IOWA STATE UNIVERSITY
Digital Repository

1931

Band spectra produced by certain explosion mixtures

Harley A. Wilhelm
Iowa State College

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Physical Chemistry Commons

NOTE TO USERS

BAND SPECTRA PRODUCED BY CERTAIN EXPLOSION

MIXTURES

BY

HARLEY A. WILHELM

A thesis submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject Physical Chemistry

Approved:

In charge of Major work

Head of Major Department

Dean of Graduate College

Iowa State College
1931

UMI Number: DP12003

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI®

TABLE OF CONTENTS

1126-65

I. INTRODUCTION

This paper deals with the excitation of molecular spectra by the explosion of mixtures of solids and gives the results so far obtained on the spectra emitted by MgS and PbS.

This work was begun with the idea of producing emission spectra of intermetallic compounds, photographing these spectra and interpreting them. Although a large number of intermetallic compounds was studied, the ordinary methods of excitation which were used failed to produce any molecular spectra assignable to such compounds. The arc and spark spectra between electrodes of the compounds were investigated in the region 2400. to 6700. A. Due to the failure to obtain molecular spectra of intermetallic compounds, other compounds were studied with the object of developing suitable methods for exciting these spectra. The plan of this part of the work was to follow the periodic table passing from the oxides of the metals, which are relatively easy to excite and photograph, to the more metallic compounds formed by elements lower in the same family. Out of this work has developed the production of band spectra by explosion mixtures. The development and use of this method of excitation are presented herein.

II. HISTORICAL

The work of Barrat (1) on absorption of mixed
metallic vapors, and the observation by Newman (2) that bands
are emitted by excitation of mixed sodium and potassium vapors,
have shown that intermetallic compounds exist in the vapor
state and are capable of absorbing and being excited to emit
spectra similar to other non-metallic compounds. In previous
work in this laboratory several intermetallic compounds were
made up and excited in the arc and spark in air. A few were
arced in an atmosphere of hydrogen. The results of this work
indicated that no band spectra were produced, which were assign-
able to intermetallic compounds. The spectrum produced in each
case was a qualitative summation of the spectra of the two
metals, each excited under the same conditions as the compound,
and showed only reversals and variations in relative intensities.
Similar observations were made by Tammen (3) who examined the
spectra emitted by Cu_2Sb, Zn_2Cu_2, Bi_2Mg_2 and Mg_2Sn when arced
in air. Wache (4), in his observations of the spark spectra of
copper in aluminum and of copper in zinc, found only atomic
spectra. Wheatstone and Ångström (5) made observations similar
to those of Wache, on spark spectra of amalgams and brasses.

Due to the apparent inability to excite inter-
metallic compounds by arc and spark in the ordinary way, the
work on these compounds was dropped temporarily for a study of
excitation of less metallic compounds. Since the spectra of
the oxides of many of the metals were already known and analyzed,
and the combination of metals with elements lower in the same
family of the periodic table as oxygen would produce compounds
more metallic, the next step was to produce and analyze band
spectra of the sulfides of the metals. A search of the litera-
ture revealed that no metallic sulfide spectra had been analyzed.
The only molecular spectra involving sulfur, which have been
found to have been analyzed (6) were those of sulfur atoms with
carbon (7), oxygen (8) and other sulfur (9) atoms.

The excitation of the sulfides was then tried by
arcing metallic electrodes having cores of sulfur. This excita-
tion produced no spectra assignable to the sulfide of a metal.
Some metals were then arced in atmospheres containing sulfur,
such as H_2S and CS_2. In the former, the outstanding molecular
spectra produced were those of the hydrides of the metals, with
no evidence of sulfide spectra. In the latter case no metallic
sulfide spectra were found. Strong Swan bands were produced
regardless of the metal used as electrodes when arced in CS_2.
The production of spectra of metals in pure sulfur vapor was
then tried, but the strong absorption of the low temperature

sulfur vapor around the arc and the difficulties encountered in the operation of the arc made the method quite undesirable. The only evidence of sulfide spectra obtained by this method, was that obtained by copper, Figure 1a.

Due to the observation that a flashlight powder produced band spectra, it was decided to try the explosion of mixtures as a means of exciting the sulfide spectra. This method was found to be suitable for the production of spectra of sulfides and applicable to many other compounds. A search of the literature showed that a method similar to the one being developed in this laboratory was used by Ghosh, Mahanti and Mukkerjee (10) to excite the blue-green system of MgO. In their work, a mixture of magnesium nitrate and magnesium powder was ignited by means of a sparking arrangement.

III. THEORETICAL

The relations existing between the energy changes
in a gaseous diatomic molecule and its spectrum have been very
ably presented by Jevons (11). More recently Meggers and
Wheeler (12) have applied the notation recommended by Mulliken
(13) to the treatment of molecular spectra by Jevons. A
theoretical treatment, which is sufficient for the interpreta-
tion of the present work, is presented here.

The energy which may change by absorption or radia-
tion, in a gaseous diatomic molecule in any particular electronic
state, when the molecule is vibrating longitudinally along the
line joining the centers of the atoms and rotating on an axis
perpendicular to this line, is represented by the equation,

$$E = E_e + E_v + E_r \qquad \text{Equation 1.}$$

Here E_e is electronic energy, E_v is vibrational energy, and E_r
is rotational energy. A change in this energy, either by
radiation or absorption, such change being any combination of
possible changes in the three practically independent variables,
may be represented by the equation,

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_r \qquad \text{Equation 2.}$$

Of these changes, the shift in electronic energy ΔE_e is by far
the greatest and a system of bands is determined by any single

electron jump. ΔE_v is next in magnitude and determines the bands of a system. ΔE_r is of small magnitude compared with the other changes and furnishes the fine line structure to the bands. Since E_r is indirectly proportional to the moment of inertia I, it may be seen that a molecule having a high moment of inertia would furnish a fine line structure, which could not be resolved except on a spectrograph with high resolving power. Since the molecules dealt with in this paper are molecules with relatively high moments of inertia, the rotational structure is not defined by the spectrograph used. Since the origin of a band is not distinguishable without fine line structure, the band heads, which bear nearly a constant difference with the band origins throughout a system, are the only measurable quantities to determine in the analysis of a system. Equation 2 then becomes for this work,

$$\Delta E = \Delta E_e + \Delta E_v \qquad \text{Equation 3.}$$

The energy of vibration of this diatomic molecule is given approximately by the new quantum mechanics as

$$E_v = hc\left[\omega_o(v + 1/2) - \omega_o x (v + 1/2)^2\right] \qquad \text{Equation 4.}$$

v (the quantum number for vibrational states) = 0, 1, 2, 3, ----. $c\omega_o$ per second is called the frequency of vibration of infinitesimal amplitude and x is a small constant. Since the electronic change causes changes in both ω_o and $\omega_o x$

$$\Delta E_v = hc \left[\omega_o{}'(v' + 1/2) - \omega_o{}'x'(v' + 1/2)^2 \right] -$$

$$hc \left[\omega_o{}''(v'' + 1/2) - \omega_o{}''x''(v'' + 1/2)^2 \right] \quad \text{Equation 5.}$$

The (')s refer to the upper electronic state and the (")s refer to the lower electronic state. The energy accompanying a radiation or absorption is

$$\bar{E} = \frac{hc}{\lambda} = \Delta E \text{ (for the molecule)} \qquad \text{Equation 6}$$

where h is Planck's constant, c the velocity of light and λ the wave length of the light.

The wave number ν , i.e. the number of wave lengths of the light per centimeter in a vacuum is equal to $1/\lambda_{vac}$. Since the wave number associated with electronic and vibrational changes in a molecule is represented by,

$$\nu = \nu_e + \nu_v ,$$

and $\qquad \nu_v = \dfrac{\Delta E_v}{hc}$,

$$\nu = \nu_e + \left[\omega_o{}'(v'+1/2) - \omega_o{}'x'(v'+1/2)^2 \right] -$$

$$\left[\omega_o{}''(v''+1/2) - \omega_o{}''x''(v''+1/2)^2 \right] \qquad \text{Equation 7.}$$

ν_e is the energy in (cm^{-1}) units contributed to the light effect by the electron shift and defines the origin of the system.

In order to assign proper values to the variables and constants in equation 7, a table like Table 4 is constructed for the wave numbers of bands in a system. For making the assignments of v' and v", the following partial quotation from Meggers

and Wheeler (12), who modified the statements of Jevons (11) to conform with the notation recommended by Mulliken (13) is exceedingly helpful:

Bands for which v' (or v'') is constant and v'' (or v') varies constitute a v'' (or v') progression; thus the bands for which v', v'' are, respectively, 0,0, 0,1, 0,2, 0,3---form the v'' progression v'= 0, and the 0,2, 1,2, 2,2, 3,2---bands form the v' progression v'' = 2. Bands for which the change $v''-v'$ is constant form a sequence, thus the $v''-v'$+1 sequence consists of the 0,1, 1,2, 2,3, 3,4---bands. In analyzing a system it is usually expedient to arrange the wave numbers of the heads in a table such that the 0,0 band appears in, say, the left-hand top corner, each v'' progression runs horizontally, each v' progression runs vertically and each sequence runs diagonally from top left to bottom right. The vibrational quantum analysis may, indeed be said to consist of the correct construction of such a table, for when this is achieved, the values of v' and v'' can be assigned with almost complete certainty, and the coefficients in equation (11)* often evaluated.

Criteria for the v', v'' assignments are:

1. ν increases with decreasing v'' in a v'' progression and with increasing v' in a v' progression.

2. The intervals $\Delta\nu$ between successive bands of a progression decrease with increasing v' or increasing v'', very nearly in arithmetical progression if Q heads or band origins are tabulated, and less nearly in arithmetical progression if R or P heads are used.

3. A decrease of I is accompanied by an increase of ω_e, and vice versa; hence, if the bands degrade toward the infra-red $I'' < I'$, $\omega_e'' > \omega_e'$, and the above intervals $\Delta\nu$ are larger in a v'' progression than in a v' progression; the reverse is true if the bands degrade toward the ultra-violet.

4. As a consequence of (1) and (3), along a sequence v' and v'' increase in the direction in which the bands degrade.

*Equation 11 refers to an equation similar to 7 of this paper.

5. When the directions of increase of v' and v'' are thus settled, their values are decided by the sudden cessation of a v'' progression (say $v' = 0$ or 1) at its low-ν end, and of a v' progression (say $v'' = 0$ or 1) at its high-ν end; the test is applied by verification of the entire absence from the spectrogram of bands whose ν's are obtained by extrapolations beyond the top row and left-hand columns of the above table.

. . . .

7. The distribution of intensity among the bands of a system is normally of the type in which a progression (say $v' = 4$ or $v'' = 4$) has two intensity maxima separated by a minimum, and the locus of all the maxima is a curve of nearly parabolic form (the Franck-Condon parabola) such that (a) its axis approximately coincides with the 0 sequence, and represents a rapid decline of intensity from a maximum to zero; (b) if the change $I'' - I'$ or $\omega_0'' - \omega_0'$ is very small, its vertex coincides with the 0,0 band (which is the strongest of the system), and its two limbs are close to one another and to the 0 sequence (which is the strongest, if not the only, sequence present); (c) as the change $I'' - I'$ or $\omega_0'' - \omega_0'$ increases, the vertex of the curve recedes from the 0,0 band, and the limbs of the curve become wider apart; thus the wide curve of maxima which characterizes a large change cuts the 0 sequence not at the 0,0 band, but at a higher v', v'' band.

8. The vibrational isotope effect, if present and precisely measurable, furnishes an absolute check on the v', v'' numeration and is, in fact, the experimental evidence for the use of $(v + 1/2)$ instead of v in the vibrational energy terms in equations[*] (2), (3), and (11).

Such a table has been constructed for a system of MgS bands in Table 4. The difference between two adjacent wave numbers in the progressions is shown in the columns indicated by $\Delta \nu_{\frac{v}{2}}$, which refers to the difference between the two

---

[*] Equations (2), (3), and (11), refer to equations similar to 4, 5 and 7 of this paper.

wave numbers with average v equal to $\frac{y}{2}$.

The constants $\omega_o"$, $\omega_o"x"$, ω_o', and $\omega_o'x'$ of equation 7 can be evaluated from Table 4. A general method for such a calculation will be developed at this point.

From equation 7 it may be seen that in a $v"$ progression the difference between two adjacent wave numbers is

$$\Delta \nu_{\frac{y}{2}}" = - \left[\omega_o"\left(\frac{y}{2}\right) - \omega_o"x"\left(\frac{y}{2}\right)^2\right] + \left[\omega_o"\left(\frac{y}{2} + 1\right) - \omega_o"x"\left(\frac{y}{2} + 1\right)^2\right]$$

from which

$$\Delta \nu_{\frac{y}{2}}" = \omega_o" - (y + 1)\omega_o"x"$$

Similarly $\quad \Delta \nu_{\frac{y+2}{2}}" = \omega_o" - (y + 3)\omega_o"x"$

The difference between these two adjacent $\Delta \nu$'s of a $V"$ progression is then,

$$\Delta \nu_{\frac{y}{2}}" - \Delta \nu_{\frac{y+2}{2}}" = \omega_o" - (y+1)\omega_o"x" - \omega_o" + (y+3)\omega_o"x" = 2\omega_o"x"$$

Also $(y+3)\Delta \nu_{\frac{y}{2}}" - (y+1)\Delta \nu_{\frac{y+2}{2}}" = (y+3)\omega_o" - (y+1)\omega_o" = 2\omega_o"$

In the same way ω_o' and $\omega_o'x'$ may be evaluated and the whole summed up as

$$\omega_o'x' = \frac{\Delta \nu_{\frac{y}{2}}' - \Delta \nu_{\frac{y+2}{2}}'}{2}$$

$$\omega_o' = \frac{(y+3)\Delta \nu_{\frac{y}{2}}' - (y+1)\Delta \nu_{\frac{y+2}{2}}'}{2} , \quad \text{(when } \Delta \nu_{\frac{y}{2}}' = \nu_{v'=\frac{y+1}{2}} - \nu_{v'=\frac{y-1}{2}})$$

and

$$\omega_o"x" = \frac{\Delta\nu_{\frac{y}{2}}" - \Delta\nu_{\frac{y+2}{2}}"}{2}$$

$$\omega_o" = \frac{(y+3)\,\Delta\nu_{\frac{y}{2}}" - (y+1)\,\Delta\nu_{\frac{y+2}{2}}"}{2} \quad \left(\text{when } \Delta\nu_{\frac{y}{2}}" = \nu_{v"=\frac{y-1}{2}} - \nu_{v"\frac{y+1}{2}}\right)$$

The value for ν_e can be calculated after the above constants have been determined.

IV. MATERIALS

The compounds used in this work were all marked C.P.
except the BaO_2. The compound $MgSO_4$ (dried), on which consider-
able weight is placed in the proof of a carrier of a band
system presented herein, was

Cl	0.010%
As	0.001%
Alkali Metals (as Na)	0.500%
Fe	0.003%
Other Heavy Metals	None

The sources of magnesium besides that in the $MgSO_4$,
were the following:

(a) A metal which contained at least 99.6% magnesium.
The impurities possible were

Cu less than	0.01%	Al less than	0.006%
Mn less than	0.01%	Ba	0.003%
Fe less than	0.03%	Ca	0.012%
Si about	0.04%	Alkali metals - trace	
Oxide	0.2 to 0.3 %		

(b) A portion of the above magnesium metal was sublimed
here and the product used as the second source. This product
was not analyzed.

The source of aluminum, which was used in the work, was bronzing aluminum, labelled chemically pure.

Flowers of sulfur was the source of free sulfur.

V. APPARATUS AND MANIPULATIONS

The spectra discussed herein were photographed with a Hilger El Quartz spectrograph. The dispersion of this instrument varies from about 47 A per millimeter at 6500 A to 8.5 A per millimeter at 4000 A, the region so far used in the study of explosion spectra. The photographic plates which were used were Wratten and Wainwright panchromatic. These plates were sufficiently fast to register the band systems up to 6500 A, with very short exposures. Since several of the systems excited gave spectra which progressed farther to the red than the limit of these plates, plates sensitized to the far red by kryptocyanine and to the infra red by neocyanine were tried. These sensitized plates were entirely too slow for this work.

Various materials for supporting the charge were tried, the most satisfactory for general use being a 1/4 inch carbon rod having a cone shaped cup drilled in one end. The mixture was placed in this cup in the upright position in such a way that the exploding material would pass up before a lense which focused the light on the slit of the spectrograph. To produce the MgS bands for final measurement, the charge was ignited in a cup in a magnesium rod. The use of this material eliminated any bands due to carbon which would interfere with measurement of the MgS bands.

The most satisfactory method found for igniting the mixture was to strike an arc on the rod in the vicinity of the charge. The rod holding the charge was connected to the positive pole of a 100 volt storage battery. Other methods of ignition such as by flame, spark and fuse were tried. The arc method proved to be best in that mixtures which required considerable heating before reaction started could easily be so treated by heat from the arc.

The spectra were compared with the iron arc spectrum at 100 volts D.C. through the use of a Hartmann diaphram. Measurements of the spectra were found to be quite difficult to make with the high magnification of the microscope of the Societe Genevoise Measuring Machine, which can be read to .0001 centimeter. The magnification showed plate graininess and made the location of bands difficult. Other methods of measurement were tried, such as projecting the image at about 25 diameters magnification on a screen, where the band heads could be seen much better than under the microscope. The image was measured, but the amount of error, due to the chromatic aberration of the projector and the change in temperature of the plate by the light source, was too great.

The graininess of the plate was eliminated and good contrast was brought about by an attachment made in the College Instrument Shop for the microscope of the Measuring Machine.

This attachment was designed in this laboratory. Due to the simplicity of the apparatus, and marked increase in the accuracy of the work by its use, it is described here. It will be seen that the image produced and the control of the apparatus gives it advantages over some of the methods reviewed by Wright (14).

The mechanism is merely a small metallic cube, which rotates between the objective and the object on an axis perpendicular to the axis of the microscope and perpendicular to the spectral lines. The cube has large holes drilled through from face to face along the other two axes. Over these four holes are cemented thin glass plates. This rotating cube is housed to prevent the image being dimmed by reflected light. Only a small aperature, sufficiently large for the field to be observed, is left between the object and the rotating cube. This attachment is fastened to the microscope and the rotator driven by means of a belt from a small electric motor to a pulley on the axis shaft extended outside the housing. In order to correct for the change in focus as the angle between the faces of the cube and axis of the microscope changes, a small correcting lens is placed over the aperature between the object and the cube. This lense was found unnecessary for the thickness of glass plates used in this instrument. In order that the axis of rotation may be perpendicular to the lines on

the plate, an adjustment is provided for turning the attachment through a sufficient angle. During each revolution of the cube, four views of the field are received, therefore, the slow rate of four or five revolutions per second is sufficient to fuse the grains into a solid well defined line. Each grain is elongated into a straight line. The amount of elongation depends upon the thickness of the plates used on the cube. The image of a grain always travels in one direction across the field, making a line of even intensity throughout its length. The field may easily be examined for spots not due to lines by merely stopping the rotator. By this arrangement, no errors due to shift of prisms or parts are introduced.

After the band systems and the iron arc spectrum were measured, the micrometer readings for the iron arc were plotted against wave lengths on a large graph. From this curve, the wave lengths in air of the band heads were determined. These wave lengths were then changed over to wave lengths in vacuum by the addition of a correction taken from tables worked out by Meggers and Peters (15) and given by Baly (16). The wave numbers were obtained from vacuum wave lengths by dividing one by this wave length expressed in centimeters. A Munroe calculation machine was used to carry out the calculations in the work.

VI. EXPERIMENTAL

In the course of the work, the spectrum produced by
a flashlight powder made of powdered magnesium and powdered
barium peroxide was photographed. This photograph showed a
strong emission band system, shown in Figure 2d to the red end
of the spectrum. A few measurements were made of the system
which showed it to be due to BaO, which had already been analyzed
by Mecke (8). Manganese dioxide was then mixed with powdered
magnesium. The burning of this mixture gave the MnO system,
Figure 2c, also treated by Mecke (8). A mixture made of lead
dioxide and magnesium gave the PbO system, Figure 2b, analyzed
by Bloomenthal (17). By using aluminum in place of the magnesium
in the above mixtures, the same spectra were observed as before
except that the AlO system was produced by these mixtures while
the MgO system was present in the spectra produced by the first
mixtures.

When powdered sulfur was added to the explosion mix-
tures the spectrum emitted by each mixture changed considerably.
In place of the oxide spectra of barium, manganese and lead, new
systems appeared when the constituents were mixed in the proper
proportions. This appeared to be the solution to the problem
of exciting the metallic sulfides to emission. It being necessary

to prove that the new systems were due to the sulfides, a study
of band spectra produced by explosion mixtures was undertaken.
In the course of the work, several new band systems were excited
by the explosion method and an analysis given for one MgS
system. Due to the complicated structure of the PbS spectrum,
only a partial analysis has been given for the bands of PbS.
The work has included some previously known systems in order to
show the character of the spectra produced by this method of
excitation.

The character of the combustion was found to depend
upon the constituents of the mixture and the proportions used.
In some cases, the reaction was explosive as in the case of red
phosphorus and lead dioxide. In other mixtures, the combustion
was of the nature of a steady flame as was observed when the PbS
system was produced by a mixture of aluminum, sulfur and lead
dioxide. Due to the short duration of the excitation in an
explosion, several explosions were necessary to register the
spectrum on the photographic plate; while the flamelike combustion
required only a few charges per setting.

The temperature reached during the combustion can
only be estimated or given rough calculation. From the appear-
ance of the O— O band of AlO (18) in the burning of the mix-
ture of aluminum, lead dioxide and sulfur, which has probably
the lowest maximum temperature limit of any reaction yet studied,

it is estimated that temperatures reached are at least 3000° absolute.

The advantages of the explosion method as found from the work in this laboratory are: (a) The reduction of the relative intensity of the atomic spectrum which so often covers up bands when excited by the arc of the metal in the proper atmosphere. Figure 2a shows the visible PbO bands produced by an are between lead electrodes.in air, while Figure 2b shows the same system excited by explosion of a mixture of magnesium and lead dioxide. (b) Systems are produced which are difficult to produce otherwise. The CuS system obtained by arcing between copper electrodes in sulfur vapor, Figure 1a, an excitation which is very difficult to produce and photograph is compared with the same system excited by the explosion of a mixture of magnesium and copper sulfate, Figure 1b. (c) As has been seen in a description of the apparatus used, a minimum of equipment is necessary to excite spectra by this method.

The disadvantages of this method of excitation are:

(a) That the spectra which do extend far into the ultra violet are very weak in this region. Compare (a) and (b) of Figure 2 in which the band at left or violet end are much weaker for the spectrum by explosion. This, weakness is to be expected from the small amount of energy of reaction for the mixture which was used.

(b) Some explosions give a weak continuous background to their

spectra. This background makes it difficult to locate weak band heads. These continuous spectra can be reduced by adjusting the position of the charge and the relative amounts in the mixture to give an explosion rate which will allow the solid particles to exist for only a short time in focus with the slit of the spectrograph as compared with the time of existance of the excited gas in that position. Ghosh, Mahanti and Mukkerjee (10) have observed that the background produced by their mixture is much less than that obtained by exciting the MgO bands by burning magnesium ribbon. (c) Possibly the large number of kinds of atoms involved during an explosion makes the assignment to the proper carrier less certain. The method of elimination herein used seems to limit the possibilities to quite definite assignments. (d) Unless very fast photographic plates are used, this method requires a long time to record the spectra. The broadening of bands due to collisions (19) and pressure which no doubt would be enhanced in the explosion was not noticeable in the spectra as photographed by the low dispersion of the apparatus used.

A Band System of MgS

Figure 3 shows several bands produced during the explosion of a mixture of magnesium, mercuric oxide and sulfur.

To show that MgS is the carrier of a system observed in the blue region of the spectrum, when mixtures containing magnesium and sulfur are exploded, the observations on a number of different explosions are recorded in Table 1. Column 1 gives the mixture; column 2, the supporting electrode and column 3, gives the observation, positive if the system is observed in the spectrum, or negative if not observed.

<u>Table 1</u>

Mixture	Electrode	Observation
Mg and PbO_2	Carbon	+
Mg, PbO_2 and S	"	-
Al, PbO_2 and S	"	+
Mg and $PbSO_4$	"	+
Mg and $Bi_2(SO_4)_3$	"	+
Mg and CuO	"	-
Mg and $CuSO_4$	"	+
Mg, HgO and S	"	-
Mg, HgO and S	"	-
Mg and HgO	"	-
Mg and BaO_2	"	+
Mg and MnO_2	"	+
Mg and $MgSO_4$	"	+
Al and $MgSO_4$	"	+
Mg and $MgSO_4$	Magnesium	+

It is evident from these observations that magnesium and sulfur are both necessary in the mixture to produce the system under investigation. Other bands in the violet are common with this system, and it is quite probable that these bands

belong to other MgS systems corresponding to other electron transitions in the molecule. The vibrational quantum analysis is given for this system in Table 4.

The PbS Bands

Figure 4 shows the bands produced during the combustion of a mixture containing aluminum, lead dioxide and sulfur.

Table 2, similar to Table 1, is here constructed to show that PbS is the carrier of a number of bands, throughout the visible, which are produced when mixtures containing lead and sulfur are excited by their combustion.

Table 2

Mixture	Electrode	Observation Figure
Al and PbO_2	Carbon	−
Al, PbO_2 and S	"	+
Mg and PbO_2	"	−
Mg, PbO_2 and S	"	+
Mg, HgO and S	"	−
Mg, HgO, S and Pb	"	+
Mg, HgO, S and PbO	"	+
Mg, HgO, S and $PbCl_2$	"	+
Mg, HgO, S and PbF_2	"	+
Mg, HgO, S and PbO_2	"	+
Mg and $PbSO_4$	"	+
Mg, BaO_2 and S	"	−
Mg, SnO_2 and S	"	−
Mg, MnO_2 and S	"	−
Mg, CuO and S	"	−

These observations show that the two elements Pb
and S are both necessary constituents for the production of
the bands. The large number of sources of Pb and S seem to
eliminate the possibility of any impurities producing the
spectrum. Since the system is in appearance quite like that of
S_2 molecules, a very careful comparison was made between the
data on the S_2 bands (20) and these bands which showed them to
be entirely different. Since the origin of the system is some-
what indefinite, only a temporary analysis is included, as
given in Table 5.

Figure 1. (a) Copper arc in sulfur vapor. (b) The explosion of magnesium with copper sulfate.

Figure 2.
(a) PbO bands by arc of lead in air.
(b) PbO bands by explosion of Mg and PbO$_2$ mixture.
(c) MnO bands by explosion of Mg and MnO$_2$ mixture.
(d) BaO bands by explosion of Mg and BaO$_2$ mixture.

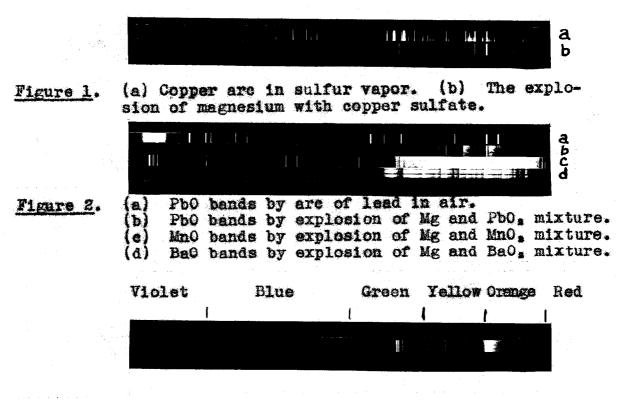| Violet | Blue | Green | Yellow | Orange | Red |

Figure 3. Bands produced during the explosion of a mixture of magnesium mercuric oxide and sulfur.

Figure 4. (a) Spectrum produced by burning 4 charges of a mixture of aluminum, lead dioxide and sulfur. (b) The iron arc spectrum. (c) Spectrum produced by burning 2 charges of a mixture of aluminum, lead dioxide, and sulfur.

VII.   RESULTS

A system of bands of MgS (Figure 3) has been obtained which shows four distinct sequences in the blue part of the spectrum. About 20 band heads have been measured for the system. Other band heads belonging to the same system are no doubt present, but too weak to measure accurately. There appears to be some doubling in the very weak bands of the (+2) sequence. The overlapping of this system in the voilet with other bands, possibly due to another system of MgS, has prevented measuring the weak heads in that region. The system degrades to the red as shown by the (0) sequence.

The wave lengths, estimated relative intensities (from 00 the very weak to 4, the strongest), wave numbers and v'v" assignments for this MgS system are shown in Table 3.

The vibrational quantum analysis for this MgS band system is given in Table 4, which was constructed according to the criteria for v'v" assignments. An approximate equation for the system based on the above data and assignments is

$$\mathcal{V} = 23{,}055.8 + \left[495.3\ (v' + 1/2) - 2.8\ (v' + 1/2)^2\right] - \left[525.2\ (v'' + 1/2) - 2.93\ (v'' + 1/2)^2\right]$$

Table 3

Data on MgS band heads

λ (Hd.)(I.A.)	Intensity	ν (cm^{-1})	v'	v"
4547.6	00	21,983.8	2	3
4543.8	00	22,002.2	1	2
4467.0	2	22,380.4	6	7
4462.7	2	22,401.9	5	6
4458.6	2	22,422.5	4	5
4454.5	2	22,443.2	3	4
4449.4	3	22,468.9	2	3
4444.4	3	22,494.2	1	2
4439.6	3	22,518.5	0	1
4356.0	00	22,950.5	3	3
4349.8	1	22,983.2	2	2
4344.2	2	23,012.8	1	1
4338.9	4	23,040.9	0	0
4278.9	00	23,363.9	6	5
4272.8	00	23,397.3	5	4
4267.1	0	23,428.5	4	3
4260.3	0	23,465.9	3	2
4254.2	1	23,499.6	2	1
4247.9	1	23,534.4	1	0

TABLE 4. *Vibrational Quantum Analysis of MgS Band System No. 1.*

v' \ v''	0	Δν1/2	1	Δν3/2	2	Δν5/2	3	Δν7/2	4	5	6	7	AVERAGE
0	23,040.94	522.4	22,518.53	516.3	22,002.200								
Δν1/2	493.5		494.3		492.0								493.3
1	23,534.41	521.6	23,012.82	518.6	22,494.23	510.4	21,983.800						
Δν3/2			486.8		489.0		485.1						487.0
2			23,499.61	516.4	22,983.21	514.3	22,468.93						
Δν5/2					482.7		481.6						482.2
3					23,465.90	515.4	22,950.500	507.3	22,443.22				
Δν7/2							478.0						478.0
4							23,428.50			22,422.52			
5									23,397.300		22,401.92		
6										23,363.900		22,380.42	
AVERAGE		522.0		517.1		513.4		507.3					

The spectrum of PbS (Figure 4a and c) which has been obtained shows strong bands throughout the entire visible region. The limit of the photographic plate is about 6700 A and in that part of the spectrum the bands are very strong, so no doubt extend farther to the red than the data indicate. Over 100 bands have been measured in the region photographed. All bands degrade to the red and show no rotational structure.

Table 5 gives the data which has been obtained on the spectrum. These data include all bands observed on the photograph produced by the combustion of a mixture of aluminum, lead dioxide and sulfur on a carbon electrode. No doubt some of these bands cannot be assigned to PbS.

A complete analysis of the PbS bands has not yet been obtained because of the difficulty met with in selecting an origin. The bands seem to fit into two or three schemes only partially. Further study of these bands is needed.

The band spectrum produced by the explosion of mixtures of Pb and S resembles closely the band systems for PbO as reported by Bloomenthal (17). However, a careful comparison of these two spectra reveals that the explosion spectrum contains many new bands which when analyzed can be definitely ascribed to a PbS system.

Table 5

λ(Hd.) IA	Intensity	ν (cm^{-1})	λ(Hd.) IA	Intensity	ν (cm^{-1})
6660.	0	15,015.0	5275.5	00	18,950.2
6542.6	1	15,280.0	5268.1	00	18,976.8
6482.0	4	15,423.0	5249.4	2	19,044.7
6372.3	2	15,688.5	5229.4	4	19,117.5
6314.1	4	15,833.3	5194.0	00	19,246.8
6285.3	00	15,905.8	5184.2	2	19,284.2
6270.7	2	15,942.9	5159.2	4	19,377.6
6153.8	4	16,245.6	5132.7	00	19,485.2
6113.7	2	16,352.2	5115.3	4	19,543.8
6087.7	1	16,422.0	5092.4	1	19,631.7
6073.2	1	16,461.2	5084.8	1	19,661.0
6033.5	0	16,569.5	5069.1	2	19,721.9
6001.5	4	16,657.8	5048.6	4	19,802.0
5964.0	1	16,762.8	5026.0	00	19,891.0
5926.1	0	16,869.9	5004.9	1	19,974.8
5909.3	1	16,917.9	4983.1	4	20,062.2
5872.0	1	17,025.3	4978.2	1	20,081.9
5854.1	4	17,077.4	4943.9	00	20,221.2
5767.3	4	17,334.3	4920.2	4	20,318.6
5733.2	1	17,437.4	4901.1	00	20,397.8
5714.8	0	17,493.5	4876.1	1	20,502.3
5701.4	00	17,534.6	4865.3	1	20,547.8
5630.2	4	17,756.3	4859.4	4	20,572.7
5603.9	00	17,839.6	4841.8	1	20,647.5
5580.6	0	17,914.4	4811.5	1	20,777.5
5566.0	00	17,961.4	4800.2	1	20,826.4
5550.0	4	18,013.1	4778.7	1	20,920.1
5520.2	2	18,110.4	4762.6	00	20,990.8
5500.4	2	18,175.5	4742.3	00	21,080.6
5462.5	00	18,301.6	4724.4	1	21,160.4
5443.1	0	18,366.8	4715.0	1	21,202.6
5422.9	4	18,435.2	4707.0	1	21,238.6
5414.7	0	18,463.1	4698.6	00	21,276.6
5385.2	0	18,564.2	4685.8	0	21,334.7
5375.1	2	18,599.1	4668.2	0	21,415.1
5347.5	4	18,695.1	4652.3	1	21,488.3
5321.8	2	18,785.3	4631.0	00	21,587.1
5301.3	4	18,858.0	4622.6	2	21,626.3

4595.5	1	21,753.8	4352.2	00	22,970.6
4583.0	0	21,813.1	4342.0	00	23,024.5
4563.5	3	21,906.8	4328.5	00	23,096.3
4554.2	00	21,951.5	4317.3	3	23,156.2
4548.2	00	21,980.4	4267.0	3	23,429.1
4533.0	3	22,054.1	4246.9	1	23,539.9
4517.8	00	22,128.3	4238.4	00	23,587.1
4506.3	1	22,184.8	4233.6	00	23,613.9
4493.5	00	22,247.9	4217.8	0	23,702.3
4481.6	0	22,307.0	4198.2	00	23,812.9
4475.9	1	22,335.4	4181.1	00	23,910.3
4427.5	0	22,580.0	4158.2	00	24,041.9
4421.7	2	22,609.6	4125.6	0	24,231.9
4375.4	00	22,848.8	4107.1	1	24,341.
4368.4	3	22,885.4			

VIII. INTERPRETATION OF RESULTS

The moment of inertia of the MgS molecule with the electron in the more excited state is, when $V'=0$, represented by I_0' and similarly for the less excited state is I_0''. From the observation that the bands degrade to the red

$$I_0' > I_0''.$$

Since $I_0 = r_0^2 \mu$, where r_0 is the nuclear separation of the two atoms in the zero vibrational state and μ is the reduced mass,

$$r_0' > r_0''$$

The electronic levels which produce this system of MgS bands are separated by 2.85 volts or a difference in level corresponding to 65,800 calories per gram molecule.

The energy of dissociation of the MgS (gas) molecule to give Mg (gas) + S (gas) may be calculated by the equation developed by Birge and Sponer [20]. This equation is

$$D = \int_0^{V_0} \omega_v \, dv$$

where D is energy of dissociation, $\omega_v = \omega_0 - 2\omega_0 xv$ and V_0 is the value of V which makes $\omega_v = 0$. This equation when applied to the more excited state of the molecule becomes

$$D' = \int_0^{V_0'} \omega_v' \, dv'$$

and gives for the MgS molecule in that state the value
$D' = 62,000$ cal/mole. Similarly the dissociation of the less
excited molecule gives $D'' = 67,000$ cal/mole.

IX. SUMMARY

1. The method of exciting band spectra by explosion mixtures has wide applicability and should lead to the study of many new systems.

2. The spectrum of MgS has been excited by this method and a band system obtained which degrades to the red.

3. The heat of dissociation of the MgS molecule in two different states of excitation has been calculated.

4. The spectrum of PbS molecules is easily photographed by the explosion method. The spectrum of PbS which resembles that of PbO is not easily analyzed.

5. The advantages outweigh the disadvantages of the method for production of many spectra in the longer wavelength regions.

X. LITERATURE CITED

1. Barratt, Molecular Spectra and Molecular Structure, p.758, The Faraday Society (1929).

2. Newman, Phil. Mag. 48, 159 (1924).

3. Tammen, Z. anorg. allgem. Chem., 92, 76 (1915).

4. Wache, Compt. rend., 177, 39 (1923).

5. Wheatstone and Ångström, Z. anorg. Chem., 92, 77 (1915).

6. Birge, International Critical Tables Vol. V, p. 411 (1929).

7. Jevons, Proc. Roy. Soc. (London), 117, 351 (1928).

8. Mecke, Zeits. f. Physik. 42, 390 (1927).

9. Rosen, Zeits. f. Physik, 43, 69 (1927).

10. Ghosh, Mahanti and Mukkerjee, Phys. Rev., 35, 1491 (1930).

11. Jevons, Proc. Phys. Soc. (London), 41, 538 (1929).

12. Meggers and Wheeler, B.S.Jour. Research, 6 (RP 273), 239 (1931

13. Mulliken, Phys. Rev., 36, 611 (1930).

14. Wright, Jour. Opt. Soc. Amer., 21, 485 (1931).

15. Meggers and Peters, Scientific Papers of Bureau of Standards, No. 327 (1918).

16. Baly, Spectroscopy Vol. I, p. 128, Longmans, Green and Co. Ltd. (1927).

17. Bloomenthal, Phys. Rev., 35, 34 (1930).

18. Ornstein and Brinkman, K. Akad. Amsterdam Proc., 34, No. 4, 498 (1931).

19. Lasareff, Zeits. f. Physik., 64, 598 (1930).

20. Birge and Sponer, Phys. Rev., 28, 259 (1926).

XI. ACKNOWLEDGMENT

The writer wishes to take this opportunity
to express his sincere thanks to Dr. W. H. Jennings,
who suggested the problem and gave valuable suggestions
throughout the work.