correlation energy correction is included in the energies of Table III. Before correction, the  $^3\Pi_1$  (configuration II) and  $^3\Sigma^+$  (III) were approximately 12 000 and 9 000  $\text{cm}^{-1}$  lower in energy than the  $^1\Sigma^+$  (I). The uncertainty in the use of a limited basis set and in application of correlation effects leaves open the possibility that MgO has a triplet electronic ground-state. The calculations suggest at least two low-lying triplet electronic states.

A qualitative analysis\* of the configurations I, II and III shows the  $5\sigma$  orbital is very largely 2s AO centered on the oxygen atom; the  $2\pi$  orbital is largely  $2p\pi$  AO centered on oxygen with some  $3p\pi$  and  $3d\pi$  on Mg and the  $7\sigma$  orbital is mostly 3s AO on Mg with some  $3p\sigma$  on Mg and some  $2p\sigma$  on O. The  $6\sigma$  orbital is 45% 3s on Mg and 55%  $2p\sigma$  on O in

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\*A partial population analysis was used in ref. 22 for estimation of correlation energies. Ref. 21 contains information on calculations with a larger basis set for configuration I from which estimates of a population analysis may be made.

configuration I while it is almost entirely  $2p\sigma$  in configuration III.<sup>22</sup> So the low-lying molecular orbital configurations are quite ionic in character being very nearly like  $Mg^+$  and  $O^-$  for configurations I, II and III. The  $3\pi$  orbital is largely  $3p\pi$  on Mg.

It is difficult to assign the observed electronic states of MgO to particular molecular orbital configurations because configuration mixing can be expected to be quite important. There are five  $^1\Sigma^+$  states and three  $^1\Pi$  states listed in Table II which may interact. From the atomic viewpoint, the four molecular states from the ground-state atomic ions can be expected to interact with molecular states from neutral atoms causing unusual and irregular potential curves.

It is postulated that the  $X^1\Sigma^+$  state of MgO is associated with configuration I and the  $A^1\Pi$  state with configuration II. The  $B^1\Sigma^+$  state is likely a mixture of configurations, perhaps very complex. Its steep potential curve (see Table IV and Fig. 2) suggests unusual behavior and irregularities in vibrational structure<sup>23</sup> suggest interaction of potential curves. Further information is needed to determine the nature of this state.

The electronic states from configuration VII are of interest since the only  $^1\Sigma^-$  state comes from this configuration. It will be assumed in this discussion that the assignment of all MgO electronic states is correct. A discussion of the possibility that the assignment is incorrect will be presented later in this paper. The splitting of the states of the  $\pi^3\pi$  configuration has been discussed<sup>24</sup> for  $N_2$  and they may be represented relative to the  $^3\Delta$  as

$$\Delta E(1\Sigma^+) = -2B + 4C$$

$$\Delta E(3\Sigma^+) = -2B$$

$$\Delta E(1\Sigma^-) = 2B$$

$$\Delta E(3\Sigma^-) = 2B$$

$$\Delta E(1\Delta) = 4D$$

where the constants B, C and D are 5 000, 36 900 and 4 200  $\text{cm}^{-1}$  in the  $\text{N}_2$  molecule.<sup>23</sup> Assuming the C and D states of MgO to be derived from molecular orbital configuration VII and assuming the constant B to be about 5 000  $\text{cm}^{-1}$  in MgO, the energies of all states of configuration VII, except the  $1\Sigma^+$  which is assumed to be very high in energy as in  $\text{N}_2$ , may be predicted.

$$E(3\Sigma^+) = 10\,000\ \text{cm}^{-1}$$

$$E(1\Sigma^-) = 30\,000$$

$$E(3\Sigma^-) = 30\,000$$

$$E(1\Delta) = 30\,000$$

$$E(3\Delta) = 20\,000$$

Although the energies of these states cannot be accurately predicted without further information, the present assignment combined with available experimental data does predict five electronic states from configuration VII whose energies are less than 30 000  $\text{cm}^{-1}$ . Small changes in the constants B and D change the energies of the  $3\Sigma^+$  and the  $3\Delta$ . For example, if B is 7 500  $\text{cm}^{-1}$  the  $3\Sigma^+$  from this configuration will be degenerate with the  $X^1\Sigma^+(I)$  state. Furthermore the  $3\Sigma^+$  state from this configuration will interact with the  $3\Sigma^+$  from configuration II. The mutual repulsion will depress the lower energy  $3\Sigma^+$  thus increasing the possibility of a very low-lying triplet state.

Since configuration VII appears to be the only reasonable configuration to account for a  ${}^1\Sigma^-$  electronic state as low in energy as  $30\,000\text{ cm}^{-1}$ , this configuration assignment is most probably correct. There are two configurations giving  ${}^1\Delta$  states, but in view of the extreme similarity of the spectroscopic constants of the C and D states (see Table I) it seems quite likely that they are from the same molecular orbital configuration. From consideration of the calculated orbital energies<sup>21</sup> and the assignment of the C and D states of MgO to configuration VII, it seems probable that all eight configurations of Table II have low-lying electronic states. By applying the normal selection rules for electronic transitions to the states of Table II, ten triplet transitions whose lower state is either  ${}^3\Pi_1$ (II) or  ${}^3\Sigma^+$ (III) and sixteen singlet transitions whose lower state is either  ${}^1\Sigma^+$ (I) or  ${}^1\Pi$ (II) would be predicted. Not all of these transitions would be expected to be easily accessible for analysis due to overlap, inherent weakness, or location of the spectrum in an inconvenient spectral region.

The Morse potential curves of the known states of MgO are shown in Fig. 2 and Table IV summarizes the Morse dissociation limits and total energy of dissociation products. The lowest energy dissociation products giving a  ${}^1\Sigma^+$  state are the Mg( ${}^1S$ ) and O( ${}^1D$ ) (see Fig. 1) so this excitation energy ( $15\,868\text{ cm}^{-1}$ ) must be subtracted from the Morse curve limit of the  $X^1\Sigma^+$  state to obtain the dissociation energy. This value of  $13\,400\text{ cm}^{-1}$  (1.66 eV or 38.3 kcal/mole) is considerably less than the corrected<sup>22</sup> "Third Law" mass spectrometric<sup>25</sup> value of 81 kcal/mole ( $28\,000\text{ cm}^{-1}$  or 3.5 eV). Transpiration experiments<sup>26,27</sup> have been corrected to give a dissociation energy of  $82 \pm 5\text{ kcal/mole}$  which is felt to be reliable.<sup>28</sup> Even higher dissociation energies have been proposed.\*

\* See Ref. 29 p. 240 or Ref. 28 for summaries.

Although the vibrational structure of the  $X^1\Sigma^+$  state appears<sup>23</sup> normal to  $v=7$ , interactions nearer the dissociation limit could make the potential curve behave anomalously. Another suggestion to explain the lack of agreement between the spectroscopic experimental dissociation limits is that MgO has a triplet state (or states) lower in energy than the  $X^1\Sigma^+$ .

A third alternative explanation is that the previously discussed ionic character of the MgO bonding makes the Morse curve approximation very inaccurate. The alkali metal halides extrapolate to dissociation energies in the Morse potential approximation that are lower than the accepted values.<sup>29</sup> It is felt that evidence for this occurrence in MgO should be the failure of a two term expansion in  $(v + \frac{1}{2})$  to fit the vibrational levels of the  $X^1\Sigma^+$  state. This evidence is not available and some evidence to the contrary exists.<sup>23</sup> Since the discrepancies in the alkali metal halides are often as large or larger than the discrepancy in MgO, this explanation must be considered possible for all or part of the difference. A study of the higher vibrational levels of the  $X^1\Sigma^+$  state would be useful to clarify this point.

Attention should be called to the dissociation limits of other states in Table IV. The  $A^1\Pi$  state goes to nearly the same limit as the  $X^1\Sigma^+$  state. This is consistent with dissociation to  $Mg(^1S)$  and  $O(^1D)$ . The  $B^1\Sigma^+$  state is exceptionally stable and may be considerably affected by the molecular states from  $Mg^+$  and  $O^-$ .

The  $C^1\Sigma^-$  and  $D^1\Delta$  states have shallow potentials apparently going to the same limit. The lowest dissociation products giving both a  $^1\Sigma^-$  and a  $^1\Delta$  state are  $Mg(^3P)$  and  $O(^3P)$ . The corresponding dissociation energy of  $26\,700\text{ cm}^{-1}$  (3.31 eV or 76.3 kcal/mole) is considerably closer to an acceptable value than that obtained from the extrapolations of the  $A^1\Pi$  and the  $X^1\Sigma^+$  states. The molecular orbital configuration VII assigned to the  $C^1\Sigma^-$  and  $D^1\Delta$  states comes from the promotion of a  $2\pi$  electron which is largely  $2p\pi$  on oxygen to a  $3\pi$  orbital which is largely  $3p\pi$  on magnesium. The bonding in these two states therefore is considerably less ionic in character than in the  $A^1\Pi$  (II) and the  $X^1\Sigma^+$  (I). Extrapolation by Morse curves may be expected to be more reliable and hence the dissociation energy determined from these states is probably more accurate.

It is possible that the  $C^1\Sigma^-$  and  $D^1\Delta$  dissociate to more highly excited products, but this seems unlikely since it would require a large number of additional electronic states lower in energy than these two if the non-crossing rule holds. It may be concluded that if there are electronic states lower in energy than the  $X^1\Sigma^+$ , they are probably not very much lower. This correlation provides a more stringent limit on states lower than the  $X^1\Sigma^+$  than does the discrepancy between the extrapolations of the  $X^1\Sigma^+$  and the "correct" dissociation energy.

If the correlation of the  $D^1\Delta$  to  $Mg(^3P)$  and  $O(^3P)$  dissociation products is correct, then another  $^1\Delta$  state must exist below  $30\,000\text{ cm}^{-1}$  which correlates to the  $Mg(^1S)$  and  $O(^1D)$ . Most probably this  $^1\Delta$  comes from configuration IV of Table II. Since by Hund's rules the  $^3\Sigma^-$  from this configuration is lower in energy than the  $^1\Delta$ , this correlation gives further evidence for the existence of a low-lying triplet state.

The correlations presented seem reasonable and consistent with available data. Additional experimental work will be necessary to unambiguously solve the discrepancy between the spectroscopic and thermodynamic data. The determination of the energies of low-lying triplet states is of prime importance.

## EXPERIMENTAL

### A. Computer Program

The rotational energy of MgO requires three terms in the expansion of  $J(J + 1)$  in order to adequately represent the observed rotational energy levels at high  $J$ .<sup>18</sup> Many band heads of the violet system occur at high  $J$  due to the similarity of  $B_v'$  and  $B_v''$ . The complex violet spectrum of MgO and MgOH has two assigned transitions, the  $C^1\Sigma^- - A^1\Pi$  and the  $D^1\Delta - A^1\Pi$  of MgO. Only lines of the (0,0) and (1,1) bands of each transition have been rotationally analyzed.<sup>17,18</sup> In order to properly assign other band heads in the spectral region 3600-4000 Å, accurate calculations were needed for the wavelengths of other vibrational bands of these known transitions.

A computer program was written to calculate the wavelength in air and wave number in vacuum of band heads belonging to electronic transitions for which the spectroscopic constants of both states are known. Eq. (1) is the cubic equation to be solved to determine the  $J$  value at which a P-branch forms a head.

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$$J^3 + J^2 \frac{3(D_v'' + D_v')}{2(D_v'' - D_v')} + J \frac{(B_v' - B_v'' - D_v' + D_v'')}{2(D_v'' - D_v')} + \frac{(B_v' + B_v'')}{4(D_v' - D_v'')} = 0 \quad (1)$$

This equation is derived from approximating the rotational energies of the upper and lower states by

$$F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 \quad (2)$$

where  $B_v = B_e - \alpha_e(v + \frac{1}{2})$  and  $D_v = D_e + \beta_e(v + \frac{1}{2})$ . A cubic equation similar to Eq. (1) must be solved to determine the J value of an R-head. Q-heads are easily calculated since they occur at the origin.

It should be noted that determination of the band head by approximating  $F_v(J) = B_v J(J + 1)$  gave erroneous and inaccurate results. In some cases this approximation predicted a band head in the wrong branch.

## B. Magnesium Oxide Arc

In order to reduce contamination of the MgO spectrum by OH and MgOH, a vacuum arc system was constructed. Background pressures less than  $10^{-5}$  Torr were obtained with a 10 cm diameter oil diffusion pump and by passing the oxygen gas over phosphorous pentoxide and through a liquid nitrogen trap. The arc electrodes were tungsten rods passed through pyrex with Kovar seals. A copper adapter to the cathode held magnesium metal. An air flow outside the vacuum system cooled the anode. Exposure times were limited to 30 to 90 seconds by over-heating of the anode. A variable resistance adjusted the D.C. current flow to 1.0 to 1.5A. The arc was run in a closed system with about 1-10 Torr of oxygen.



The image of the arc was focussed onto the slit of a 0.75 m Spex spectrograph having a Czerny-Turner kinematic mount. A one micron blaze grating with 600 line/mm was used in third order for study of the violet band systems. The reciprocal linear dispersion was about  $7.1 \text{ \AA}/\text{mm}$  and with a ten micron spectrograph slit the resolution was  $0.07 \text{ \AA}$ . The spectrum was photographed on Kodak 103a-0 photographic plates. An Osram Hg/Cd spectral lamp was used as the source of standard lines.

The photographic plates were measured with a comparator. All standard line wavelengths in air were taken from the M.I.T. Tables.<sup>30</sup> A computer program was written which calculated a least-squares polynomial fit for the wavelengths in terms of the measured comparator distance using the standard line wavelengths. This polynomial was then applied to the comparator measurements of the unknown spectral features. Second order polynomial fits were used since higher order fits exceeded the accuracy of the comparator measurements.

Both the wavelengths in air and wave numbers in vacuum are reported. The formula of Edlen<sup>31</sup> was used with a small correction to the refractive index of air for water vapor content. All wavelengths and wave numbers reported are the average of a minimum of five independent measurements.

A Steinheil prism instrument was used in part of this work in a Raman Spectral arrangement. The collimator focal length was 195 mm and the camera focal length was 255 mm. The instrument aperture was  $f/4$ . Both a three-glass-prism and a two-quartz-prism arrangement were used. Kodak 103a-F 35 mm film was used in a curved-focal-plane holder to obtain simultaneous focus of all wavelength of interest.

## RESULTS

A.  $C^1\Sigma^- - A^1\Pi$  and  $D^1\Delta - A^1\Pi$  Band Heads

Table V compares the computer calculated band heads of the  $C^1\Sigma^- - A^1\Pi$  and  $D^1\Delta - A^1\Pi$  transitions to the observed band heads and to the unassigned band heads reported by Pesic and Gaydon.<sup>7,12</sup> Barrow and Crawford<sup>6</sup> observed many of the same band heads, but their spectrum was considerably overlapped and their observations are not as complete. Verhaeghe<sup>10</sup> first reported the wavelengths for a number of these band heads. None of the previous workers were able to assign the observed band heads to a particular electronic transition. All band heads reported in Table V are given as  $Qv'v''$ ,  $Rv'v''$ , etc., and the  $J$  at which the P or R-heads occur is given. Fig. 3 shows a densitometer tracing of the (0,0) sequence of both band systems.

The agreement between the computer calculated band heads and those observed is always within  $1.0 \text{ cm}^{-1}$  and usually within  $0.2 \text{ cm}^{-1}$ . A noticeable exception is the R44 band head of the  $C^1\Sigma^- - A^1\Pi$  transition. The agreement of the measurement of this band head with that of Pesic suggests that either an unknown feature in the same region obscured the band head or that the head is perturbed.

The assignment of the (0,1) sequence of the  $C^1\Sigma^- - A^1\Pi$  band system is difficult due to overlap from some violet degraded features which do not appear to form a regular series of band heads. No previous workers have reported heads that correspond to the calculated heads of this sequence. Special attention was directed toward the observation and measurement of this sequence, but all photographic plates gave obscuring features in this wavelength region. The Franck-Condon

factors of the (0,0) sequence are very much larger than those of the (0,1) sequence for the  $D^1\Delta-A^1\Pi$  transition<sup>32</sup> and by inference for the  $C^1\Sigma^- - A^1\Pi$  transition also. Due to the much greater exposure times required for plates in this wavelength region, it is felt the obscuring features are probably due to impurities present in trace amounts and to lines from the P branches of the known transitions rather than features due to unidentified MgO bands.

Only the Q-heads of the (0,1) sequence of the  $D^1\Delta-A^1\Pi$  transitions were observed because of the high J value of the head for the first few members of the sequence of R-branches. Fig. 4 shows the densitometer tracing of this sequence.

No other sequences of either the  $C^1\Sigma^- - A^1\Pi$  or the  $D^1\Delta-A^1\Pi$  transitions could be observed. The computer calculated band heads are included in Table V for other sequences which might appear in strongly overexposed plates. No heads are listed where the J of the head is larger than 100.

The average error of experimental observation and measurement is about  $0.1 \text{ cm}^{-1}$  for the strong features and is slightly larger for some weaker ones. An uncertainty of about  $0.2 \text{ cm}^{-1}$  should be attached to the leading members of each sequence.

The isotope  $\text{MgO}^{18}$  molecule has been observed by Pesic<sup>7</sup> in this spectral region. Comparison is made elsewhere<sup>33</sup> of computer calculated band heads to these observations. Little additional information is gained by this comparison:  $\text{Mg}^{25}$  and  $\text{Mg}^{26}$  constitute slightly more than 10% each of naturally occurring magnesium and might be expected to contribute weak feature to the violet spectrum. None of the observed band heads could be assigned to either isotope oxide. Calculated band heads for these isotopic oxides are reported elsewhere.<sup>33</sup>

## B. New Violet Band Systems

Of primary importance in this work is the determination of unassigned band systems belonging to the MgO molecule. The complex violet spectrum has band heads due to two MgO transitions which have now been accurately calculated including isotopic band heads. Substantial reduction of the intensity of the OH band heads in the region 3000 to 3100 Å and total elimination of the band heads in the region from 3600 to 4000 Å attributed to MgOH,<sup>12</sup> implies that any remaining band heads are most probably due to the MgO molecule.

In the region from 3600 to 4000 Å, two unassigned band systems appear to be due to MgO. Table VI gives the wavelengths and wave numbers of six members of a red-degraded sequence beginning at 3672 Å. Pesic<sup>7</sup> observed the first four members with both MgO<sup>16</sup> and MgO<sup>18</sup> and the corresponding isotope shift indicated a (0,0) sequence. Fig. 5 shows a densitometer tracing of this system. Its intensity is less than the (0,0) sequences of the two known transitions, but greater than that of the (0,1) sequence of the D<sup>1</sup>Δ-A<sup>1</sup>Π. The band heads are represented with an average error of less than 0.1 cm<sup>-1</sup> by the following formula.

$$\nu = 27\,233.32 - 17.50(\nu + \frac{1}{2}) - 1.06(\nu + \frac{1}{2})^2$$

The second band system, which was observed but not measured in this work, is the strongest feature in this wavelength region. It has violet degraded band heads<sup>34</sup> at 3720.7, 3721.0 and 3721.4 Å. These band heads overlap the expected band heads of the (1,0) sequence of the D<sup>1</sup>Δ-A<sup>1</sup>Π transition, but are not due to this transition. The observed isotope shift<sup>7</sup> of these bands indicates a (0,0) sequence. The close spacing of the bands is indicative of a transition between states with similar spectroscopic constants.

A search of the spectral region from 2500 to 4000 Å was carried out in an attempt to find new band systems of MgO. Particular attention was paid to the region around 3000 Å which is totally dominated by OH bands in spectral sources where OH is not suppressed. No band systems could be found although several features were measured<sup>33</sup> which could not be attributed to MgO or suspected impurities.

### C. Possible MgO Triplet States

As pointed out earlier the  $C^1\Sigma^-$  and  $D^1\Delta$  states have extremely similar spectroscopic constants and a small energy separation (see Table I). To test the hypothesis that these two reported electronic states are actually triplet state sub-levels some tests were made. The closeness of the constants suggests that they might be a single state.

The most unambiguous determination of two electronic transitions having a state in common is a comparison of the second differences. For a given vibrational level the second differences are identical for all electronic transitions involving that state even if that state is perturbed by other electronic states.

$$\begin{aligned}\Delta_2 F''(J) &= R(J-1) - P(J+1) \\ &= (4B_v'' - 6D_v'')(J + \frac{1}{2}) - 8D_v''(J + \frac{1}{2})^3 \\ \Delta_2 F'(J) &= R(J) - P(J) \\ &= (4B_v' - 6D_v')(J + \frac{1}{2}) - 8D_v'(J + \frac{1}{2})^3\end{aligned}\quad (3)$$

From the available experimental data, the second differences were calculated for the lower state of the red system and the two violet systems ( $A^1\Pi$ ) for the  $v'' = 0$  and  $v'' = 1$  levels. Agreement was found among the second differences within experimental error. Theoretical second differences were calculated from the known spectroscopic constants using Eq. (3). For the  $A^1\Pi$  these theoretical values agree well with the experimentally determined ones.

The theoretical second differences for the  $C^1\Sigma^-$  and  $D^1\Delta$  were found to differ significantly from each other only at J values greater than about 65. This is just outside the experimental range of observation. The second differences calculated from the experimental rotational lines are found to be the same within experimental error for the  $C^1\Sigma^-$  and  $D^1\Delta$  states.

The agreement among the second differences would allow analysis of the violet systems either with a common upper state or a common lower state. The reported lack of  $\lambda$ -type doubling in the  $C^1\Sigma^- - A^1\Pi$  transition, the observed  $\lambda$ -type doubling in the  $D^1\Delta - A^1\Pi$  transition and the observation that the R(0) line is missing in the  $D^1\Delta - A^1\Pi$  transition<sup>18</sup> is consistent with the present assignment. However it is also consistent with the expected behavior of transitions between components of a  $3\Pi - 3\Sigma^+$  transition with some case c character.

It would be expected that the f-value of a singlet-triplet transition would be at least a factor of  $10^2$  smaller than the f-value of an allowed transition. The violet, red and green band systems were photographed simultaneously on 103 a-F film using the Steinheil. Qualitative account was taken of the film spectral sensitivity, transmission of the prisms and the variation of spectrograph dispersion with wavelength.

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Calculations show that the rotational lines of the violet and green systems, where the rotational constants of the upper and lower states are similar, are closely spaced leading to enhanced band head radiances with low resolution compared to the red system, where  $B_v''$  and  $B_v'$  are substantially different so that the P-heads occur near the origin and the spacing of P-lines increases rapidly away from the head. The red and green systems have a common upper state so their emission radiances are directly comparable. The violet upper states may have populations which are not easily comparable to the  $B^1\Sigma$ .

It was qualitatively concluded that the four known band systems of MgO are of comparable radiance. The experimental results indicate  $f_{em}$ -values are probably within an order of magnitude.

To further test the possible assignment of the violet bands to a  $3\Pi-3\Sigma^+$  transition, calculations were made using the formulas of Budo<sup>35</sup> for the twenty seven branches of a  $3\Sigma-3\Pi$  electronic transition. These Hönl-London formulas or line strengths give the intensity of a rotational line apart from the Franck-Condon factor, the Boltzmann factor and the electronic f-value. Relative branch intensities as a function of J were determined for various degrees of coupling intermediate between Hund's cases a and b. For a  $3\Pi$  in case a, the sublevel splittings between the  $\Omega = 2, 1$  and 0 components are both equal to A, the spin-orbit coupling constant.<sup>36</sup> From the observed energy splitting between the C-A and D-A transitions, the value of the hypothetical triplet A value is  $229 \text{ cm}^{-1}$  for the  $3\Pi$  assuming the splitting to be negligible in the  $3\Sigma$ .

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The exact relative intensities are a function of  $J$ . The following qualitative conclusions were drawn for a  $J$  of about fifty. In the case  $b$  limit ( $A=0$ ), only the  $P_1, Q_1, R_1, P_2, Q_2, R_2, P_3, Q_3$  and  $R_3$  branches are of significant intensity (one  $P, Q$  and  $R$  branch per sublevel). In the case  $a$  limit where  $A$  is large, twenty-seven branches have some intensity and twenty-four of them are within a factor of five at a  $J$  of fifty. Using the  $A$  value of  $229 \text{ cm}^{-1}$  and the  $B_0$  value of the  $A^1\Pi$  state, the case  $a$  limit is closely approached.

#### CONCLUSIONS

Although generally states of the same molecular configuration have similar spectroscopic constants, the constants of the  $C^1\Sigma^-$  and  $D^1\Delta$  states of  $\text{MgO}$  are experimentally indistinguishable. It does not appear possible to explain this occurrence on the basis of strong mixing of the two states since the  $\Delta\Lambda$  selection rule<sup>29,36</sup> forbids it. It is highly unlikely that a  $^3\Sigma-^3\Pi$  transition (or vice-versa) might be mistaken for multiple singlet transitions in any coupling case intermediate between  $a$  and  $b$ . If the  $C$  and  $D$  states of  $\text{MgO}$  were components of a  $^3\Sigma-^3\Pi$  transition, one would expect a large additional number of branches whose radiance is comparable to the observed branches. Furthermore, the four known electronic transitions have radiances which are qualitatively the same order of magnitude, apparently ruling out a possible intercombination transition assignment. The reason for the similarity of the spectroscopic constants of the  $C^1\Sigma^-$  and  $D^1\Delta$  states of  $\text{MgO}$  remains to be explained. However it does now appear unlikely that the  $C^1\Sigma^-$  and  $D^1\Delta$  states are triplet sublevels.



Many of the previously unassigned band heads in the violet spectrum of magnesium oxide are now assigned. The (0,0) sequence band heads of the  $C^1\Sigma^- - A^1\Pi$  and  $D^1\Delta - A^1\Pi$  band systems have been calculated and observed. Some of the weaker heads have been observed and they also agree with the computer calculated wavelengths. This agreement, where comparison can be made, suggests the calculated but unobserved band heads are accurate thus allowing confidence in assigning band heads in this spectral region to other transitions.

It is concluded that the emitter of the band sequence beginning at  $3672 \text{ \AA}$  is MgO. The series of six band heads measured in this work form a (0,0) sequence which fits the expected second order equation well. High resolution analysis of this system could be of value for further understanding of MgO electronic states.

It is concluded that the strong features near  $3720 \text{ \AA}$  are due to MgO although the structure is unlike any known MgO band system. The substantial reduction of the OH bands near  $3000 \text{ \AA}$  suggests that impurities such as MgOH should appear only weakly if at all. The upper and lower states must have nearly identical  $\omega_e$  values since there is no apparent development of a (0,0) sequence.

Correlation of molecular orbital configurations and the known electronic states of MgO seems reasonable. Of particular interest is the low energy of the  $^1\Sigma^-$  whose molecular orbital configuration must include excitation of the  $3\pi$  orbital. This correlation suggests eight configurations which may have low-lying electronic states. Quantitative prediction of the energies of triplet states is not possible due to the lack of sufficient experimental data. It is concluded that several triplet states of MgO should be low-lying and it seems possible that the electronic ground-state could be a triplet.

The dissociation energy discrepancy may be explained by electronic states in MgO lower in energy than the  $X^1\Sigma^+$ , by a drastic change in the form of the potential curve of the  $X^1\Sigma^+$  state at high vibrational quantum number, or by the inadequacy of the Morse curve approximation. Consideration of the extrapolations of the  $C^1\Sigma^-$  and  $D^1\Delta$  states gives strong evidence that the ionic bonding of the  $X^1\Sigma^+$  and  $A^1\Pi$  states accounts for part or all of the discrepancy.

Although progress has been made in the understanding of MgO electronic states, a major conclusion of this work is that a great deal more experimental evidence is needed. The internal partition function of MgO will remain uncertain until the contribution of triplet states can accurately be determined. Other types of excitation of the MgO spectrum such as hollow cathode or flames might preferentially excite one band system without interference from others. Chemiluminescence experimental evidence might be useful and a more thorough search of the MgO spectrum may well show some additional band systems capable of analysis.

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TABLE I.

Spectroscopic Constants for Known States of MgO in  $\text{cm}^{-1}$ 

Constant	$X^1\Sigma^+$	$A^1\Pi$	$B^1\Sigma^+$	$D^1\Delta$	$C^1\Sigma^-$
$T_e$	0.0	3563.27	19 983.95	29 851.63	30 080.95
$\omega_e$	785.06	664.44	824.08	632.5	632.4
$\omega_e x_e$	5.18	3.91	4.76	5.3	5.2
$B_e$	0.5743	0.5050	0.5822	0.5014	0.5008
$\alpha_e$	0.0050	0.0040	0.0045	0.0048	0.0048
$D_e \times 10^6$	1.22	1.165	1.14	1.245	1.255
$\beta_e \times 10^8$	2.0	1.0	2.5	3.0	3.0
$H_e \times 10^{12}$		5.9			4.8

TABLE II.

Correlation of Molecular Orbital Configurations  
with Electronic States of MgO

Configuration Number	Orbital Population					Electronic States
	5 $\sigma$	2 $\pi$	6 $\sigma$	7 $\sigma$	3 $\pi$	
I	2	4	2			1 $\Sigma^+$
II	2	3	2	1		3 $\Pi_1$ , 1 $\Pi$
III	2	4	1	1		3 $\Sigma^+$ , 1 $\Sigma^+$
IV	2	2	2	2		3 $\Sigma^-$ , 1 $\Delta$ , 1 $\Sigma^+$
V	2	3	1	2		3 $\Pi_1$ , 1 $\Pi$
VI	2	4	1		1	3 $\Pi_r$ , 1 $\Pi$
VII	2	3	2		1	1,3 $\Sigma^+$ , 1,3 $\Sigma^-$ , 1,3 $\Delta$
VIII	2	4		2		1 $\Sigma^+$

TABLE III.

Calculated Term Values for Three Molecular  
Orbital Configurations of MgO

Outer Molecular Orbital Configuration	Electronic State	Calculated Energy $\text{cm}^{-1} \times 10^{-3}$
$5\sigma^2 2\pi^4 6\sigma^2$	$1\Sigma^+$	0.0
$5\sigma^2 2\pi^3 6\sigma^2 7\sigma$	$3\Pi_i$	2.3
	$1\Pi$	4.6
$5\sigma^2 2\pi^4 6\sigma 7\sigma$	$3\Sigma^+$	2.3
	$1\Sigma^+$	12.8

TABLE IV.

Morse Dissociation Limits and Extrapolated Energies  
of Atomic Products for MgO,  $\text{cm}^{-1} \times 10^{-3}$

State	$D_0$	$T_0$	Total Energy
$X^1\Sigma^+$	29.3	0.0	29.3
$A^1\Pi$	28.0	3.5	31.5
$B^1\Sigma^+$	35.3	20.0	55.3
$C^1\Sigma^-$	18.9	30.0	48.9
$D^1\Delta$	18.6	29.8	48.4



TABLE V.

Comparison of Computer Calculations with Observed Band Heads of MgO

Band Head	$C^1\Sigma^- - A^1\Pi$ Band System					$D^1\Delta - A^1\Pi$ Band System				
	J	Calc. Å	Calc. $\text{cm}^{-1}$	Pesic and Gaydon	This Work	J	Calc. Å	Calc. $\text{cm}^{-1}$	Pesic and Gaydon	This Work
R00	77	3766.1	26 545.0	26 545.2	26 545.0	83	3798.2	26 320.6	26.320.5	26 320.4
R11	68	71.8	504.7	505.0	505.1	74	3804.2	279.3	279.6	279.0
Q00		72.4	500.8	501.3	500.6		05.2	272.0	279.6	279.0
Q11		77.3	466.2	465.8	465.8		10.3	237.3	237.3	237.4
R22	62	77.8	463.0	462.9	463.1	66	10.4	236.5		
Q22		82.6	429.1	429.0	428.8		15.7	199.8	200.1	200.2
R33	56	84.0	419.4	418.2	418.6	60	16.0	192.0		192.0
Q33		88.3	389.2	388.4	388.8		21.6	159.5	160.3	160.1
R44	51	90.5	374.0	371.0	371.7	54	23.7	145.4		144.3
Q44		94.4	346.8		346.3		27.9	116.4		116.9
R55	47	97.4	326.3			50	30.8	96.6		
Q55		3800.9	301.8				34.7	70.5		

Table V. (continued)

Band Head	$C^1\Sigma^- - A^1\Pi$ Band System					$D^1\Delta - A^1\Pi$ Band System				
	J A	Calc.	Calc. $cm^{-1}$	Pesic and Gaydon	This Work	J A	Calc.	Calc. $cm^{-1}$	Pesic and Gaydon	This Work
R10	47	3682.5	27 147.8			49	3713.6	26 920.4		
Q10		85.9	122.8				17.3	893.9		
R21	43	88.9	100.6			45	20.2	872.7		
Q21		92.0	77.8				23.5	848.6		
Q01		3868.2	25 844.2				3902.8	25 615.4	25 616.7	25 615.6
Q12		72.3	817.4				6.9	588.5	589.1	588.2
R34	83	74.0	805.9			89	8.0	581.4		
Q23		76.7	788.1				11.4	558.8	559.2	558.4
R45	74	80.2	764.7			80	14.6	538.4		
Q34		81.5	756.0				16.4	526.3	526.5	526.2
R56	67	86.6	722.1			72	21.4	494.1		
Q45		86.7	721.4				21.8	491.0	490.3	490.8
Q56		92.3	684.2				27.7	452.9		452.3

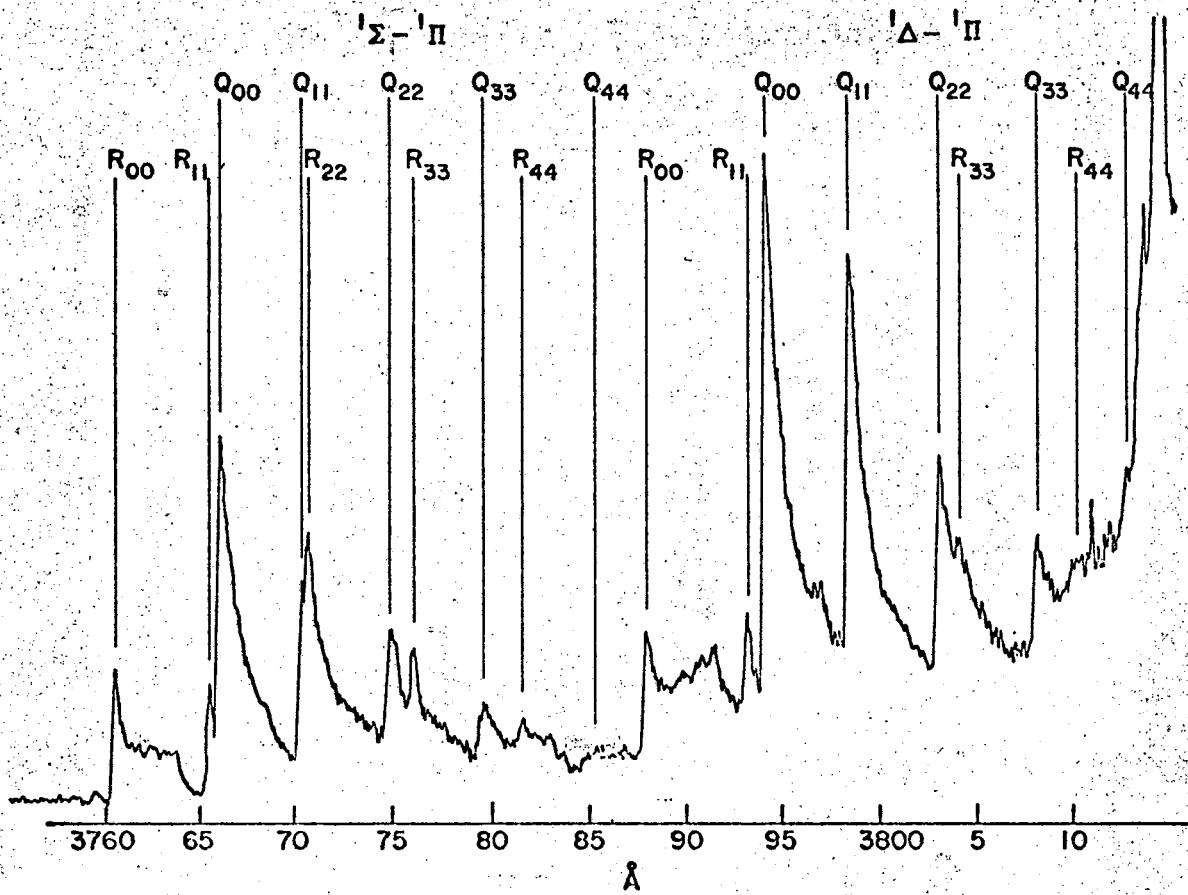
Table V. (continued)

Band Head	$C^1\Sigma^- - A^1\Pi$ Band System					$D^1\Delta - A^1\Pi$ Band System				
	J	Calc. A	Calc. $cm^{-1}$	Pesic and Gaydon	This Work	J	Calc. A	Calc. $cm^{-1}$	Pesic and Gaydon	This Work
R67	61	93.3	677.9			65	28.4	448.2		
Q67		98.4	644.4				34.0	412.0		
R20	32	3602.4	27 751.3			33	3632.3	27 522.9		
Q20		4.6	734.4				34.6	505.2		
R31	30	9.8	694.8			31	39.9	465.7		
Q31		11.8	679.0				42.0	449.3		
Q02		3967.8	25 195.4				4004.2	24 966.6		
Q13		70.8	176.4				7.3	947.5		

TABLE VI.

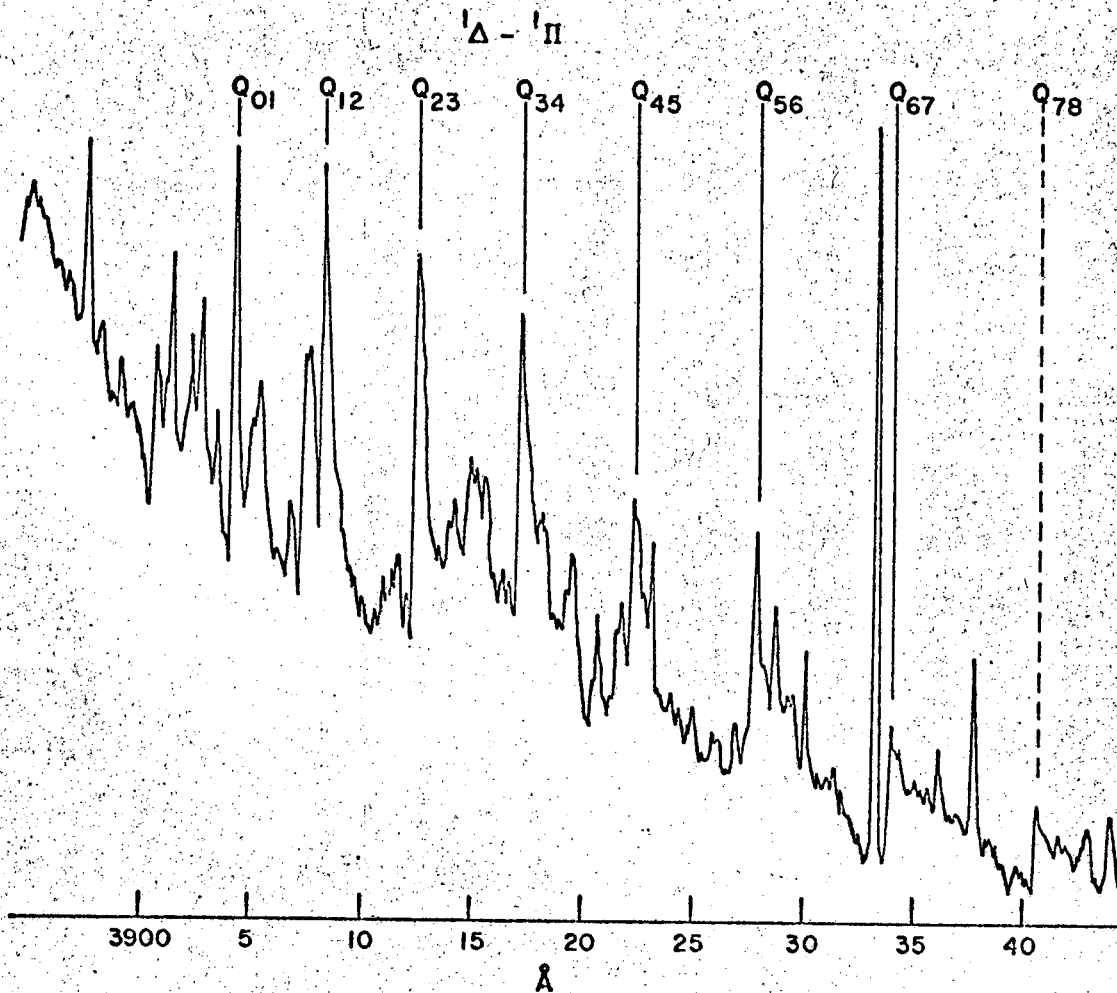
## Band System Attributed to MgO

Band Assignment ( $v'$ , $v''$ )	Observed Wavelength (Angstroms)	Observed Wavenumbers ( $\text{cm}^{-1}$ )	Pesic Wavenumbers ( $\text{cm}^{-1}$ )	Pesic Isotope Shift ( $\text{cm}^{-1}$ )
(0,0)	3672.1	27 224.4	27 224.5	-0.04
(1,1)	3674.8	204.5	204.9	-0.12
(2,2)	3677.7	182.9	183.3	-0.19
(3,3)	3680.9	159.1	159.4	-0.28
(4,4)	3684.4	133.1		
(5,5)	3688.3	104.8		



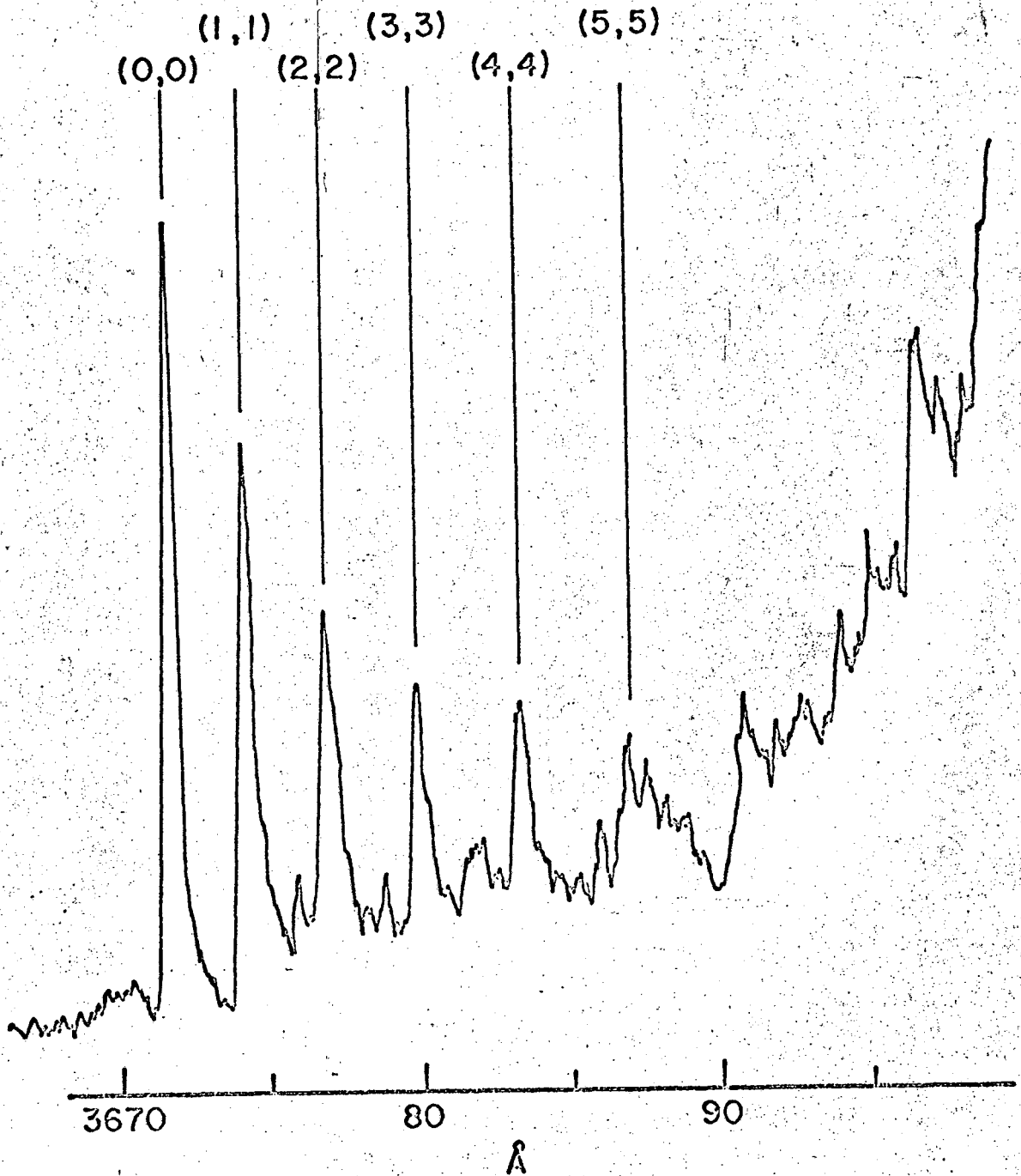
ZBL 692-119

Figure 3. Tracing of the (0,0) sequences of the  $C^1\Sigma^- - A^1\Pi$  and the  $D^1\Delta - A^1\Pi$  band systems of MgO.



XPL 682-120

Figure 4. Tracing of the (0,1) sequence of the  $D^1\Delta - A^1\Pi$  band system of MgO.



XBL 682-121

Figure 5. Tracing of a band sequence attributed to MgO.

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