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Berkeley, California

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Sandor Trajmar

(Ph.D. Thesis)

July 3, 1961

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Contents

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THE NEAR-ULTRAVIOLET SPECTRUM OF MAGNESIUM OXIDE

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ABSTRACT

The complex violet spectrum of magnesium oxide has been the subject of many investigations, but there has been little progress in identifying the molecular species responsible for this spectrum and no success at all in analyzing the spectrum.

In this work the spectrum appearing in the region 3600 to 4000 A was produced in a King furnace and vacuum arc. The spectrum was studied under different pressures of hydrogen (or water), deuterium, and oxygen as well as at different magnesium oxide activities in order to identify the species present in the vapor phase over the oxide or in a magnesium arc at temperatures above $2000^{\circ}C$.

From spectral intensity measurements it has been concluded that species involving hydrogen (most probably MgOH) and at least one kind of oxide species contribute to this spectrum. Measurements of spectral intensity versus magnesium oxide activity showed that both the oxide and hydroxide contained one magnesium oxide. From isotope-shift studies it was concluded that there is only one hydrogen atom involved in the hydroxide molecules.

The hydroxide, deuteride, and oxide bands were separately produced and photographed at high resolution. The wave lengths of the hydroxide

and deuteride band heads and of the rotational lines of the oxide bands in the region 3766 to 3820 A were measured for possible analysis.

I. INTRODUCTION

The importance of high-temperature chemistry and the need for more knowledge about the properties of such systems have been rapidly growing in recent years.

At high temperatures most chemical systems undergo changes. The characteristic oxidation states of elements and compounds are usually different from those at room temperature. In many important systems the major stable species and their energy levels are not yet known, and reliable thermochemical calculations then cannot be performed. Magnesium oxide and its vapor phase constitutes such a system.

Optical spectroscopy is an important tool for studying gaseous species at high temperatures. It supplies the necessary data for the calculation of the partition function, from which all other thermodynamic functions of the system can be obtained. The behavior of high-temperature systems can be predicted by such thermodynamic calculations with more certainty than the behavior of systems at lower temperatures, since the number of kinetic factors is reduced at high temperatures.

When Mg is excited in an arc or flame, or magnesium oxide is heated above 2200°C, a strong complex band structure is observed in the spectral region 3600 to 4000 A in addition to the well-known MgO green and red bands,[1,2,3] which have been analyzed and assigned to MgO monomer.

Many attempts have been made to analyze the violet spectrum or to identify the emitter, but with no success. In 1935 Verhaege attempted the analysis as MgO.[4] Barrow and Crawford (1945) found that the violet system is too complex, and concluded that the emitter was in doubt.[2]

Mg_2O and Mg_2 are not likely to play an important role in the vaporization of MgO, as has been shown by Brewer and Mastick[5] and by Lagerquist.[6] Brewer and Porter published a comprehensive study of the vaporization of MgO in 1954.[7]

From vapor pressure measurements Brewer and Porter have concluded that MgO does not vaporize into only elements at around $1800^{o}C$, but that molecular species also contribute appreciably to the vapor. From measurements of spectral intensity versus temperature they claim that the species responsible for the violet spectrum is more important at about $2200^{o}C$ than the MgO $^1\Sigma$ state, which is the lower electronic state of the green transitions. Wigner-Witmer correlation rules would not allow singlet molecular states from magnesium and oxygen ground states. This indicates the probable existence of lower-lying triplet states. From simultaneous measurements of intensities of the green and violet bands at different MgO activity they have concluded that the violet emitter contains only one magnesium and one oxygen per molecule and, therefore, that it is monomer MgO. A partial vibrational analysis has been carried out in accordance with this assumption, but the rotational structure of the spectrum is not completely resolved even at 0.65 A/mm linear dispersion. Their final conclusion has been that more than one electronic transition between triplet states is involved in the violet spectrum.

James and Sugden have suggested, from comparing the spectral regions of occurrence of Ca, Sr, and Ba halide bands and that of the complex alkaline-earth oxides, that these bands are due to MOH (M = Ca, Sr, or Ba).[8] Following this suggestion Gaydon[9,11] and Gaydon and Charton[10] have carried out extensive studies of the alkaline earth

oxide spectra. By producing the spectrum in flame and in "vacuum arc" in oxygen, water, and heavy water they have concluded in the case of Ca, Sr, and Ba that both oxide and hydroxide are present in the vapor phase.

The violet spectrum of the magnesium oxide seems to be the most complex. From the complexity of the spectrum and from the fact that it has not been observed in stellar spectra one has an indication of a polyatomic emitter.

Gaydon and Pesic produced the spectrum in vacuum arc under water, heavy water, oxygen, and hydrogen atmospheres in high dispersion (0.59 A/mm).[12] They were not able to make a vibrational or rotational analysis or to explain the observed isotope shift, but found that the spectrum was different in water from that in oxygen. They assigned part of the bands to MgOH and part to the Mg_2O_2 as the two most probable species, similar to the case of the other alkaline earth oxides.

Ba_2O, Ba_2O_2, BaO, Ba_2O_3, and SrO species have been found in the vapor of the corresponding oxides by mass spectroscopic methods.[13,14,15] In magnesium oxide no evidence of Mg_xO_y has been found[15] at temperatures around $1800^\circ C$. This can be attributed to the low temperature and the reducing effect of tungsten shieldings.

This was roughly the situation when, on Professor Brewer's suggestion, I started to work on this problem.

The spectrum appeared to be too complicated for one to expect an analysis in the near future; therefore another way was necessary for identification of the species present in the vapor. A promising approach seemed to be the study of spectral intensities under equilibrium conditions in different atmospheres and at different pressures.

From this, by application of the mass-action law, one should be able to identify the species responsible for the spectrum.

Such experiments were carried out and are described in the following sections.

II. DESCRIPTION OF APPARATUS

A. King Furnace

The King furnace used in this investigation has been described by Hicks[16] and by Engelke.[17] Except for various modifications which had been added through the years, it was the furnace constructed and described by Brewer, Gilles, and Jenkins.[18] It consisted of a graphite resistance tube in a vacuumtight, water-cooled brass chamber.

The heater tubes were machined from graphite. They were 12.5 in. long and 7/8 in. i.d., and a 1/2-in. bore was drilled through the length of the tube. A 6-inch heating zone at the center of the tube was maintained at uniform temperature by tapering the outside diameters symmetrically from 7/8 in. at the center to 3/4 in. at the minimum cross sections, which were located 3-1/4 in. from either end, where the diameter increased in one step to 7/8 in. Cylindrical graphite baffles 1/2 in. long and with 1/8 in. holes drilled along their axes were placed inside the tube at both ends. They served to improve definition of the hot zone and to minimize the diffusion of the gaseous species from the hot zone.

The graphite tube was lined with 0.001-in.-thick sheets of tantalum and tungsten, so that the magnesium oxide was in contact only with the tungsten. The graphite reacting with the tantalum formed a TaC layer, and the carbon could not readily penetrate the tungsten. Consequently, except for some attack by the tungsten, rapid reduction of the MgO was prevented.

The potential drop across the furnace was 12 to 18 volts, and power requirement about 20 kva for temperatures of 2000 to 2300°C.

Power was supplied by a 100-kva step-down transformer, which was operated from a 440-volt single-phase source. Temperature control was obtained by manually adjusting a Powerstatt connected to a control transformer, whose secondary was in series with the secondary of the step-down transformer.

The furnace windows were made of 1/6-in.-thick optical quartz, and they could be easily replaced and cleaned. Two brass disks with 1/4-in. apertures were positioned in the bore of the window assembly, which helped to keep the window clean. To avoid multiple reflections the windows were tilted 2 degrees from vertical.

The furnace was connected to a vacuum line and valve system which allowed the attainment of different atmospheres in the furnace.

The temperature was read with a Northrup optical pyrometer which had been calibrated by comparison with a NBS-calibrated pyrometer.

B. Vacuum Arc

The arc used to produce the spectrum in oxidizing atmosphere is shown in Fig. 1.

It consisted of a 2-liter pyrex bulb with quartz window, of adjustable electrodes with magnesium tips, and of ground glass joints to vacuum and to gas inlet lines. Both electrodes had kovar-to-glass joints and were mounted to the bulb by tapered ground-glass joints. The upper electrode was connected to the bulb by a vacuumtight bellows system which made possible the adjustment of the electrode distance under vacuum.

The pressure could be read by mercury manometer or by thermo-couple gauge. Power was supplied by 200 v dc line and could be regula-
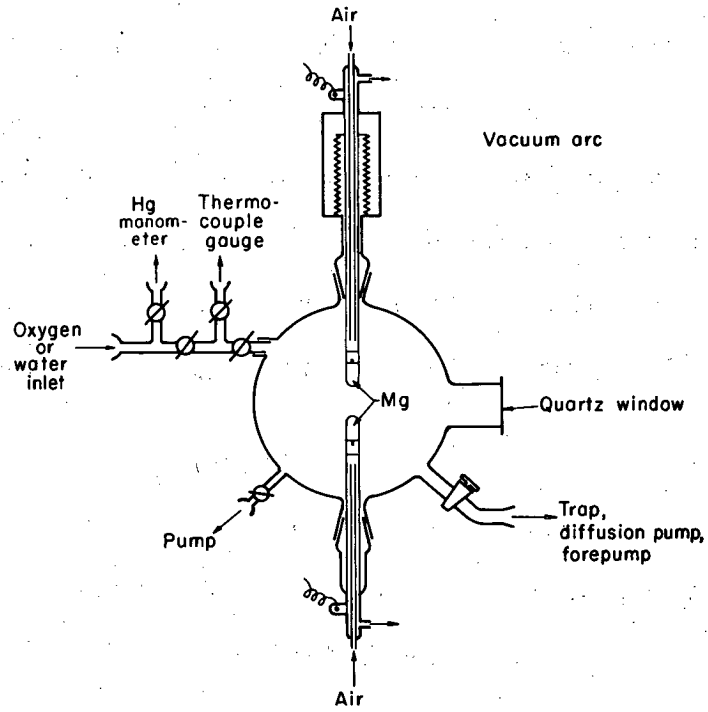
Fig. 1. Vacuum Arc.

ted between 1 and 5 amperes by a resistor. The arc was started by a
Tesla coil. The electrodes could be cooled by air, but for short
operations it was not necessary. The window was mounted on a side
arm to keep it free of depositing magnesium oxide. A small glass bulb
was connected to the main bulb which contained the water or heavy
water. The water pressure was adjusted by keeping this flask at the
required temperature. When the arc was run in oxygen, this bulb was
removed and the system was connected to dry oxygen supply. One of the
two pumps was simultaneously operated with the arc, while the other
pump system, which consisted of a liquid nitrogen trap, oil diffusion
pump and fore-pump, served only for degassing of the system.

C. Spectrograph

In most of this work a 3-meter concave grating spectrograph was
used in first and second order. It had a linear dispersion of
2.8 A/mm and revolving power of 0.027 at 4000 A in second order. The
spectrograph could be mounted either with a scanning device or a
photographic plate holder. A slit width of 20 to 50 μ was used on
both the spectrograph and photocell during spectral scannings, and of
about 10 μ when the spectrum was photographed.

The spectrum was also produced in very high dispersion by a 21-
ft concave grating spectrograph in second and third order. It had a
linear dispersion of 0.58 A/mm in second and 0.28 A/mm in third order.

D. Electronic Spectrum - Scanning Device

The scanning device was designed and described by Phillips.[19]
A 1P-21 photomultiplier (RCA) located on the Rowland circle of a
3-m concave grating spectrograph generated a dc current which was

proportional to the intensity of the light hitting the photocathode. The current went through a load resistor, and the voltage drop across the resistor was power-amplified after being changed to ac by a Brown converter. The output from the amplifier was converted to dc and used to drive a Brown "Electronic" strip-chart recorder.

A vacuumtight container with silicone rubber gaskets and double quartz window was constructed which made it possible to keep the photomultiplier tube at dry ice temperature. By cooling, the signal-to-noise ratio was increased by a factor of more than two. The container was filled with argon for better heat conduction, and the space between windows was evacuated to prevent moisture condensation. The argon was dried, because moisture condensation on the tube pins caused considerable noise.

E. Optics

For best illumination of the spectrograph the image should be sharply focused on the slit, and cover the entire slit and the entire grating. To satisfy all these requirements in the case of a narrow, extended source like the King furnace requires special optics. This could be achieved by the use of a cylindrical lens in front of the slit, but the more complicated optical system would have no advantage over a simple lens system in this work. Therefore the second requirement was not satisfied.

The furnace was located 3 m from the slit and a quartz lens of 5 cm diameter and 30 cm focal length was used. For the arc the distance was 1 meter and the quartz lens had a diameter of 5 cm and focal length of 20 cm.

The spectrum obtained by the King furnace is not equally intense across its full width, because of imperfection of the system. There was, however, a wide enough homogeneous substrip in the spectrum, and this was scanned with the microdensitometer.

III. PRELIMINARY EXPERIMENTS

The purpose of the preliminary experiments was to find the best conditions for producing the spectrum and to make qualitative observations on the behavior of the spectrum in different atmospheres.

A. King Furnace Excitation

The sample consisted of small magnesium oxide crystals, which had some advantage over powder: namely, they made possible a greater charge density and caused much less dust formation. The result of the analysis of the sample is summarized in Table I.

The crystals were placed in the hot zone of the furnace and had contact only with the tungsten lining. They lasted for about 40 minutes at $2220^{\circ}C$. This temperature was found the most suitable for the experiments. At and above $2300^{\circ}C$ the dust concentration was very high, the MgO was reduced too rapidly, and rapid crystal growth starting at different points of the tube completely closed up the hole. Below $2100^{\circ}C$ the violet spectrum was not observable with reasonable exposure times. Since the comparison of the violet bands with the green MgH and MgO bands was also planned, and the latter did not appear below $2200^{\circ}C$ with convenient exposures, the temperature $2220^{\circ}C$ was accepted as best for the King furnace experiments.

The upper temperature limit could be pushed up to $2400^{\circ}C$ in argon atmosphere, if a few percent of SiO_2 was added to the MgO crystals. The small amount of eutectic melt that was formed this way helped in trapping the dust particles. In hydrogen atmosphere the same method did not work.

The spectrum was scanned with the above-described photoelectric

Table I.   Sample Analysis (in wt %)[a]

Weight Analysis		Spectral Analysis			
Ignition loss	0.27	Al	0.06	Ca	0.005
CaO	0.10	Fe	0.03	Ba	0.05
SiO_2	0.04	Si	0.04	Mn	0.005
R_2O_3	0.10	Cr	0.0006	Li	0.01
		Cu	0.0008		

a   Analysis has been done at the Analytical Laboratories of
Mineral Technology and Ceramics Department, University of
California, Berkeley.

device, but it seemed impossible to achieve good reproducibility. The irregular changes in the King furnace, change in dust concentration, and crystals growing across the tube showed up as peaks on the chart. The scanning method was therefore abandoned, and a photographic technique was applied which smooths out time-dependent deviations in the furnace.

Kodak plates were used, type 103 a-O or II a-O for the region 3000 to 4000 A, and type 103 a-F for the region 5000 to 6000 A.

Hg, Mg, and Fe lines served as reference lines. From these, 90 contamination atomic lines were identified and used as further reference points. (See Table II.) For more accurate wave-length measurements a thorium spectrum was applied.

The plates were calibrated by step weakener, and a Leeds-Northup microdensitometer was used for scanning.

B. Influence of Hydrogen Pressure on Spectral Intensity

The violet spectrum was believed to belong at least partially to MgOH. To check this assumption the spectrum was photographed in the region 3600 to 4000 A, with gradually increasing hydrogen pressure.

The results are shown on Fig. 2. The first photograph was taken in 20 cm argon atmosphere (part a); "x" indicates the unknown hydropressure corresponding to the water present in the sample and tube. The hydrogen pressure was then increased to 5 cm (part b) and to 10 cm (part c). The figure shows a microdensitometer scan of a part of the spectrum under these three conditions. The region 3773.5 to 3882.5 A where three strong hydroxide bands are very close together, is marked by vertical lines on the figure.

Table II. List of atomic lines observed in the furnace spectrum

Wave length (A)	Element		Wave length (A)	Element		Wave length (A)	Element	
4077.83	Hg	I[a]	3865.53	Fe	I	3734.87	Fe	I
4063.59	Fe	I	3864.11	Mo	I	3733.32	Fe	I
4046.76	Cr	I(?)	3859.91	Fe	I	3732.03	Co	I
4046.56	Hg	I[a]	3856.37	Fe	I	3727.62	Fe	I
4045.82	Fe	I	3849.97	Fe	I	3722.56	Fe	I
4044.42	A	I	3841.05	Fe	I	3719.94	Fe	I
4034.39	Mn	I	3840.44	Fe	I	3709.26	Fe	I
4033.07	Mn	I	3838.29	Mg	I	3707.83	Fe	I
4030.75	Mn	I	3834.22	Fe	I	3705.57	Fe	I
3998.65	Ti	I	3832.30	Mg	I	3687.46	Fe	I
3989.77	Ti	I	3829.35	Mg	I	3683.05	Fe	I
3981.77	Ti	I	3825.88	Fe	I	3679.91	Fe	I
3968.47	Ca	II	3824.44	Fe	I	3663.28	Hg	I[a]
3961.52	Al	I	3820.43	Fe	I	3662.88	Hg	I[a]
3958.21	Ti	I	3815.84	Fe	I	3654.83	Hg	I[a]
3956.28	Ti	I	3812.96	Fe	I	3653.50	Ti	I
3948.66	Ti	I	3799.55	Fe	I	3650.14	Hg	I[a]
3944.00	Al	I	3798.51	Fe	I	3647.84	Fe	I
3933.66	Ca	II	3798.26	Mo	I	3642.67	Ti	I
3930.30	Fe	I	3795.00	Fe	I	3639.80	Cr	I
3927.92	Fe	I	3787.88	Fe	I	3635.46	Ti	I
3922.91	Fe	I	3767.19	Fe	I	3631.46	Fe	I
3920.26	Fe	I	3763.79	Fe	I	3619.39	Ni	I
3906.48	Fe	I	3758.27	Fe	I	3618.77	Fe	I
3902.96	Mo	I	3752.86	Ti	I	3608.86	Fe	I
3899.70	Fe	I	3749.49	Fe	I	3605.33	Cr	I
3895.66	Fe	I	3748.26	Fe	I	3593.49	Cr	I
3886.28	Fe	I	3745.90	Fe	I	3581.19	Fe	I
3878.57/02	Fe	I	3745.56	Fe	I	3578.68	Cr	I
3872.50	Fe	I	3737.13	Fe	I	3570.10	Fe	I

[a] Reference lines from auxiliary exposure
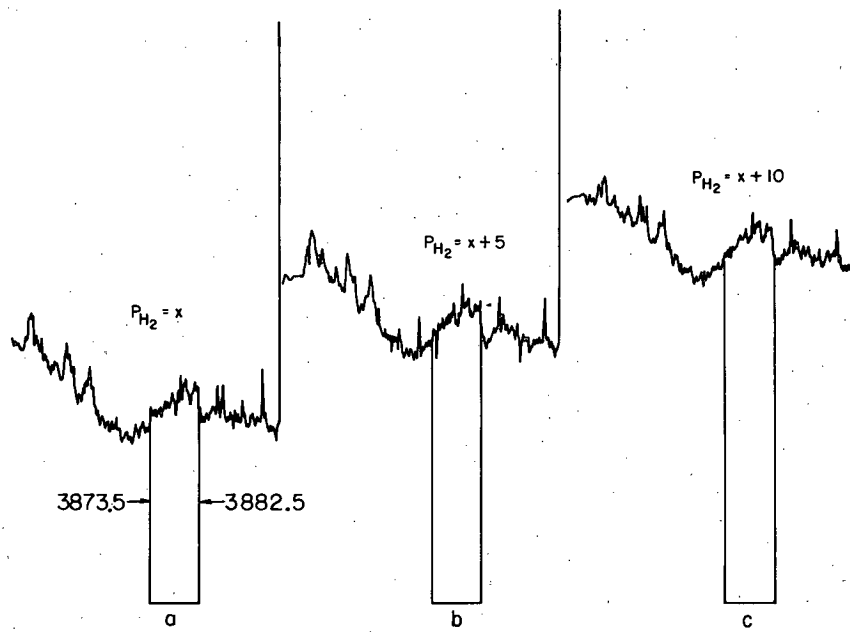
Fig. 2. Microdensitometer scan of a part of the MgOH spectrum at three different H_2 pressures.

Most of the 44 bands listed by Gaydon as hydroxide bands were present in the King furnace spectrum.[12] The intensity of these bands increased with increasing hydrogen pressure. The increase was roughly proportional to the square root of the hydrogen pressure. Several other bands which responded the same way were also observed.

The hydroxide bands were quite strong even when no hydrogen but only dry argon (20 cm Hg) was present in the furnace. This was attributed to the presence of water in the furnace and the sample.

Several of the strongest bands listed by Gaydon as oxide bands were also observed in the furnace spectrum under argon atmosphere, but they were obscured when hydrogen was introduced into the furnace.

In the first-order pictures, where the complex violet bands and the green MgH and MgO bands were simultaneously photographed, close parallelism was observed between the behavior of the violet hydroxide and green MgH bands. The latter were also present in the furnace when hydrogen was not yet added. Their response to increasing hydrogen pressure was very similar.

In another experiment an attempt was made to eliminate the water present in the sample and King furnace. The furnace without charge and lining was evacuated and gradually heated up to $2500^{\circ}C$ in 24 hours and was kept at that temperature for about 2 hours under continuous pumping. The vacuum was less than 10 μ at the end of the 2-hour period. The water was trapped with liquid N_2. The furnace was then filled with dry argon, and the lining and charge were introduced. The sample was then degassed at $800^{\circ}C$ for 2 hours. Following this the spectrum was photographed in first order, covering both the violet and green bands, at 2.5-hour intervals.

A continuous decrease of the intensity of both the hydroxide and the MgH green bands was observed. The intensity of the violet oxide bands and the green MgO bands did not change appreciably, but as the hydroxide bands disappeared the oxide bands dominated the spectrum.

The experiment was repeated and the spectrum was photographed in second order covering only the violet bands. The above observation concerning the hydroxide and oxide bands was confirmed. Finally hydrogen was introduced into the King furnace and very strong hydroxide bands were observed again. This proves that the decrease of the intensity was not due to the reduction of the sample. The midrodensitometer scannings of these plates are shown on Fig. 3.

The spectrum was also observed in deuterium atmosphere. It had a quite different appearance from the spectrum in hydrogen. An isotope shift was definitely indicated, but the spectrum was too complex to allow correlation between the two band systems.

E. Vacuum Arc Excitation

In order to study the spectrum in oxidizing atmosphere, the vacuum arc described above was built. In air or in oxygen atmosphere without special care, N_2 and CN as well as the mixture of the magnesium oxide and hydroxide bands were present.

To produce the oxide spectrum free of disturbing bands the water and nitrogen had to be excluded. The arc was therefore degassed at less than 0.1 μ for several days, water was trapped with liquid nitrogen, and water and nitrogen-free oxygen were used. Under these conditions the dominant features of the spectrum were the oxide bands. The presence of water could be very well confirmed by the simultaneous observation of

Before degassing   After degassing   H₂ added
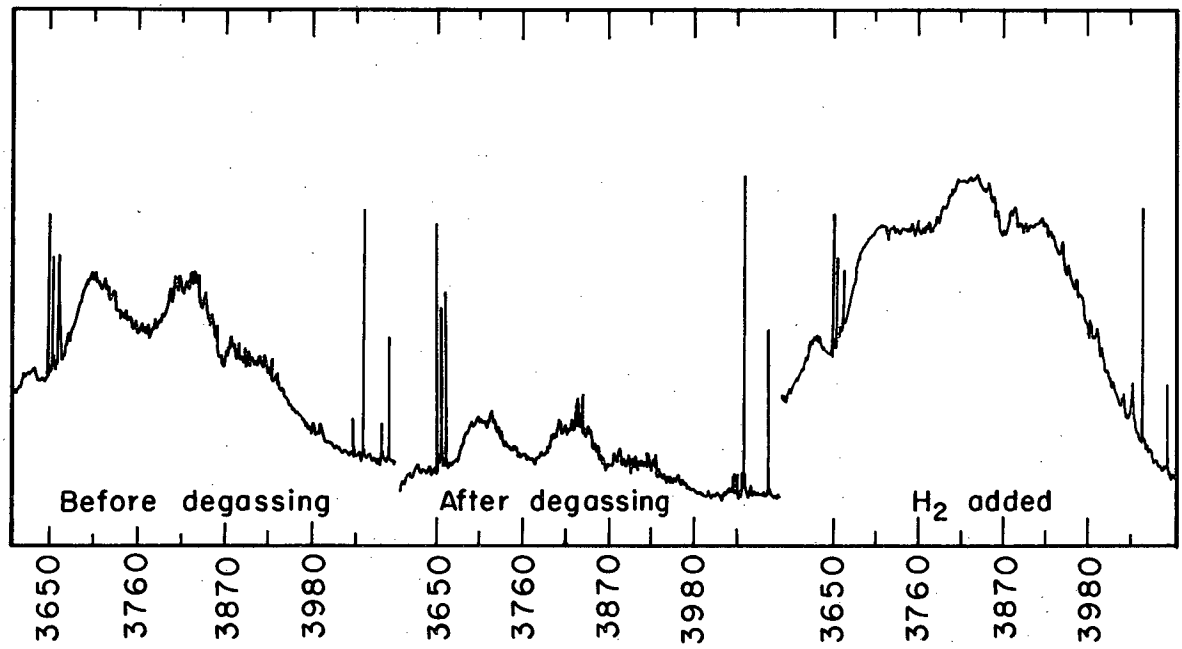
Fig. 3.   The effect of degassing on the violet bands.

the 3064-A OH band. Fig. 4a shows the arc spectrum in water and in oxygen and the corresponding OH band. Fig. 5 shows the microdensitometer trace of the violet region.

When the arc was operated in water atmosphere the hydroxide bands observed in the King furnace were very strong (as were the MgH and the 3064-A OH bands). Under these conditions only the strongest oxide bands were present with noticeable intensities.
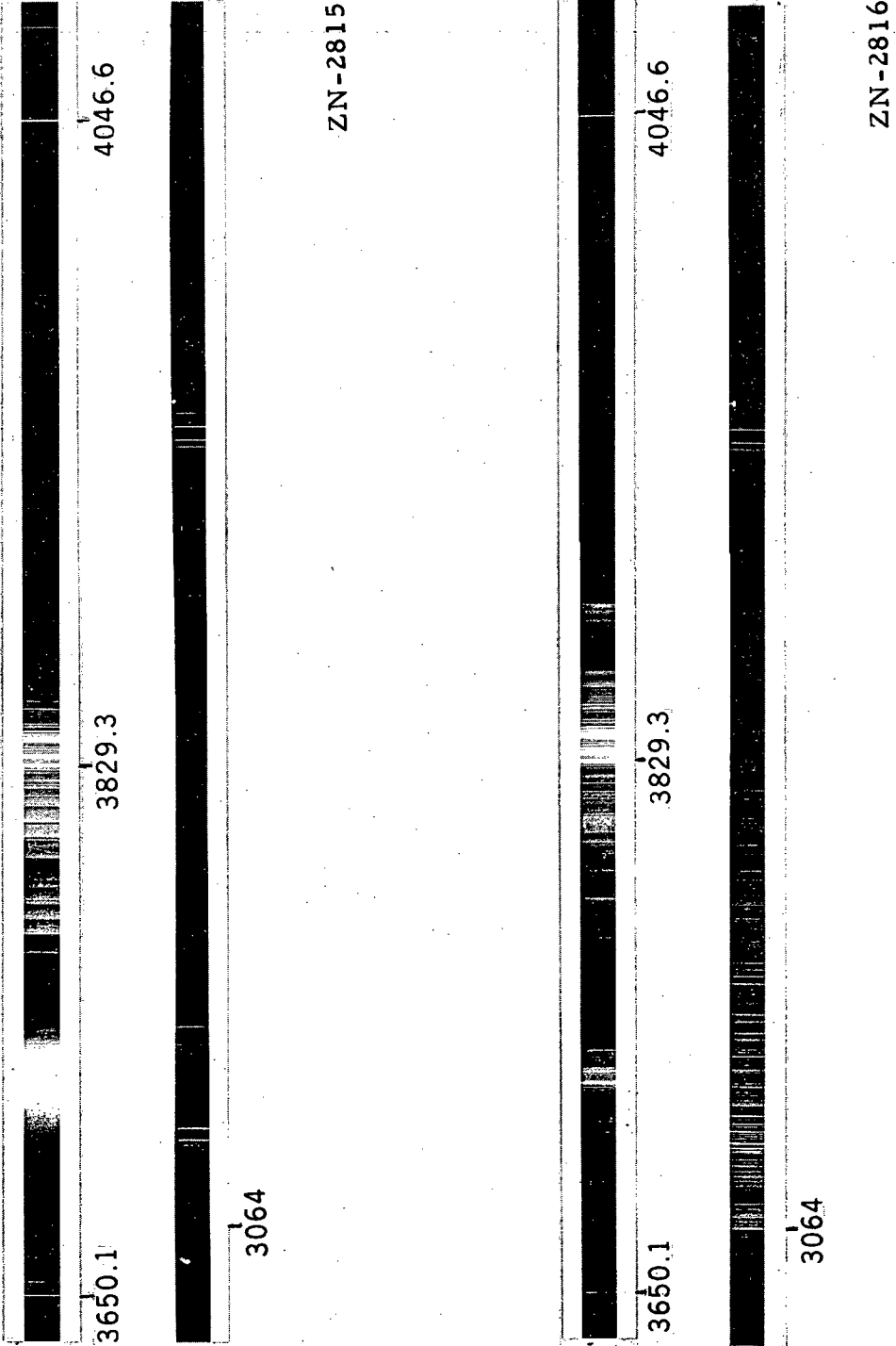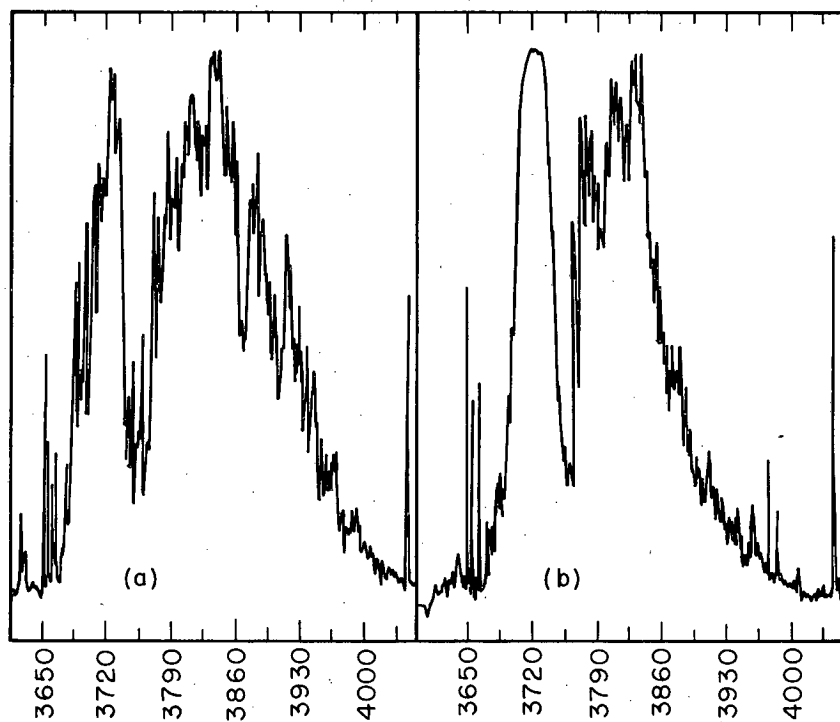
ZN-2815

ZN-2816

Fig. 4. The arc spectrum in oxygen.
The arc spectrum in water.

3650 3720 3790 3860 3930 4000 3650 3720 3790 3860 3930 4000

(a) (b)

MU—24174

Fig. 5. Arc spectrum in H_2O.
Arc spectrum in O_2.

IV. DISCUSSION OF PRELIMINARY EXPERIMENTS

In the preliminary experiments the optimum conditions for producing the spectrum were established, qualitative effects of the hydrogen pressure were observed, and it was shown that hydrogen-containing species as well as oxide species contribute to the spectrum.

The King furnace at the temperatures of the experiments is considered as an equilibrium source of radiation, therefore mass-action law considerations can be applied: namely, the vapor pressure (fugacity) and therefore the intensity of the bands originating from a species containing hydrogen should increase proportionally with increasing hydrogen pressure.

The bands assigned to hydroxide emitter were found qualitatively to behave in this manner. The presence of hydrogen in the emitter responsible for this spectrum was therefore almost certainly established.

The close parallelism of the MgH bands with these bands and their disappearance when the sample and furnace were degassed at elevated temperature were a further assurance of the correctness of this assumption. These bands were called "hydroxide" bands although there was no rigorous proof concerning the composition of this molecule yet.

Porter's intensity measurements on the violet and green magnesium oxide bands at different MgO activity showed that there was only one MgO present in the species responsible for the violet spectrum.[7] Therefore he concluded that it was also MgO. More rigorously, however, one could deduce from his results only that the emitter contained one MgO, but it could also be a reaction product of MgO with some element commonly present in flame, arc, or furnace.

The experiments described above showed that the King furnace spectrum contained mostly hydroxide bands. Porter's measurements also were carried out with the King furnace and he actually observed these bands; his results, therefore, apply to the hydroxide not to the oxide bands, and are in agreement with the assumption that these belong to MgOH.

Bulewicz and Sugden studied the magnesium violet spectrum in flames of oxygen-hydrogen-nitrogen gas mixtures.[20] The magnesium was applied in the form of a spray of magnesium salt solutions. They found that the intensity of bands changed proportionally with the concentration of solution in the atomizer, indicating only one magnesium atom per molecule. One could say again that in a flame of an oxygen-hydrogen-nitrogen gas mixture mostly the MgOH bands occurred, and the possible overlap of some weak oxide band structure would not influence appreciably their measurements even if the oxide bands were due to a dimer.

The assumption that the hydroxide species contains one magnesium and one oxygen has been quite well established by these experiments, but there is no proof of the number of hydrogen atoms in the emitter, although from the occurrence of magnesium halide bands and the complex violet bands in the same spectral region we have support for the MgOH assumption. (See Fig. 6).

The general appearance and wave lengths of the band heads of the hydroxide spectrum are discussed later in connection with the high-resolution pictures.

In theory, analysis of the spectrum or a study of the isotope shift would supply the necessary data, but the compexity of the spectrum seems to make analysis difficult. The isotope shift has been studied and is described in Chapter VI.

Another way of proving this assumption would be to select regions of the spectrum where only "hydroxide" bands are present and study quantitatively the variation of intensity with respect to hydrogen pressure. These experiments are discussed in Chapter V.B.

It was observed on plates taken with the King furnace as a source that, when an attempt is made to minimize the water in the sample and furnace, the intensity of most of the features decreases, but several bands remain strong. These bands are overlapped by strong hydroxide bands when water is present, but when the water of H_2 pressure is low they dominate the spectrum. The wavelength of these features agrees with the wavelength of strong oxide bands assigned by Gaydon to Mg_2O_2. In the King furnace the atmosphere is always reducing; the intensity of these oxide bands is understandably low.

The vacuum arc built for better observation of the oxide features proved to be a very convenient source for the production of magnesium oxide and hydroxide spectra together and separately. The arc is not suitable for mass-action-law considerations, because one does not know how far off one is from equilibrium and because the pressure cannot be varied over a wide enough region. Because the temperature of the arc is higher than that of the furnace, the spectrum is more complex. In spite of this the arc gives very nice spectra, because the dust problem is absent.

The spectra obtained by the vacuum arc gave further evidence that

the complex violet band system consisted of overlapping hydroxide and oxide bands.

The oxide band system consists of four groups of bands: (a) A weak group of bands centering at about 3640 A. (b) A very strong, complex band group around 3720 A. Both sides of this group show fine rotational structure. The center part consists of bands degrading in both directions and has a very complex structure. (c) A somewhat weaker group of bands in the region 3766 to 3830 A. These bands all degrade toward the red and are partially resolved even with the 3-meter spectograph. (d) A weaker group of bands, which is the continuation of the third one and extends up to about 4000 A.

V. QUANTITATIVE STUDIES OF SPECTRAL INTENSITIES

A. Oxide Bands

In order to fix the formula of the violet-emitting oxide, the variation of the intensity of these and the green bands were studied together under equilibrium vapor pressure conditions at constant temperature, but at varying thermodynamic activity of the solid MgO. In order to carry out this experiment a spectral region had to be found where only oxide bands were present. King furnace excitation was applied and sufficient time was allowed for the establishment of thermal equilibrium.

The chemical equilibria equations are

$$MgO\ (s,a_1) = MgO\ (g,{}^1\Sigma) = 1/x\ (MgO)_x\ (g).$$
$$MgO\ (s,a_2) = MgO\ (g,{}^1\Sigma) = 1/x\ (MgO)_x\ (g).$$
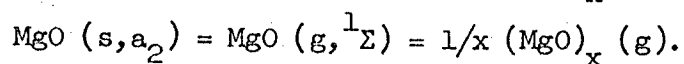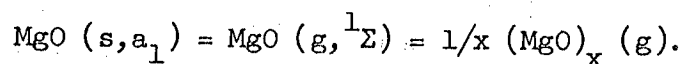
The thermodynamical relationship expressed in terms of intensities is

$$\left(\frac{I\ (green,\ a_1)}{I\ (green,\ a_2)}\right)^x = \left(\frac{I\ (violet,\ a_1)}{I\ (violet,\ a_2)}\right),$$

where $I\ (green,\ a_1)$ = intensity of a green MgO band at solid MgO activity of a_1. The other symbols have similar meanings. From this equation, by observing the ratio of the intensities of the green bands (which are known to belong to MgO monomer) and those of the violet oxide features, one can obtain the value of x.

The furnace and sample were freed of water to a certain extent (by degassing) in order to decrease the intensity of the hydroxide bands and make the oxide bands eaily observable. The spectrum was then photographed in argon atmosphere.

In the first series of experiments the 5007-4962 A green MgO bands and the violet bands were photographed simultaneously in first order on

the same plate at two different MgO activities. The change in the activity was achieved by bringing the sample to about $2500^{\circ}C$ for 1 to 2 minutes, at which it reacted quite fast with the tungsten lining. In the compound formed the activity of the MgO was less than unity. Temperature, spectrograph settings, and optics were kept the same during the two exposures. Each plate was calibrated by a step weakener at 3600 and 5100 A.

In a second series of experiments only the violet bands were photographed in second order and the intensity ratios of oxide and hydroxide features at two different activities were compared. The MgOH bands should behave like MgO monomer in this experiment. At higher dispersion the green bands could not be included because the spectrograph covers a range of only about 1000 A.

The results are shown in Tables III and IV. The first column shows the spectral regions or the wave length of the features chosen for the measurements. On the first-order pictures it is hard to distinguish individual bands, therefore, a spectral region has been chosen, where mostly one kind of features are present. Whenever contributions from other types of molecules could occur they are indicated in square brackets. "At." means contribution from atomic features. I/t is the intensity calculated for unit exposure time and "r" is the ratio of the intensities at two different MgO activities. The corresponding activities are also shown in the head row. Both the first- and second-order activity experiments were performed twice ("a" and "b" in the tables.).

No difference is observable in behavior for any of the violet bands compared with the green bands or with the MgOH bands. The value

of x calculated from the above equation is unity.

Table III. The effect of the variation of MgO activity on spectral
intensities. (First-order spectrum).

Wave length region	Species	a			b		
		I/t at a = 1	I/t at a < 1	r	I/t at a = 1	I/t at a < 1	r
3680-3716	(MgO)x [MgOH]	3.23	1.44	2.14	2.20	1.03	2.13
3716-3725	(MgO)x	3.26	1.50	2.17	2.43	1.15	2.11
3725-3746	(MgO)x [MgOH]	2.88	1.30	2.22	1.93	0.92	2.11
3766-3830	(MgO)x [MgOH]	2.86	1.29	2.22	1.87	0.85	2.20
3873-3882	MgOH	2.31	1.12	2.08	1.36	0.63	2.16
4974-5007	MgO	3.60	1.59	2.26	2.50	1.35	1.90

Table IV. The effect of the variation of MgO activity on spectral
intensities. (Second-order spectrum).

Wave length region	Species	a			b		
		I/t at a = 1	I/t at a < 1	r	I/t at a = 1	I/t at a < 1	r
3720.7-3721.4	(MgO)x	2.08	0.97	2.14	2.50	1.17	2.13
3724.9	(MgO)x [MgOH]	1.80	0.83	2.17	2.05	1.11	1.93
3731.8	(MgO)x [MgOH]	1.60	0.72	2.24	1.78	1.00	1.78
3766.1	(MgO)x	1.56	0.64	2.44	1.12	0.50	2.22
3771.8-3772.3	(MgO)x	1.56	0.64	2.44	1.10	0.50	2.20
3777.4-3777.8	(MgO)x	1.50	0.64	2.32	1.12	0.50	2.22
3782.6-3784.2	(MgO)x	1.56	0.65	2.40	1.16	0.51	2.27
3798.3	(MgO)x [At.]	1.32	0.63	2.10	1.70	0.93	1.84
3805.3-3824.4	MgOH	1.40	0.67	2.09	1.62	0.96	1.69
3848.56	MgOH	1.40	0.70	2.00	1.67	0.98	1.72
3873.5-3882.5	MgOH	0.96	0.43	2.24	1.15	0.71	1.61

In each case the activity has been decreased by a factor of roughly two (calculating from the green bands). If some of the bands had originated from a dimer the intensity ratio would be 4 instead of 2, which is most probably outside the limits of experimental error. Even if one of the oxide bands or regions chosen had a 50% contribution to the intensity from MgOH, which is very improbable, a ratio of 2.7 instead of 2 would have to be observed.

The discrepancy showing up in the intensities of the same band under the same conditions on different plates may be partially caused by slight difference in temperature, but are mainly due to the difference in spectrograph settings and optics. These had to be reset for every plate separately, because of the step-weakener exposure.

The error introduced by the uncertainty in the temperature must be quite small, on the one hand, because the temperature was measured at least within an accuracy of $\pm 10^{\circ}C$; on the other hand, the error introduced in comparing the intensity of the green and violet bands is proportional to the difference in heats of vaporization of the green and violet species.

These experiments show that the oxide bands appearing in the King furnace belong to monomer species. This could be expected probably for the oxide bands in the region 3766 to 3830 A, which appear very regular and are partially resolved with the 3-m concave-grating spectrograph. The results are interesting as far as the 3720 A complex oxide bands are concerned. The 3720.66 -, 3720.96 -, 3721.40 -, and 3724.9 - A oxide bands are very complex, and Gaydon has classified them as Mg_2O_2 bands. These bands are very well recognized on the plates and are not disturbed by atomic lines or overlapping MgOH bands.

There is another "complex" oxide band at around 3732 A, not listed by Gaydon, which behaves also as a monomer.

We conclude from these results that there is no dimer contribution to the violet spectrum under the conditions of these experiments, and all oxide bands present in the furnace spectrum are due to a diatomic MgO.

Quite recently Pesic studied the isotope shift in the green and violet magnesium oxide bands, using vacuum arc excitation and running the arc in ^{16}O, in ^{18}O, and in a mixture of them.[21] He did not observe extra bands in the last case, therefore only one oxygen was involved in the oxide emitter. He found, however, that the isotope shift in the violet bands was quite irregular -- which, he concluded, may be attributed to a polyatomic emitter Mg_xO.

This raises again the question of the probable importance of the Mg_2O species in the vapor phase. Mg_2O may be formed according to the equation

$$MgO\ (g) + Mg\ (g) = Mg_2O\ (g).$$
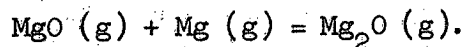
If equilibrium is maintained, then

$$p_{Mg_2O} \propto p_{MgO} \cdot p_{Mg}$$

There are three possibilities:

(a) p_{Mg} is proportional to the MgO solid activity. In this case p_{Mg_2O} is proportional to the square of the solid MgO activity.

(b) p_{Mg} is not proportional to the solid MgO activity and not constant either. In this case the spectral intensities of the near-ultraviolet features belonging to the oxide emitter should not be proportional to the MgO solid activity.

(c) If p_{Mg} is approximately constant as the solid activity is varied,

then the intensities of the oxide features are proportional to the first power of the activity and so they behave similarly to the monomer.

An isotope shift experiment with Mg isotopes would yield further useful data for settling this question.

B. Hydroxide Bands

It was found in the preliminary experiments that certain features of the violet bands were sensitive to hydrogen pressure. As a matter of fact, their intensity varied roughly in proportion to the square root of hydrogen pressure. The numbers of oxygen and magnesium atoms in the molecule responsible for these bands were quite well established.

In connection with the studies of spectral intensity of the violet oxide bands as a function of MgO solid activity, some of the most intense hydroxide bands were also observed. It was shown that these also behave as monomers, that is, they contain one magnesium and one oxygen.

We have no real proof concerning the number of hydrogens, but only some indication for one hydrogen because of the nice fit of the spectral region of the hydroxide bands into the MgX scheme (where X is a halogen or OH). This is demonstrated in Fig. 6.

Under equilibrium conditions it is necessary to satisfy the equation

$$\left(\frac{I_1}{I_2}\right) = \left(\frac{p_1}{p_2}\right)^{n/2}$$

where I_1 and I_2 are the intensities of the hydroxide bands at hydrogen pressures of p_1 and p_2 and n is the number of hydrogens contained

by the emitter. This equation holds, of course, only in the linear region of the concentration-versus-intensity plot. In a gaseous system at low pressure the intensity is far from black-body intensity, and this requirement is satisfied. This equation offers a convenient way for the determination of n. With the King furnace used as an equilibrium source, the spectral intensity of the hydrogen bands was studied as the function of the hydrogen pressure for this purpose. Several difficulties arose, however, in connection with these experiments.

(a) There was always water present in the King furnace and sample, corresponding to an unknown hydrogen pressure. This had to be taken into account as a parameter and it amounted to approximately 10% of the maximum tolerable hydrogen pressure.

(b) Dust present in the furnace gave a continuous background radiation which changed with hydrogen pressure. The dust had another effect too: the intensity of the spectral features itself decreased-- while the dust concentration and background radiation increased--because of the scattering of radiation on the solid particles.

(c) The hydrogen pressure could not be increased over about 30 cm Hg because the disturbing effect of the dust became intolerable, the sample reduced too fact, and fast transport of the material closed up the hole. On the other hand, the intensity was proportional only to the square root of the hydrogen pressure.

(d) The sample reduced quite fast, and this made it impossible to cross-check by taking several exposures with the same sample.

(e) The final difficulty, which turned out to be prohibiting, was that equilibrium could not be maintained even with moderately high
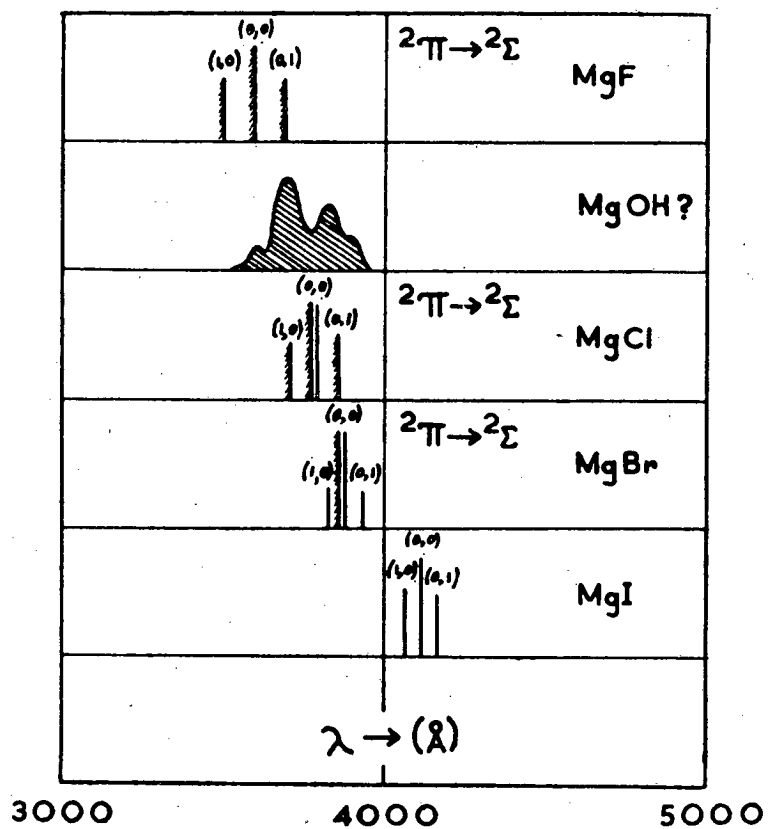
Fig. 6. Diagrammatic spectra of magnesium halide radicals, compared with the contour or the Mg ultraviolet bands.

*Taken from Reference 20.

hydrogen pressures. This last point is demonstrated in Fig. 7, which shows the violet and green spectrum obtained in 8 cm argon and in 28 cm hydrogen pressure. Going from the argon to hydrogen the intensity of the green MgOH bands increased parallel with the violet hydroxide bands, as one expected, but at the same time the intensity of the green MgO bands very greatly decreased. This indicated that equilibrium was not maintained. If it had been maintained, the intensity of the MgO bands should have remained the same when the intensity of bands belonging to hydrogen-containing species increased owing to the increase of the hydrogen pressure.

The explanation for the failure to maintain equilibrium may be the following: material is transferred from the hot zone to the cold parts of the tube, and this transfer is speeded up by the increase of the hydrogen pressure. When the rate of disappearance of the gaseous species from the hot zone approaches the vaporization rate of the MgO, equilibrium can no longer be established.

It has been found by Dreger and Margrave in Langmuir vaporization experiments that the vaporization coefficient of MgO is very small.[22] This indicates that the equilibrium considered here can be easily upset by processes using up MgO in the vapor phase.

We therefore conclude that the King furnace is not an appropriate source for studying the hydrogen pressure effect quantitatively.
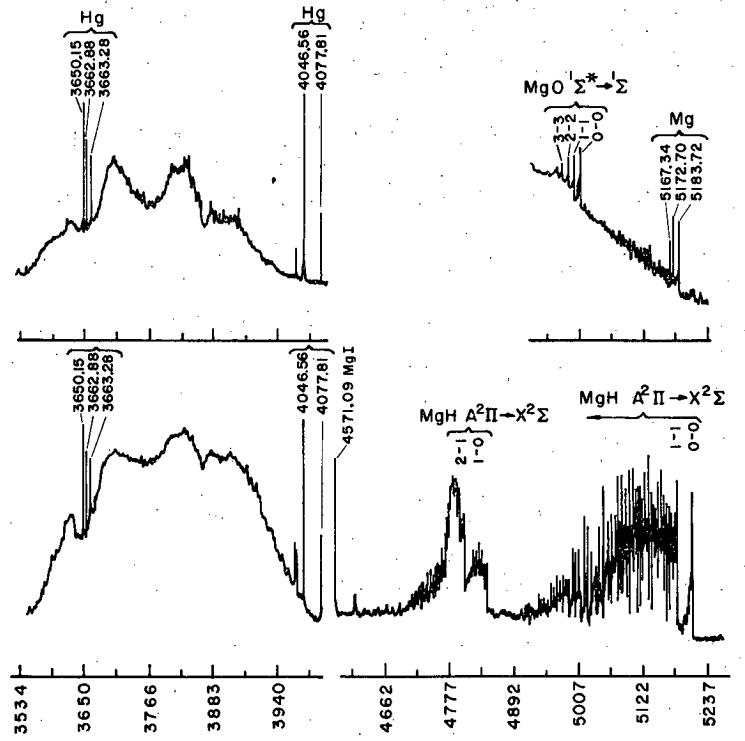
Fig. 7. Violet bands in argon atmosphere.
        Green bands in argon atmosphere.
        Violet bands in hydrogen atmosphere.
        Green bands in hydrogen atmosphere.

VI. ISOTOPE SHIFT IN THE MgOH SPECTRUM

For the determination of the number of hydrogens in the hydroxide emitter a study of the isotope shift was undertaken. The spectrum was produced by running the vacuum arc in water, in heavy water, and in a mixture of them. The photographs of the spectra were taken on the 3-m concave-grating spectrograph in second order covering the region 3600 to 4000 A as well as the 3064 OH band. The shift was easily observable on the OH band and clearly present in the hydroxide bands, as evidenced by the different appearance of the two spectra. On plates taken with the mixture both the hydroxide and deuteride features were easily observable, but no extra features were found.

Although the correlation between the two band systems must be complex, it is possible to recognize the hydroxide and deuteride bands photographed on top of each other. It seems also certain that the appearance of extra bands corresponding to mixed species would be observable. The absence of these extra features is interpreted therefore as proof that there is only one hydrogen atom per molecule.

VII. HIGH-RESOLUTION SPECTRA

The hydroxide, deuteride, and oxide spectra produced by the vacuum arc were photographed in high resolution with the 21-ft concave-grating spectrograph on Kodak IIa-O plates. A partially overlapping thorium spectrum was exposed on each plate to serve as standard. All plates were calibrated with step weakener. The wave lengths were obtained by a program (developed by Professor John Phillips and Professor Sumner Davis) using an IBM 704 computer.

The hydroxide bands were obtained in second order in the region 3668 to 3937 A. They are shown on Fig. 8. The spectrum looks quite complicated, not resembling at all a diatomic molecular spectrum. There are bands present degrading to both directions or to neither, and many headless high-intensity regions. At some parts of the spectrum the rotational structure is resolved, but in most parts it is not. With few exceptions it is hard to tell where a band head is at all. The piling up of the overlapping rotational structure of different bands gives high-intensity regions which one should not call band heads. The most intense points more or less similar to a diatomic band head have been measured and their wave lengths and intensities are given and compared to those of Gaydon in Table V.

Wave lengths joined by brackets represent the two edges of a band with no visible degradation in either direction.

Gaydon lists 44 MgOH bands; 38 of them agree quite well with bands measured on these plates, four do not seem to be bands in the present spectra (they are marked with "n"). One band is not definitely recognizable, and one of his bands is out of the region of exposure. Besides these 21 more bands are listed.
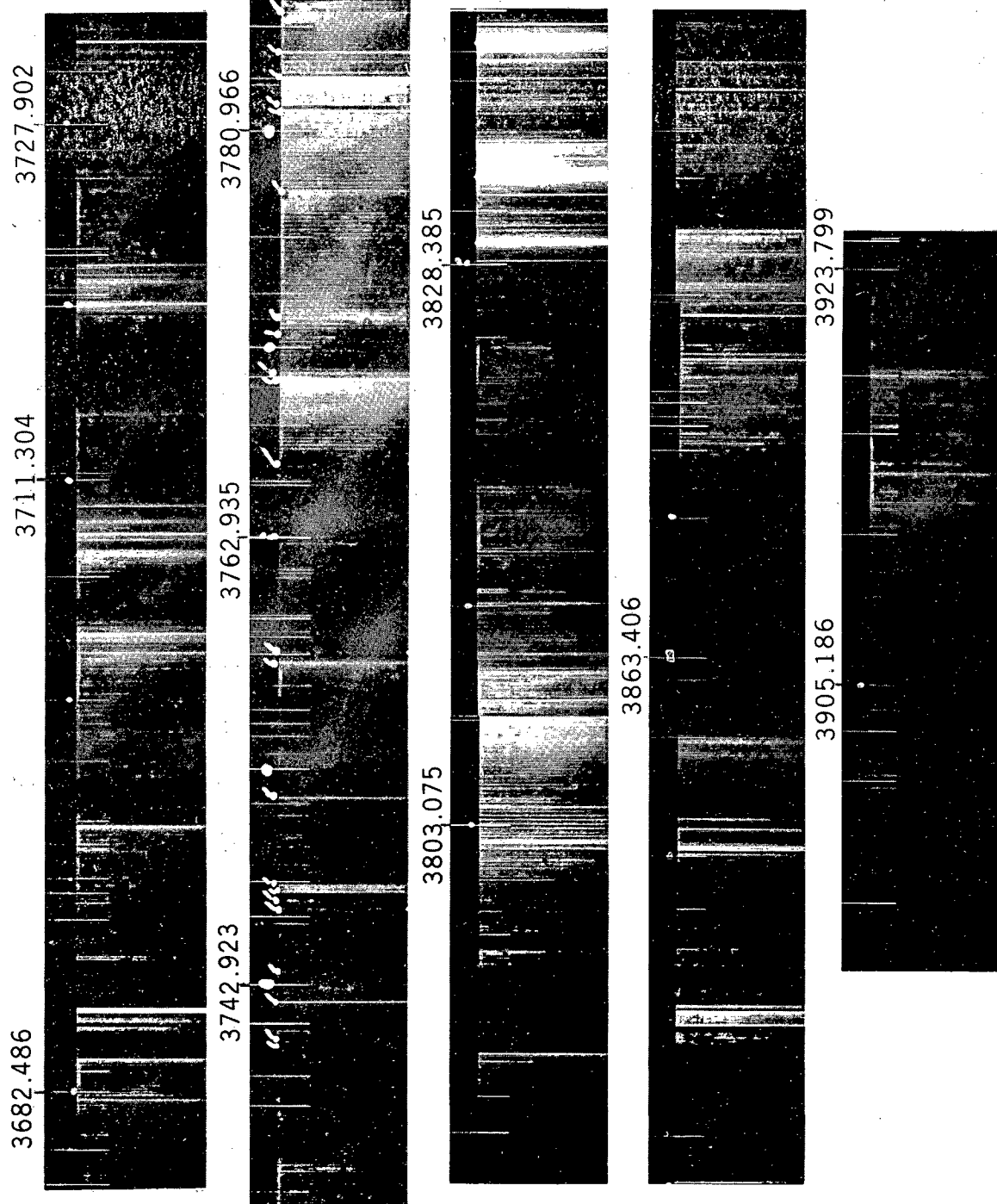
Fig. 8. MgOH Spectrum.

ZN-2817

The deuteride spectrum has also been produced with this high dispersion by running the arc in heavy water. The spectrum is shown on Fig. 9. The wave lengths of the most prominent features are given in Table VI.

Gaydon lists 39 MgOD bands. In 26 cases the observations agree, 10 do not look like bands on these plates, and three are out of the range of exposure. Fourteen more new MgOD bands are listed here.

The observations described in Chapter VI concerning the isotope shift were further confirmed by the high-resolution pictures. There is no doubt about the occurrance of a shift, but the correlation between the two spectra must be very complex.

From the appearance of the hydroxide spectrum in the same region as the halide spectra we can deduce that the bonding in the molecule is Mg-O-H, and it is very probably a bent molecule. In this case the two larger moments of inertia are almost the same and we have the case of a prolate asymmetric top. The substitution of deuterium for hydrogen does not appreciably affect the two larger moments of inertia, but will affect the small one very much. The three normal modes of vibrations are also differently affected by the hydrogen-deuterium isotope-shift. This may account for the complicated isotope shift. The theoretical considerations for isotope shift in a triatomic molecule are briefly summarized in Appendix II.

The general appearance of the oxide spectrum has been described above. The two most intense groups of these bands have been photographed in second order on the 21-ft spectrograph. The 3720 A region is quite complex, but not as much as the hydroxide bands, and when the spectrum is produced with very short exposure so that only the most intense part of it shows up, the rotational structure is quite well

Table V. The most prominent features of the MgOH bands.

This work			Gaydon		
λ (A)	I	Deg	λ (A)	I	Deg
			3660.1^a	4	V
3675.86	54	V	76.0	4	V
84.04	84	V	84.06	4	V
86.47	86	V	86.4	8	V
95.05	86	V	95.09	7	V
3703.21	90	V	3703.25	6	V
04.09	92	V	04.09	8	V
04.42	64	V			
07.83	89	V	07.9	8	V
08.84	80	V	08.80	8	V
09.31) 09.42)	76) 73)	M	09.38	6	M
10.05	89	R			
14.39	61	M			
18.89	61	V			
19.54	94	V	19.60	10	V
24.74	65	M	24.8	4	M
30.84	55	V			
31.75		?	31.76	8	V
32.31	55	R	32.37	4	M
42.17	72	V	42.19	5	M
47.06) 47.40)	48) 36)	M	47.07	4	M
51.31	46	V	51.34	4	M
57.36	55	V			
59.40			59.37	2	M
70.00	85	V	70.63	7	V
72.74	65	M	72.9	5	M
81.88	91	V			
82.12	84	R	82.0	5	V
83.36	87	V	83.36	8	V
84.47	86	V	84.52	5	V
92.72	92	V	92.78	5	V
93.62	80	V			
			97.44^s	3	V
3802.39	93	M	3802.40	8	M
08.81	93	V	08.82	8	V
10.13	91	V	10.17	8	V
			19.23^n	6	V
			26.41^n	5	V
33.85	95	V	34.80^n	6	M
			45.08^n	5	M
46.60	80	V			

Table V. (cont.) The most prominent features of the MgOH bands.

This work			Gaydon		
λ (A)	I	Deg	λ (A)	I	Deg
46.92	93	M	46.93	6	M
47.59	93				
48.56		M	48.56	8	M
49.68	71	V	49.68	8	V
50.35	85	M			
54.80	94	M	54.9	7	V
54.90	92				
55.74	90	V			
56.19	81	V			
56.45	70	V			
59.74	77	V	59.7	6	V
62.65	60	M			
73.06	75	V			
76.83	83	V	76.82	6	V
80.19	81	V	80.16	6	V
81.50	86	V			
82.56	68	V	82.5	6	V
90.01	69	V			
93.66	73	V			
3901.15	61	V	3901.16	5	V
14.64	64	M	14.64	4	M
19.20	57	V	19.1	5	V
27.85	45	M			
31.70	41	V			
36.36	37	V	36.2	4	V

a Outside exposed range

s not definitely recognizable

n does not seem to be a band on the recent exposures
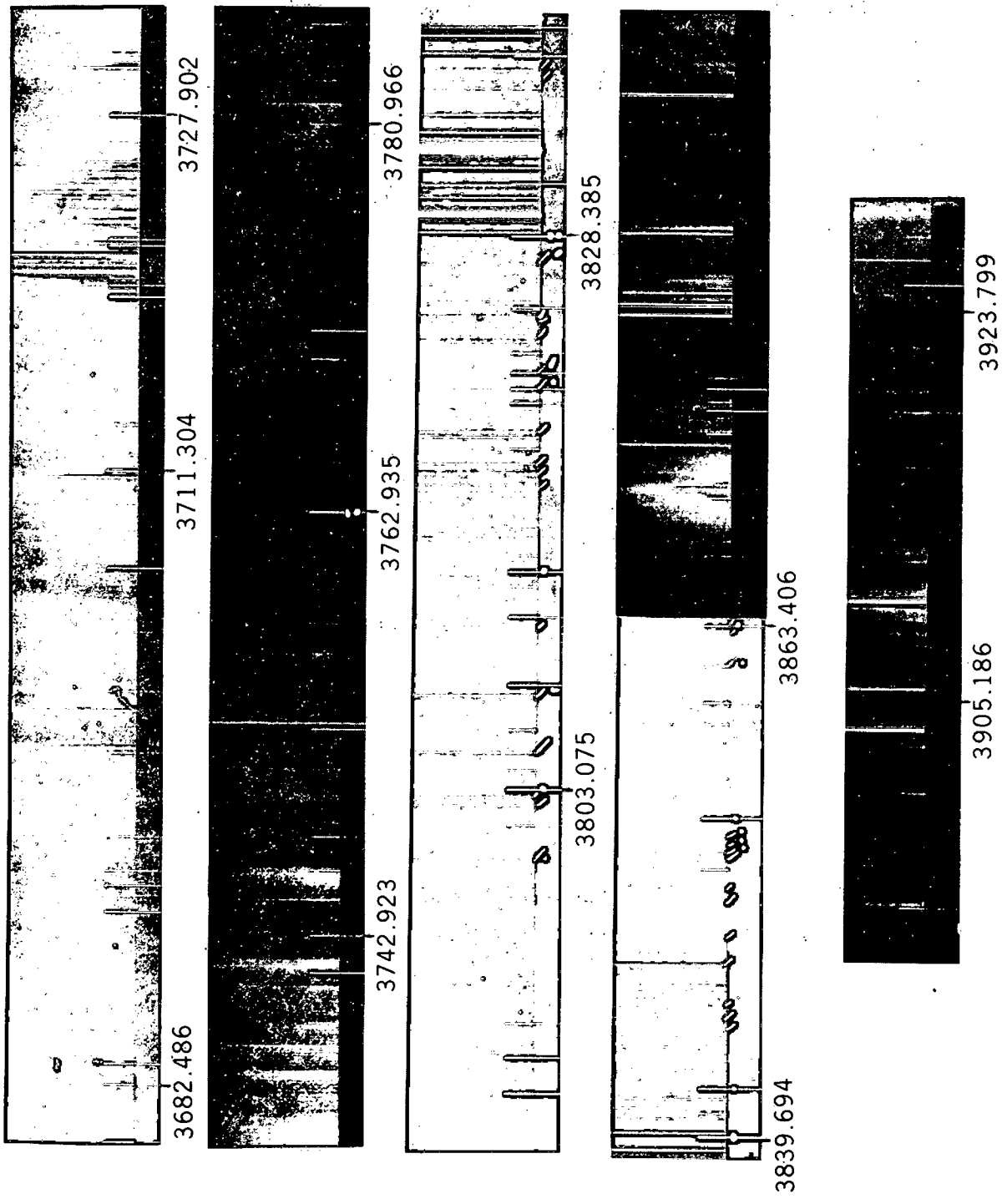
Fig. 9. MgOD Spectrum.

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Table VI. The most prominent features of the MgOD bands.

	This work			Gaydon		
λ (Å)	I	Deg		λ (Å)	I	Deg
				3650.23^a	3	M
				56.2^a	3	V
				65.52^a	5	V
3668.49	23	V		68.44	4	V
71.70	26	V		71.76	6	V
76.29	20	V		76.22_n	3	V
				79.64	4	V
82.87	20	V		82.85	4	V
98.37	36	V		98.3	6	V
3700.10	35	V		3700.08	6	V
01.13	21	V		01.1	6	V
11.03	47	V		11.05	4	V
13.47	38	R		13.51	4	V
23.00	39	M				
24.34	51	M				
30.69	35	V				
33.				33.	3	M
				36.60^s	4	V
37.78	36	V		37.81_n	3	V
				38.5	3	R
40.57		M		40.6	3	M
41.78	25	M		41.3	3	M
46.09	22	V		46.2	4	V
56.26	20	V		56.21	4	V
63.82	21	V				
81.91	36	V				
82.99	39	V		82.84_s	3	V
				94.5_n	2	V
				97.33_n	3	M
				97.79_n	3	R
99.85	35	V		99.92	4	V
3807.39	46	M		3807.46	3	M
21.37	35	V				
22.17	47	R				
27.15	41	V				
52.91	48	V		52.8	4	V
53.26	36	V				
53.67	29	V				
61.57	42	V				
70.11	60	M		70.1	8	M
				78.32_n	5	M
78.52	43	M		78.6	3	M
79.27		M		79.38	5	M
80.		M		80.0	3	M

Table VI. (cont.) The most prominent features of the MgOD bands.

This work			Gaydon		
λ (A)	I	Deg	λ (A)	I	Deg
82.42	39	M			
90.			92.7	6	V
			3903.90[n]	5	M
3905.78		M			
09.93	61	M	09.8	8	M
			11.3[s]	4	V
			15.20[s]	4	R
19.98	24	V	20.04	3	V
34.59	25	V			

[a] outside exposed range

[s] not definitely recognizable

[n] does not seem to be a band on the recent exposures.

resolved and the band structure is very similar to the region 3766 to 3830 A.

The bands of the third group (3766 to 3830 A) all degrade to red, and--except for the regions near the band heads--are quite well resolved in second order. This group has also been photographed in third order. The wave lengths of the rotational lines have been measured and a complete analysis of these bands will be attempted and described in a separate paper. These oxide bands are shown in Fig. 10. They look very much like a $^1\Pi \longleftrightarrow {}^1\Sigma$ transition.

On the basis of the activity experiments described in section V/a and the general appearance of the spectrum, the bands of both groups are assigned to diatomic magnesium oxide, although some contribution from Mg_2O_2 species to the 3720 A region is possible at the arc temperature. The most probable reason for the complexity of this region is the overlapping of bands with different directions of degradation.

The two weaker groups of oxide bands have not been studied in detail.
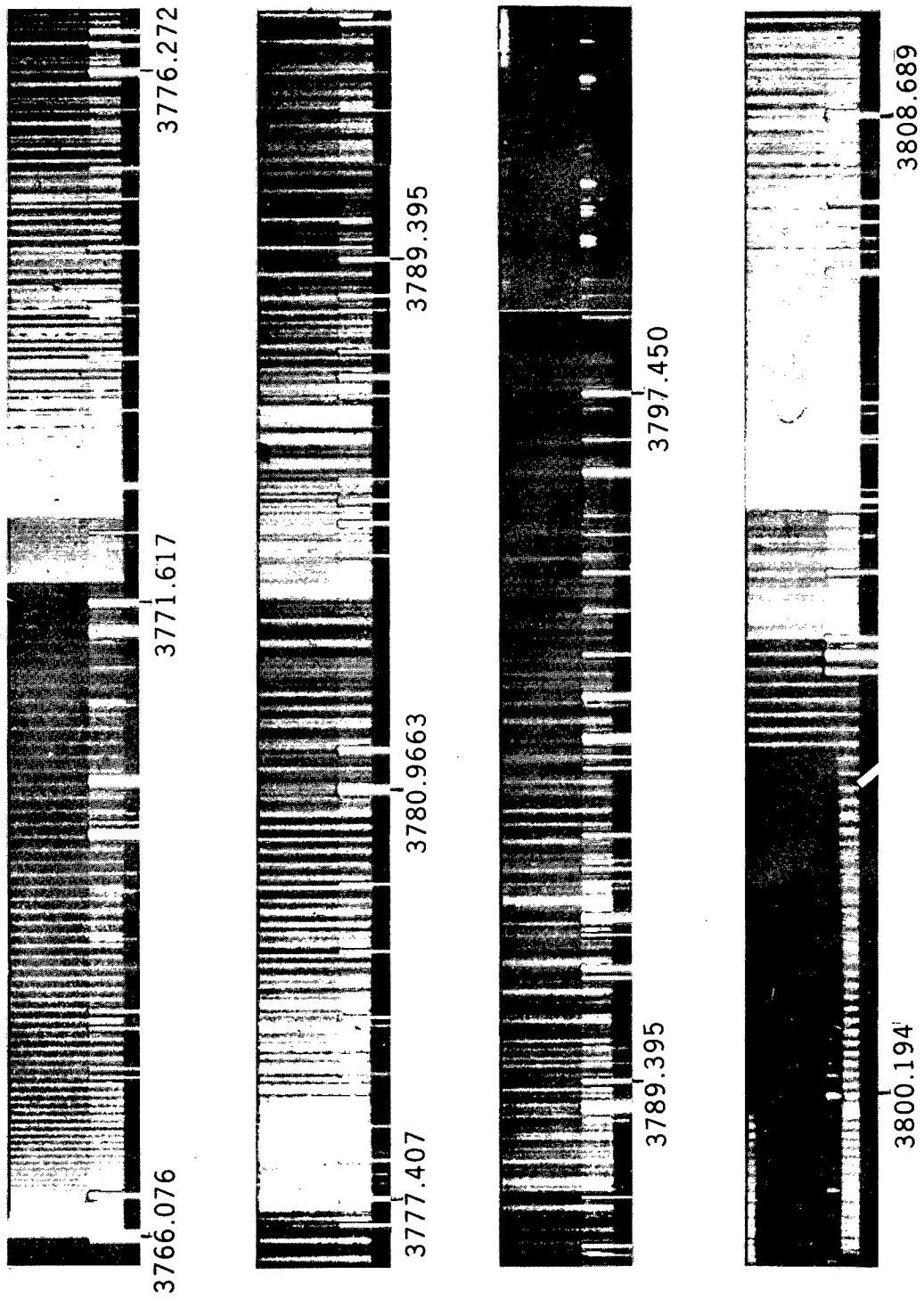
Fig. 10. Magnesium oxide spectrum.
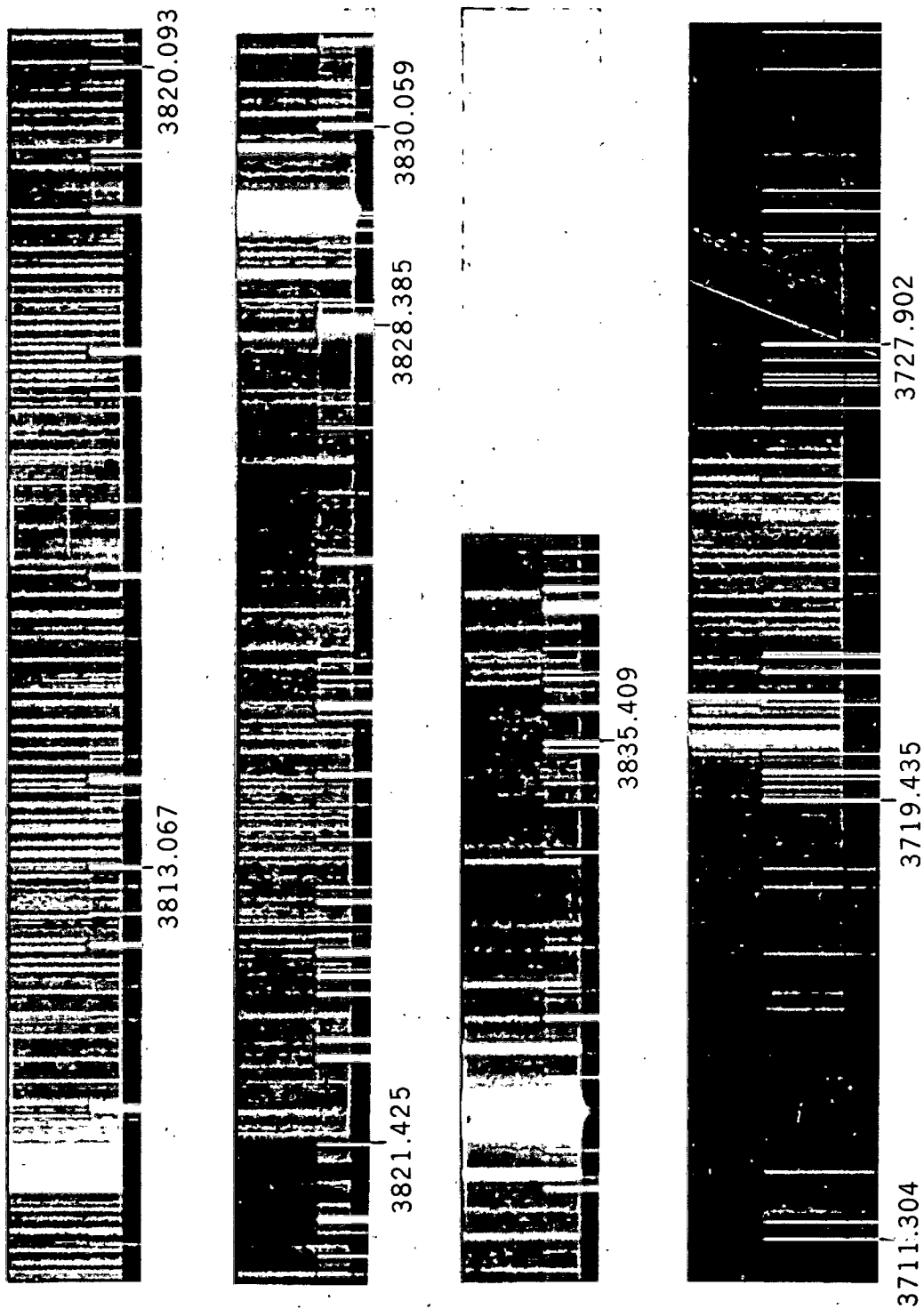
Fig. 10

VIII.   SUMMARY AND SUGGESTION FOR FURTHER WORK

The near-ultraviolet spectrum has been produced with the King furnace and a vacuum arc. It has been shown that the complex spectrum observed in the region 3600 to 4000 A is due to overlapping MgOH and MgO bands. These formulae have been verified by considerations of mass action law and of isotope shift. The prominent features of the MgOH and MgOD spectrum are listed. The rotational lines in the region 3766 to 3820 A of the oxide bands have been accurately measured for possible analysis.

In connection with magnesium oxide there are still many unsolved problems. To mention just a few: The ground state of the molecule is still ambiguous. The dissociation energy is not known. Observation of triplet-singlet transitions or perturbations might settle the first problem. By extending the regions of the known transitions to higher vibrational and rotational levels or to higher-lying new electronic transitions the second question could be answered. In the past, spectral intensities of the ultraviolet bands have been studied as a function of the temperature, but the oxide and hydroxide spectra have not been carefully separated. These experiments should be repeated, with each system produced separately to obtain the heat of vaporization by the Σ - plot method. The King furnace, however, is not a well suited source for these experiments. In case of MgOH the equilibrium is not maintained, as has been demonstrated above, and in case of the oxide bands serious problems are presented by the narrow temperature range available for producing the spectrum, the low oxide vapor pressure due to the reducing atmosphere, the presence of the dust and by the over-

lapping of the hydroxide features. The analysis of the near-ultraviolet oxide and hydroxide bands looks quite difficult, but certainly would be of great value. The study of the near-ultraviolet spectra produced by a hollow cathode or by microwave excitation should be very useful because the rotational excitation in these sources is very low compared with the arc.

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APPENDIX A

1. The Thermodynamic Stability of $MgO(g)$

The vapor pressure of $MgO(g)$ can be calculated at any temperature by considering the equilibrium

$$MgO(s) = MgO(g), \quad K_p = p_{MgO(g)}.$$
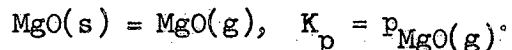
The free-energy functions for the species involved have been tabulated.[23] Depending on whether we consider the $^1\Sigma$ or $^3\Sigma$ ground state of gaseous MgO, the value of the free-energy function at $2300^\circ K$ is 60.78 or 62.96, respectively. For the heat of vaporization of MgO a value of 153 ± 3 kcal/mol has been obtained by Altman and Searcy[24] at $0^\circ K$ by the transpiration method, assuming $^1\Sigma$ ground state. This corresponds to 154 kcal/mol at $298^\circ K$. If the ground state were $^3\Sigma$, their value would have to be increased by 4.3 kcal/mol. For the dissociation energy of MgO an upper limit of 90 kcal/mol has been obtained by Inghram, Chupka, and Berkowitz,[25] applying mass-spectroscopic techniques. Birge-Sponer extrapolation for the $^1\Sigma$ state yields a dissociation energy of 85 kcal/mol.[24,26] The higher values of dissociation energies obtained by other investigators by flame techniques[27,28,29] or King-furnace excitation[7] can be discounted because of the disturbing influence of MgOH. By forming the appropriate thermodynamic cycle one can obtain the relationship

$$\Delta H_{f,298}(MgO,s) + \Delta H_{v,298}(MgO) + D_{298}(MgO) - E$$

$$= \Delta H_{v,298}(Mg) + 1/2 D_{298}(O_2),$$

where $\Delta H_{f,298}$, $\Delta H_{v,298}$, and D_{298} are the heat of formation, heat of vaporization, and dissociation energy at $298^\circ K$ and E is the energy of

excitation of the state to which $D_{298}(MgO)$ refers. Taking

$\Delta H_{f, 298}(MgO,s) = -143.7$ kcal/mol,[30]

$\Delta H_{v,298}(Mg) = 35.6$ kcal/mol,[31] and

$D_{298}(O_2) = 119.1$ kcal/mol,[32]

we have

$\Delta H_{v,298}(MgO) = 238.9 - D_{298}(MgO) + E.$

Assuming $^1\Sigma$ ground state, one has $\Delta H_{v,298}(MgO) = 152.9$ kcal/mol, which

is in close agreement with the value of 154 obtained by Altman and

Searcy.

From the two free-energy values and heat of vaporization of

152.9 and 157.2 kcal/mol, one obtains the following vapor pressures for

$MgO(g)$ at 2300°K.

$\Delta H_{v,298}(MgO)$	Ground state	$P_{MgO(g)}$
152.9 kcal/mol	$^1\Sigma$	$10^{-5.48}$
	$^3\Sigma$	$10^{-5.00}$
157.2 kcal/mol	$^1\Sigma$	$10^{-5.89}$
	$^3\Sigma$	$10^{-5.41}$

The vapor pressure of $Mg(g)$ at 2300°K has been found by similar

calculation as

$$P_{Mg(g)} = 10^{-5.89}/\sqrt{P_{O_2}}$$

by considering the equilibria

$MgO(s) = Mg(g) + 1/2O_2(g)$ and $1/2O_2(g) = O(g).$
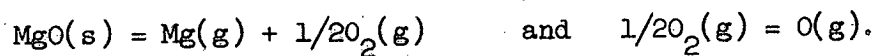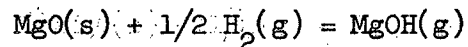
The free-energy functions have been taken from Reference 23.

From these calculations one can conclude that $MgO(g)$ species

will have similar importance to $Mg(g)$ in the vapor at this tempera-

ture only at oxygen pressures of about 1 atmosphere.

2. The Thermodynamic Stability of MgOH(g)

The vapor pressure of MgOH has been calculated from the equilibrium:

$$MgO(s) + 1/2\ H_2(g) = MgOH(g)$$

At $2300^{\circ}K$, using tabulated free-energy functions and enthalpies,[23] one obtains

$$P_{MgOH} = \sqrt{P_{H_2}} \times 10^{-5.7\pm1}$$

The uncertainty includes only that of the heat of formation of MgOH. The free-energy function for MgOH has been calculated by assuming the vibrational frequencies, internuclear distances, bond angle, and multiplicity of the ground state.

This result indicates that at hydrogen pressures above 1 atm the MgOH species are as important in the vapor at Mg(g) at this temperature.

APPENDIX B

Adel has derived formulae for the vibrational isotope effect in unsymmetrical linear and nonlinear molecules.[33,34] For the later case he assumed small mass differences, therefore his result is not applicable for the hydrogen-deuterium shift. Wilson gives equations for the normal modes of vibration of an asymmetric nonlinear triatomic molecules.[35]

In any case, in order to calculate vibrational isotope shift, all force constants and internuclear distances have to be known. In actual practice the problem is further complicated by the fact that one observes the shift of a band head which also includes the rotational isotope shift, the calculation of which is not possible without having the rotational analysis, and it would be very tedious even in that case.

The three normal modes of vibration and the three principal moments of inertia are affected differently by the isotope substitution. Assuming an Mg-O distance 1.9 A, OH distance 0.96 A, and an angle 110 deg, one calculates the three principal moments of inertia as $I_A \approx 10^{-40}$, $I_B \approx I_C \approx 70 \times 10^{-40}$ g cm^2. The molecule can be treated therefore as prolate asymmetric top. The two larger moments of inertia are not appreciably affected by a hydrogen-deuterium exchange.

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