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UNIVERSITY OF CALIFORNIA  
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DIATOMIC MOLECULES

Martin D. Shetlar  
(Ph.D. Thesis)

April 5, 1965

LOW-LYING ENERGY STATES IN NINE-VALENCE-ELECTRON  
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LOW-LYING ENERGY STATES IN NINE-VALENCE-ELECTRON  
DIATOMIC MOLECULES

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April 1965

ABSTRACT

The electronic spectra of a number of diatomic molecules with nine valence electrons were studied experimentally to determine whether unobserved low-lying energy states existed for them. The results of these experiments are correlated with previous results from the literature in an effort to clarify a number of questions pertaining to the low-lying energy states of these molecules. Problems requiring further work are pointed out throughout the body of the report.

## I. INTRODUCTION

The group of gaseous nine-valence-electron diatomic molecules present several challenging problems because their spectra have not, as a set, been thoroughly analyzed. Many spectra of nine-electron molecules have been observed under a variety of excitation conditions as well as in absorption. Vibrational analyses have been carried out in many cases,<sup>1</sup> but rotational analyses have been confined to a small number of band systems in a few molecules.

One interesting problem concerning the group as a whole is "How do corresponding states (on the basis of molecular orbital theory) in an isoelectronic sequence involving nine valence electrons vary in energy with respect to the ground state as one moves from the center of the periodic table toward the ends?" To answer this question, one must know the lowest lying electronic states in each of the molecules in the isoelectronic sequence of interest. On the basis of published experimental results and interpretations, we do not know positively that the lowest lying excited states have been observed for a number of these molecules. In this report we attempt to answer these two questions as well as a number of others pertaining to individual groups of molecules.

## II. GENERAL CONSIDERATIONS

Consider a typical isoelectronic sequence of diatomic molecules with nine valence electrons: MgF, AlO, SiN, CP, BS, BeCl. If the atoms in each molecule are labeled according to their respective columns in the periodic table, they make the following sequence: II-VII, III-VI, IV-V, IV-V, III-VI, II-VII. A similar sequence could be arranged for singly ionized molecules with nine valence electrons. Because such an analogous labeling may be carried out for any nine-valence-electron isoelectronic sequence, it follows that the set of nine-valence-electron molecules may be partitioned into subsets on the basis of the periodic group to which the constituent atoms belong.

In general, the manifold of states of diatomic molecules may be built: (a) from molecular orbital configurations, (b) from states arising when the separated atoms are brought together, and (c) from states arising when the united atom is drawn apart.<sup>2</sup>

The states arising from the lower lying molecular orbital configurations for nine-electron molecules are given in Table I in order of predicted increasing energy. As the Group IIA and IIIA atoms involved in molecule formation become heavier,  $\delta$  orbitals may move to lower energies. This movement may result in molecular orbital configurations involving  $\delta$  orbitals appearing at energies comparable to the higher lying levels in Table I. However, due to the many states of approximately the same energy, one cannot definitely assign any observed states to configurations involving  $\delta$  orbitals.

With the separated-atom approach,<sup>2</sup> a number of states are obtained



Table I. Low-lying molecular orbital configurations for nine-valence-electron molecules. The configurations are listed from the bottom of the Table in order of increasing predicted energy.

| Molecular orbital configurations                | States   |
|---|--|
| (j) $z\sigma^2 y\sigma^2 w\pi^4 y^*\sigma$      | $^2\Sigma^+$   |
| (i) $z\sigma^2 y\sigma^2 w\pi^4 z^*\sigma$      | $^2\Sigma^+$   |
| (h) $z\sigma^2 y\sigma^2 w\pi^2 x\sigma^2 v\pi$ | $^2\Pi_r, ^2\Pi_i(2), ^2\Phi_r, ^2\Pi_r$   |
| (g) $z\sigma^2 y\sigma^2 w\pi^4 x\sigma v\pi$   | $^2\Pi_r(2)$   |
| (f) $z\sigma^2 y\sigma^2 w\pi^4 w\sigma$        | $^2\Sigma^+$   |
| (e) $z\sigma^2 y\sigma^2 w\pi^3 x\sigma w\pi$   | $^2\Sigma^+(2), ^2\Sigma^-(2), ^2\Delta, ^2\Delta_i, ^4\Sigma^+, ^4\Sigma^-, ^4\Delta_r$ |
| (d) $z\sigma^2 y\sigma^2 w\pi^4 v\pi$           | $^2\Pi_r$  |
| (c) $z\sigma^2 y\sigma^2 w\pi^4 x\sigma^2$      | $^2\Sigma^+$   |
| (b) $z\sigma^2 y\sigma^2 w\pi^3 x\sigma^2$      | $^2\Pi_i$  |
| (a) $z\sigma^2 y\sigma^2 w\pi^4 x\sigma$        | $^2\Sigma^+$   |

for each combination of atoms. These are, of course, the same states obtained by molecular orbital considerations. However, if we know the dissociation energy of a certain molecule, as well as the energies of the atomic states of the separated atoms, we can predict the states which must either be below a certain energy or be repulsive. The states that arise from low-lying separated-atom configurations are given in Table II.

The united-atom approach sometimes allows one to make valuable predictions concerning stability of electronic states that have been predicted from molecular-orbital or separated-atom considerations. If a state cannot arise from a low-lying stage of the united atom it cannot be stable. In nine-valence-electron molecules this sometimes lets states of high- $\lambda$  or high-spin multiplicity be eliminated from consideration as possible low-lying states.

In general this report describes the lowest of the low-lying electronic states (those which arise from the four lowest molecular orbital configurations), for they are of thermodynamic importance and are of value in the understanding of the energy trends of states in isoelectronic sequences.

In Section III are described experiments dealing with the spectra of these molecules. In Section IV the interpretive aspects of each subset are discussed for the following reasons: (a) The molecules in each subset have dissociation products that are analogous due to the similarity of the manifold of electronic states in atoms belonging to the same periodic group; (b) all molecules in such subsets are composed of atoms with somewhat similar electronegativity differences; (c) consideration of such subsets allows one to study the effect of increasing molecular weight on energy levels in a more systematic manner; (d) certain unique

Table II. Correlations of molecular states to separated atoms.

| Separated atomic states | Molecular states  |
|-------------------------|---|
| <u>II-VII Subset</u>    |   |
| $1S + 2P^0$             | $2\Sigma^+, 2\Pi$   |
| $3P^0 + 2P^0$           | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(2), 2\Delta$<br>$4\Sigma^+(2), 4\Sigma^-, 4\Pi(2), 4\Delta$  |
| $1P^0 + 2P^0$           | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(2), 2\Delta$   |
| $3D + 2P^0$             | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(3), 2\Delta(2), 2\Phi$<br>$4\Sigma^+(2), 4\Sigma^-, 4\Pi(3), 4\Delta(2), 4\Phi$                            |
| $1D + 2P^0$             | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(3), 2\Delta(2), 2\Phi$   |
| $M(2S) + X^-(1S)$       | $2\Sigma^+$   |
| <u>III-VI Subset</u>    |   |
| $2P^0 + 3P$             | $2\Sigma^+, 2\Sigma^-(2), 2\Pi(2), 2\Delta$<br>$4\Sigma^+, 4\Sigma^-(2), 4\Pi(2), 4\Delta$  |
| $2P^0 + 1D$             | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(3), 2\Delta(2), 2\Phi$   |
| $2S + 1D$               | $2\Sigma^+, 2\Pi, 2\Delta$  |
| $2P^0 + 1S$             | $2\Sigma^+, 2\Pi$   |
| $4P + 3P$               | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(2), 2\Delta$<br>$4\Sigma^+(2), 4\Sigma^-, 4\Pi(2), 4\Delta$<br>$6\Sigma^+(2), 6\Sigma^-, 6\Pi(2), 6\Delta$ |
| $M^+(1S) + X^-(2P)$     | $2\Sigma^+, 2\Pi$   |

Table II. (Continued)

| Separated atomic states | Molecular states   |
|-------------------------|--|
| <u>IV-V Subset</u>      |  |
| $3P + 4S^0$             | $2\Sigma^+, 2\Pi, 4\Sigma^+, 4\Pi, 6\Sigma^+, 6\Pi$  |
| $1D + 4S^0$             | $4\Sigma^-, 4\Pi, 4\Delta$   |
| $3P + 2D^0$             | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(3), 2\Delta(2), 2\Phi, 4\Sigma^-(2)$<br>$4\Sigma^-, 4\Pi(3), 4\Delta(2), 4\Phi$ |
| $3P + 2P^0$             | $2\Sigma^+, 2\Sigma^-(2), 2\Pi(2), 2\Delta, 4\Sigma^+, 4\Sigma^-(2),$<br>$4\Pi(2), 4\Delta$                    |
| $1D + 2D^0$             | $2\Sigma^+(2), 2\Sigma^-(3), 2\Pi(4), 2\Delta(3), 2\Phi(2), 2\Gamma$   |
| $1S + 4S^0$             | $4\Sigma^-$  |
| $1D + 2P^0$             | $2\Sigma^+(2), 2\Sigma^-, 2\Pi(3), 2\Delta(2), 2\Phi$  |

features in several of the subsets are best treated by individual consideration of each subset. In Section V some general conclusions are drawn and a summary of the results of the present investigation is given.

This report does not deal with the molecules formed from the group IIIA atoms (Sc, Y, and La), as these very likely involve the use of d electrons in their bonding and cannot be expected to be analogous in their behavior to other nine-valence-electron molecules. Work on the spectra and states of certain molecules involving these atoms is described by Walsh.<sup>3</sup>

### III. EXPERIMENTAL ASPECTS

We investigated the spectra of a number of nine-electron diatomic molecules with the objective of answering certain specific questions.

These specific questions were:

(a) To determine if there were unobserved low-lying electronic states in the magnesium halides. The reasons for suspecting the existence of such states are discussed in Section IV.

(b) To find the missing low-lying  $A^2\Pi$  state in the IIB monohalides.

(c) To find the undiscovered  $B^2\Sigma-X^2\Sigma$  transition in the IIB fluorides. This transition has been seen in all other IIB monohalides.

(d) To observe the heretofore unseen  $A^2\Pi-X^2\Sigma$  transition of the AlO molecule.

(e) To observe the SiN  $A^2\Pi-X^2\Sigma$  transition which is analogous to the well-known Red system of CN.

The experimental methods used and the results obtained are discussed in Section III.A. The detailed interpretation of the results obtained will also be discussed in Section III.

#### A. Production of Spectra

One problem in any systematic spectroscopic study is the production of suitable spectra. Jevons<sup>4</sup> has listed several methods for obtaining spectra, and other new methods have come into use since then. However, only a few of these are useful for a specific problem. For example, in many cases an arc is not a suitable source for investigations of molecular spectra in the infrared because of the black-body continuum arising from the electrodes and from dust particles in the arc plasma. Spectroscopic

absorption experiments are not always suitable because of high-temperature requirements or problems arising from the noninertness of the container materials. Similar objections can be raised about other methods for any specific problem, the most common being that the method under consideration simply does not produce the spectra of the desired molecule. Because of the possibility of selective excitation conditions, some sources may produce certain spectra of a given molecule and not others, or some molecules may have spectra excited by a given method and yet a very similar molecule may not. Thus in many cases considerable experimental effort may be devoted to finding a source which meets the requirements for the investigation.

In our study the primary objective was to find energy states lying within 8000 to 14000  $\text{cm}^{-1}$  of the ground state. In emission, transitions from such states to the ground state would lie in the near-infrared region. Thus emission sources for consideration should not show appreciable background radiation in the infrared region.

#### B. Spectra of the Magnesium Monohalides

In low-lying energy levels of the IIA-VII subset,<sup>1</sup> the distance between the lowest excited electronic state and the ground state for calcium is much smaller than the same distance for magnesium. On this basis one might expect the magnesium monohalides to possess unobserved low-lying electronic states. This investigation was undertaken with the objective of observing these states if indeed they existed.

Since the states of all magnesium monohalides are expected to be very similar, the study of one molecule only from this group was required. MgCl was picked as the molecule.

In the past the spectra of MgCl were produced by absorption,<sup>5,6</sup> and

arcs.<sup>4</sup> Because of the unsuitability of arcs for infrared work, we developed a new emission source. This consisted of a microwave-excited electrodeless discharge tube. The method has been used in the past for the production of atomic spectra and for certain spectra of relatively volatile molecules.

#### 1. Experimental Details

A Burdick microwave diathermy unit operating at 2450 Mc and 125 W was the power source. For the closed electrodeless discharge, an A-type director supplied power to the tube.

The electrodeless discharge tube was a sealed 10-mm o.d. quartz tube approximately 15 mm long; it contained anhydrous  $MgCl_2$  and about 3 mm of argon carrier gas. These tubes were prepared as follows: A tube was attached to a vacuum manifold with the magnesium contained in a side arm. The manifold was evacuated to  $10^{-6}$  mm. The quartz tube was heated almost to the softening point with a hand torch, then re-evacuated. This procedure was repeated several times with the objective of getting rid of absorbed gases on the walls of the quartz which can produce such impurity spectra as those of  $C_2$  and CO. The magnesium was then moved into the quartz tube and sufficient chlorine gas was admitted into the system to react completely with the magnesium. This chlorine gas was solidified within the manifold at liquid nitrogen temperatures, the stopcock on the manifold was closed, and the magnesium was heated to form anhydrous  $MgCl_2$ . The excess chlorine gas was then condensed in an auxiliary vial attached to the vacuum system. High-purity argon (Linde) was then admitted to the manifold at 3-mm pressure and the tube was removed from the system by applying a hand torch at the sealoff.

The spectrographs used in this work as well as in the subsequent



investigations were low-dispersion instruments. One was a Jarrell Ash 0.75 Meter  $f/6.3$  instrument with a grating blazed for  $1\mu$  and capable of a dispersion of  $42 \text{ \AA}/\text{mm}$  in first order. The second was a Steinheil three-prism instrument with a Polaroid-film attachment. The latter instrument was primarily used for survey work in the visible region of the spectrum.

In the infrared region we used Kodak I-N and I-Z plates which were hypersensitized by the standard recommended procedure of the manufacturer.

## 2. Results

The known  $A^2\Pi-X^2\Sigma$  transition in the near-ultraviolet region was observed in emission from the electrodeless discharge source. However, thorough exploration of the region between 4000 and 12000  $\text{\AA}$  revealed no spectra corresponding to new MgCl transitions. The significance of this absence of spectra is discussed in Section IV.

## 3. Absorption Experiments

We made several attempts to observe the absorption spectra of the MgCl molecule. Quartz absorption cells containing weighed amounts of magnesium were attached to the vacuum system, evacuated to  $10^{-6}$  mm, and thoroughly outgassed with a hand torch. A calculated pressure of chlorine gas was then admitted into the calibrated system and condensed into the absorption cell by means of liquid nitrogen. The cell was then sealed with a hand torch and heated to  $1100^\circ\text{C}$  in a Hevi-Duty multiple-unit furnace. Supplementary windings near the windows on quartz extensions to the cell allowed a near-constant temperature to be maintained throughout the cell. A zirconium arc was the source of the required background continuum.

Magnesium was in such excess that the equilibrium was shifted in favor of MgCl. The exact ratios and amounts of magnesium and chlorine used were based on calculations of equilibria from known<sup>8,9</sup> and estimated thermodynamic data.

Rapid attack of the quartz windows by the magnesium vapor made it impossible for us to obtain meaningful absorption spectra. However, we were unsuccessful in reducing the excess magnesium to an extent where attack would be minimized.

### C. Studies of the IIB-VII Subset

In the observed manifold of states in the IIB-VII subset, the expected lowest lying  $^2\Pi$  state has not been seen; in the IIB fluorides, the  $B^2\Sigma$  state has not been observed. We therefore searched for these missing states.

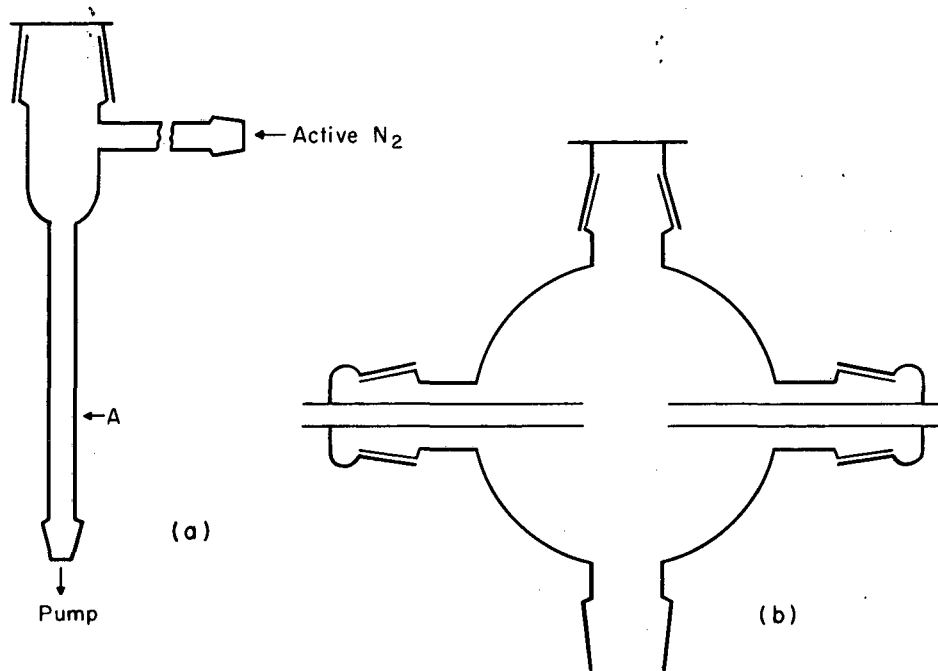
The methods of production of these spectra have usually been absorption and by use of discharge tubes. However Lord Rayleigh<sup>11</sup> and Mulliken<sup>12</sup> found that the spectrum of the HgI molecule could be excited by the reaction of active nitrogen with solid  $HgI_2$ . By investigating the effect of active nitrogen on other IIB dihalides, the author found that many spectra of the diatomic halides could be produced.

#### 1. Experimental Details

Although several designs for the reaction vessel were tried, the type shown in Fig. 1(a) was found to be the best for most solids. The solid dihalide was placed in A and when necessary a heating tape was wrapped around this portion. The reaction vessel used was made of quartz.

The active nitrogen was obtained from dry tank nitrogen passed over hot copper to remove oxygen. A Broida microwave cavity was used to produce the Lewis-Rayleigh afterglow, which extended throughout the system to the liquid nitrogen trap.

The desired spectrum was found in the reaction zone and the light produced in this zone was focussed into the spectrograph.



MU-35686

Fig. 1

## 2. Results

The spectra of the following molecules were observed in the reaction zone when active nitrogen reacted with the proper precursor: HgI, HgBr, HgCl, HgF, CdI, CdBr, CdF, ZnI, and ZnBr. With the exception of HgF and CdF, the spectra observed under these excitation conditions were transitions previously reported in the literature.<sup>1</sup> Plates taken in the infrared region out to 12,000Å showed no unreported spectra under the excitation conditions employed.

When heated in an active nitrogen stream, HgF<sub>2</sub> produced a weak green glow which could be photographed only under low dispersion on the Steinheil spectrograph with Polaroid film. The appearance of the spectrum (Fig. 3) suggests that it may be the missing B<sup>2</sup>Σ - X<sup>2</sup>Σ transition. However an assignment of this transition cannot be made with certainty without a source or conditions which produces a stronger spectrum.

When CdF<sub>2</sub> was heated in active nitrogen, a bright-green glow was observable. When photographed, this spectrum corresponded to the Cd <sup>3</sup>P-<sup>3</sup>S transition. No other spectra were observed.

The absence of the A<sup>2</sup>Π- X<sup>2</sup>Σ<sup>+</sup> transition is discussed in Section IV.

With the iodides and bromides of zinc and cadmium, an afterglow following the reaction zone was observed. Accompanying the bromides was the brick-red glow of the NBr spectrum. The afterglow of the iodine containing precursors was a bluish color and upon photographing under low dispersion appeared to be a continuum like structure, possibly belonging to NI or I<sub>2</sub>.

### D. Experimental Work on AlO

The missing A<sup>2</sup>Π-X<sup>2</sup>Σ transition in AlO poses one of the more interesting problems in the spectra of nine-valence-electron molecules. The analogous transition in BO has been observed.<sup>8</sup> For AlO, bands of this



(a)  
(b)  
(c)  
(d)

5790.66

5460.73

4358.34

ZN-4830

Fig. 2

transition would be expected in the region between 7,000 and 12,000 $\text{\AA}$ . Thus the arc, which is the usual source used for this molecule, cannot be easily used. One promising source resulted from the reaction of aluminum trimethyl with active oxygen;<sup>13</sup> this reaction produced a flame, where spectra under low dispersion were attributed to the formation of AlO. If such had been the case, an ideal source not only for AlO, but for other group III oxides would have been available.

### 1. Experimental Details

The reaction vessel was a three-liter bulb [Fig. 1(b)]. The aluminum trimethyl was purchased in cylinders from K and K Laboratories and the extra-high-purity oxygen was purchased from the Pacific Oxygen Co. The oxygen was passed through a Broida-type microwave cavity and allowed to react with  $\text{Al}(\text{CH}_3)_3$  vapor within the reaction vessel. Where the two gases met, a white flame with colored edges was formed. Upon reaction for several minutes, a layer of what appeared to be a mixture of carbon and aluminum oxide covered the walls of the vessel.

### 2. Results

All the spectra obtained were of the  $\text{C}_2$  molecule, and none were attributable to the AlO molecule.

#### E. Spectrum of SiN

By analogy with the red system of CN, an  $\text{A}^2\Pi-\text{X}^2\Sigma$  transition would be expected in the infrared region of the SiN spectrum. Our investigation was carried out in the hope of finding this transition.

Gaseous silicon nitride was produced by active nitrogen's action on  $\text{SiCl}_4$  vapor in the reaction vessel shown in Fig. 1(b). Accompanying this reaction was a purple glow that filled the whole bulb. Plates of this glow in the ultraviolet and visible regions showed the known  $\text{B}^2\Sigma-\text{X}^2\Sigma$

and  $C^2\Pi-A^2\Pi$  transitions. Our preliminary investigations in the infrared region were inconclusive, but we ceased work on this molecule upon learning that another group was also trying to find the Red system of SiN.<sup>14</sup>

#### F. Spectrum of BO

All the low-lying states of BO appear to have been seen and well characterized.<sup>1</sup> However, to eliminate the possibility that a still lower  $^2\Pi$  and  $^2\Sigma$  state remained undiscovered, we reinvestigated the spectrum of the BO molecule in the infrared.

Boron oxide was produced in a reaction vessel (Fig. 1) by the action of active nitrogen on  $BCl_3$ . The resultant blue glow which filled the reaction bulb, when photographed in the visible region, was shown to contain the known systems of BO. Plates taken in the infrared region showed the infrared bands of the  $A^2\Pi-X^2\Sigma$  system<sup>15</sup> but no new band systems.

#### G. Summary

The work reported in Sec. III showed no new band systems, with the exception of a possible  $B^2\Sigma-X^2\Sigma$  transition in HgF. The results obtained for the II-VII subset, along with previously unexplained data from the literature, allow one to make a number of conclusions concerning the states of these species. These conclusions are advanced in Sec. IV.

The prime need for further study of the AlO spectrum is a low-temperature source that would make possible conclusive studies in the infrared region. March has conducted experiments to observe the chemiluminescence of AlO formed by vaporizing aluminum atoms into an active oxygen stream,<sup>16</sup> but whether these experiments were successful is not known to us. If such a technique were to prove workable, it would provide

an ideal method of "looking" for the  $A^2\Pi-X^2\Sigma$  transition in the infrared region. Likewise it would provide a method of looking at transitions in the gallium and indium oxide molecules.

The observation of the red system of SiN should be a very promising project. Hopefully this system will be found in the near future by Broida et al.<sup>14</sup>

Further discussion and conclusions are presented in Sec. IV.



#### IV. INTERPRETIVE ASPECTS

##### A. The IIA-VII Subset

The alkaline-earth monohalides (AEM) constitute one extreme in the nine-valence-electron isoelectronic sequences. The AEM atoms have the largest electronegativity differences and would, as a group, be expected to be the most ionic of the nine-valence-electron molecules. Indeed, as recent studies have shown,<sup>17</sup> the ground states of the fluorides demonstrate ionic character. Although the small size of the fluoride ion makes ionic bonding in fluorides more energetically advantageous than in other halides, one would expect from considerations discussed in the next few paragraphs that the ground states of the other IIA halides (with the possible exception of beryllium) would also be ionic in character.

The ground states of the IIA-VII compounds probably arise initially from the separated ionic atoms  $M^{+} 2S + X^{-} 1S$ . Such a conclusion is supported by an argument presented by Herzberg.<sup>2</sup> If  $r_s$  is the internuclear distance at which the coulombic potential energy due to the separated ions is equal to the negative of the quantity [Ionization potential (metal) - Electron affinity (halogen)] and  $r_e$  is the equilibrium internuclear distance of the ground state, then when the ratio  $R = r_s/r_e$  is greater than 2.0, the ground state will be ionic. If  $R$  is less than 1.5 the ground state will be atomic, but if  $1.5 < R < 2.0$ , it is difficult to make a decision concerning the ionicity of the ground state. Morgan and Barrow have shown, in the case of  $MgCl$ , that it is a good approximation<sup>18</sup> to use the value of the M-X internuclear distance of the alkaline earth dihalides for the equilibrium internuclear distance in the monohalides. It is found that most of the alkaline earth monohalides have ionic ground states.

When this hypothesis is accepted, the next question is "What happens to the states that arise from the ground-state neutral atoms?" On the basis of discussion in this section (IV-A), it appears that these states may be either unstable or only slightly attractive. On the basis of these conclusions, it is possible for us to explain many of the puzzling features of the spectra of the IIA-VII molecules.

Many spectra of this group have been produced and analyzed vibrationally. In only a few cases have rotational analyses been done. The possibility of unobserved low-lying electronic states in certain molecules belonging to this subset provided a reason for part of the experimental work reported in Sec. III.

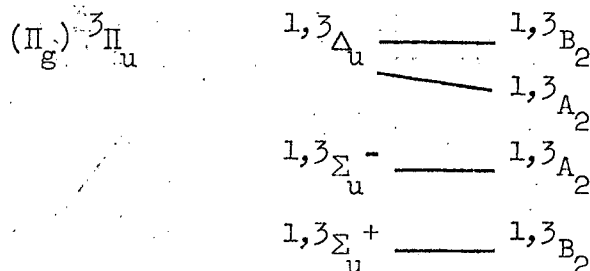
For detailed references and molecular data concerning molecules discussed in this report, consult the extensive compilations of Rosen<sup>1</sup> and Herzberg,<sup>2</sup> these are complete up to 1950. Information concerning dissociation energies is contained in the book by Gaydon.<sup>19</sup> We have included references and brief relevant reviews since 1950 in order to provide, in conjunction with the above works, an over-all coverage of the electronic states and spectra of the nine-valence-electron diatomic molecules.

1. Some Aspects of the Absorption Spectra of Alkaline-Earth Monohalide Systems

If an alkaline-earth halide is equilibrated with its vapor in a closed container at elevated temperatures, both diatomic and triatomic species will occur in the vapor phase. Absorption spectra of the vapor phase can yield transitions from the ground state to an excited state of either species. In the past none of the observed spectra of such systems have been definitely assigned to the dihalides, but many absorption spectra have been assigned to the diatomic species. However some spectra

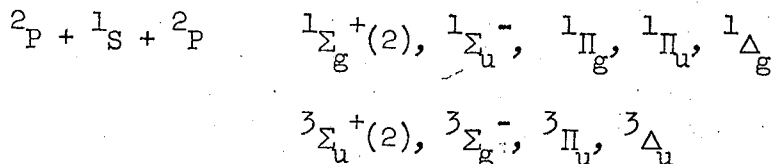
have been observed which have not been explained satisfactorily. A consideration of these spectra, which possibly belong to the alkaline-earth dihalides, leads to a better understanding of the states and spectra of the nine-valence electron monohalides.

On the basis of MO theory the alkaline-earth dihalides are sixteen-valence-electron molecules with a  $1\Sigma_g$  ground state. The lowest lying excited states result from the promotion of an electron from a bonding to an antibonding orbital, and therefore should lie rather high in energy. The states arising from this MO configuration are:<sup>20</sup>

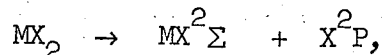


where the second column gives states in the linear molecule and the third gives the states in the bent. On the basis of selection rules, only the  $1\Sigma_u^+ - 1\Sigma_g^+$  transition would be expected to be strong.

The ground-state separated atoms correlate to form the following states:



All of these states must either (a) be below the energy corresponding to the heat of atomization of the dihalide, or (b) be repulsive. Some of them must be low enough to allow dissociation or cause predissociation leading to the process



which involves disruption of one bond and produces the diatomic halide. In the transition from the ground state to the excited state leading to

the process above, one would expect to see a continuum or very diffuse absorption region. At low temperature, at which only the lowest vibrational level of the ground state is appreciably populated, the long-wavelength edge of such an absorption would give an upper limit to the dissociation energy. However, as higher vibrational levels of the ground state are populated, the long-wavelength absorption edge will move to the red and an upper limit cannot be set from this criterion. Consideration of the short-wavelength edge of the continuum will still give an upper limit, although it may be considerably higher than the true dissociation energy. The same considerations hold for dissociative transitions in diatomic species.

A. Absorption spectra possibly belonging to the triatomic species.

Table III lists values of dissociation energies. In this table,  $D(MX_2)$  is the energy required to dissociate the  $MX_2$  molecule into its atoms in the ground state;  $D(MX)$  is the approximate predicted dissociation energy of the  $MX$  molecule calculated from application of the relation  $D(MX) = 0.46 D(MX_2)$ , which is found by Blue et al.<sup>17</sup> to hold for the alkaline-earth monofluorides. Likewise  $D(MX + X)$  is the energy required to disrupt one bond in the dihalide molecule. It must be emphasized that apart from those given for the fluorides, the values in Table III are approximate and of use mainly for the illustrative purpose which follows.

A continuum or diffuse spectrum in the magnesium chloride might be expected at about  $36\ 700\text{ cm}^{-1}$ , corresponding to the  $D(MX + X)$  process. Harrington<sup>6</sup> observed very diffuse absorption regions at  $37\ 500$ ,  $37\ 060$ , and  $26\ 590\text{ cm}^{-1}$ . In  $MgI_2$  a transition at energies greater than  $23\ 900\text{ cm}^{-1}$  would be expected leading to the same process. Morgan,<sup>5</sup> in his absorption studies of the magnesium halides, observed continuous absorptions at  $25\ 404$ ,  $25\ 575$  and  $26\ 614\text{ cm}^{-1}$ .

Table III. Dissociation-energy data for the gaseous alkaline-earth halides.  $D(MF)$  is taken from work of Blue et al.<sup>17</sup> Other  $D(MX)$  values (in parentheses) are estimated from the relation  $D(MX) = 0.46 D(MX_2)$ .  $D(MX_2)$  is taken from Brewer et al.<sup>8</sup> and  $D(MX + X)$  is calculated from  $D(MX_2)$  and  $D(MX)$ . All energies are in  $\text{cm}^{-1} \times 10^{-3}$ .

| Molecule          | $D(MX_2)$ | $D(MX)$ | $D(MX + X)$ |
|-------------------|-----------|---------|-------------|
| BeF <sub>2</sub>  | 105.0     | 48.3    | 56.7        |
| BeCl <sub>2</sub> | 77.6      | (35.7)  | 41.9        |
| BeBr <sub>2</sub> | 66.2      | (30.5)  | 35.7        |
| BeI <sub>2</sub>  | 52.5      | (24.2)  | 28.6        |
| MgF <sub>2</sub>  | 89.0      | 40.9    | 48.1        |
| MgCl <sub>2</sub> | 67.9      | (31.2)  | 36.7        |
| MgBr <sub>2</sub> | 56.6      | (26.0)  | 30.6        |
| MgI <sub>2</sub>  | 44.3      | (20.4)  | 23.9        |
| CaF <sub>2</sub>  | 93.8      | 43.2    | 50.6        |
| CaCl <sub>2</sub> | 76.5      | (35.2)  | 41.3        |
| CaBr <sub>2</sub> | 66.9      | (30.8)  | 36.1        |
| CaI <sub>2</sub>  | 54.6      | (25.1)  | 29.5        |
| SrF <sub>2</sub>  | 92.8      | 42.7    | 50.1        |
| SrCl <sub>2</sub> | 78.4      | (36.1)  | 42.3        |
| SrBr <sub>2</sub> | 68.0      | (31.3)  | 36.7        |
| SrI <sub>2</sub>  | 56.2      | (25.9)  | 30.3        |
| BaF <sub>2</sub>  | 97.9      | 45.0    | 52.9        |
| BaCl <sub>2</sub> | 82.1      | (37.8)  | 44.3        |
| BaBr <sub>2</sub> | 71.9      | (33.1)  | 38.8        |
| BaI <sub>2</sub>  | 60.4      | (27.8)  | 32.6        |

In the case of other halides (except the iodides), the absorption spectra corresponding to such a process would lie further toward the violet. Although definitive data are lacking in these cases, Fowler reports that in the absorption spectra of the fluorides, a continuum whose short-wavelength edge lies beyond the far ultraviolet edge of the plate appears in all cases.<sup>21</sup> The long-wavelength edge moves toward the red with increasing temperature, as would be expected with increasing population of excited vibrational levels in the ground state. For the chlorides and bromides, Harrington reports that continua appeared in the region below  $3000\text{\AA}$  and moved toward the red as the temperature was raised.<sup>6</sup>

Harrington also reported 19 diffuse bands in the  $\text{MgCl}_2$  absorption at about  $40\,800\text{ cm}^{-1}$ ; these he was unable to analyze. In  $\text{MgBr}_2$  he found a system at  $39\,300\text{ cm}^{-1}$  which he was not able to analyze to his satisfaction; these systems might correspond to transitions of the triatomic species.

The absorption spectra of the iodides have not been studied with any thoroughness. Thus it is unknown whether other alkaline-earth-iodide systems show transitions that might correspond to partial dissociation.

One further piece of evidence indicating that such transitions belong to the triatomic species has been supplied by recent work on the emission spectrum of  $\text{MgCl}$ . Rao and Rao found<sup>22</sup> that a  $^2\Sigma$  state is at about  $45\,000\text{ cm}^{-1}$ , but no evidence of emission from the two states found by Harrington, and attributed by him to  $\text{MgCl}$ , was observed.

B. Absorption continua and predissociations in diatomic species. The possibility that one might observe transitions that lead to dissociation or predissociation of the monohalide species is an interesting one. In this subsection spectra that appear to correspond to such processes will be discussed.

In the vapor in equilibrium with condensed  $\text{CaF}_2$ , a continuous region of absorption about  $100\text{\AA}$  wide appears with its center at about  $2\ 170\text{\AA}$ .<sup>21</sup> The short-wavelength edge must set an upper limit to the dissociative process that gives rise to this continuum. If the energy of the short-wavelength edge ( $47\ 200\ \text{cm}^{-1}$ ) is compared to the dissociation energy obtained by mass spectrometric means ( $43\ 200\ \text{cm}^{-1}$ ), it appears that the continuum may correspond to a process leading to the dissociation of the  $\text{CaF}$  molecule.

A predissociation in the spectrum of  $\text{MgBr}$  appears in the  $A^2\Pi-X^2\Sigma$  transition and places an upper limit of  $27\ 028\ \text{cm}^{-1}$  on the dissociation limit of this molecule. This value compares with a calculated approximate energy given in Table II of  $26\ 000\ \text{cm}^{-1}$ .

The above observations make it appear that there must be at least one unstable or slightly stable diatomic state, which arising from the ground-state atoms, leads to dissociation or crosses stable states and causes predissociation. The question of whether the second state arising from the ground-state atoms is stable cannot be definitely answered on the basis of present knowledge, as considerations presented in Sec. IVA.2 confirm.

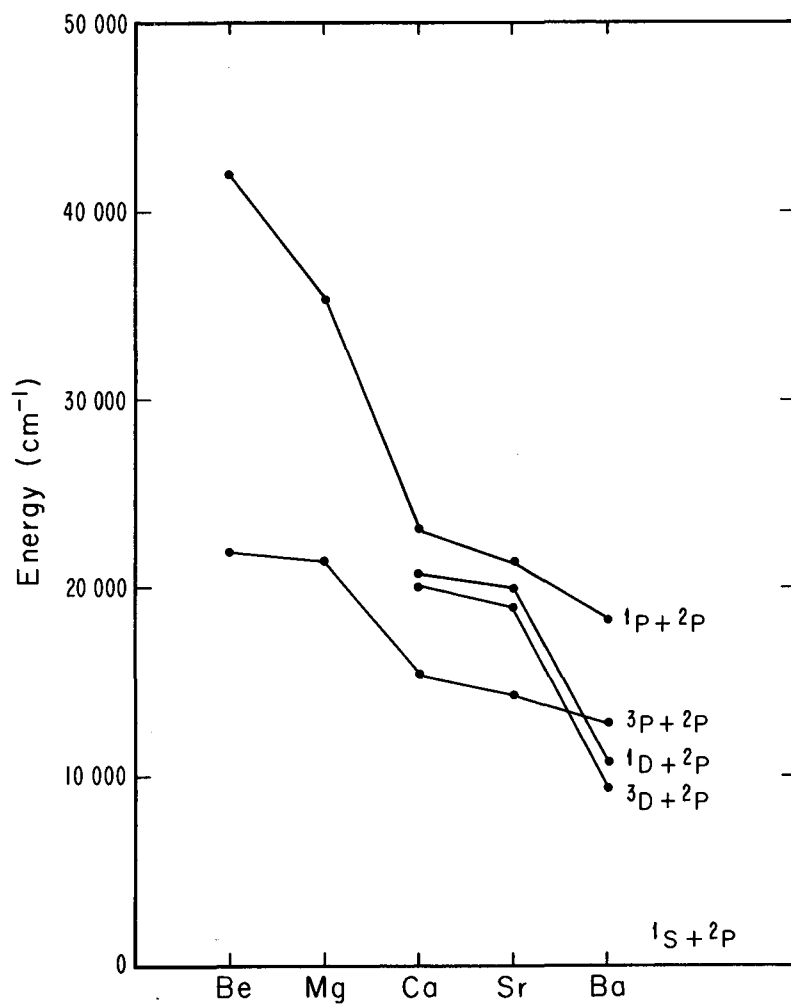
## 2. Energy Levels in the Magnesium Monohalides and Considerations Concerning the Stability of States Arising from the Ground-State Atoms

One problem in the over-all interpretation of the energy-level sequences of the alkaline-earth halides is the apparent anomaly of the magnesium monohalides. For example, in the sequence of  $\text{BeF}$ ,  $\text{MgF}$ ,  $\text{CaF}$ ,  $\text{SrF}$ , and  $\text{BaF}$  states, a large increase in the energies of these levels, relative to the ground state, occurs between  $\text{MgF}$  and  $\text{CaF}$ . Similar increases in other halide sequences might lead one to believe that several low-lying states in the magnesium monohalides might be unobserved.

Experimental work by the author (see Sec. II) on the excitation of the emission spectrum of the MgCl molecule revealed no levels lying within  $8000 \text{ cm}^{-1}$  of the ground state. A possible reason for this apparent anomaly is seen when one considers the separated atom correlations as follows: in Mg and Be the  $^3\text{P}$  states are both at about  $22\,000 \text{ cm}^{-1}$  relative to the ground state atoms, but in Ca a sudden drop to about  $16\,000 \text{ cm}^{-1}$  occurs. (See Fig. III) This leads one to believe that the  $\text{A}^2\Pi$  states do not correlate to the ground state ( $^1\text{S} + ^2\text{P}$ ) atoms, but instead correlate to the ( $^3\text{P} + ^2\text{P}$ ) configuration.

Now the question "Is there any basis for the assumption of dissociation of the  $\text{A}^2\Pi$  state to excited atoms?" must be answered. The data given in Table III justify this assumption very nicely for the Mg monohalide. The  $\text{A}^2\Pi$  state would not be expected to have much ionic character, for the state arising from the ionic separated atoms is  $^2\Sigma$  in character. A linear extrapolation of the dissociation energy of this state might be expected to give at least a very rough approximation to the dissociation energy. In the first column of Table IV are given the extrapolated dissociation energies for the magnesium and calcium monohalides calculated from the relation  $D = \frac{\omega_e^2}{4\omega_e x_e} \cdot 1,2,19$ . In the second column are given the dissociation limits that the  $\text{A}^2\Pi$  would possess if it dissociated to the ground-state atoms. (In these approximate calculations the values for the dissociation limit of the ground state of MX given in Table II have been used.) In the third column is given the dissociation limit that the  $\text{A}^2\Pi$  state would have if it were to dissociate to the ( $^3\text{P} + ^2\text{P}$ ) configuration. For the magnesium monohalides the  $^2\Pi$  state appears to correlate with the excited atoms. However a similar conclusion cannot be unambiguously drawn for the Ca monohalides. The situation for Sr and Ba monohalides is similar to that of Ca.





MU-35687

Fig. 3

Table IV. Dissociation-energy data for the  $A^2\Pi$  state of the magnesium and calcium monohalides.  $D$  is the dissociation energy calculated from a linear extrapolation of the  $A^2\Pi$  state,  $D(MX \rightarrow M^1S + X^2P)$  is the dissociation energy required to go to the ground-state atoms, and  $D(MX \rightarrow M^3P + X^2P)$  is the energy required to dissociate the  $A^2\Pi$  state to the first excited configuration of separated atoms.

| Molecule | $D$ (eV) | $D(MX \rightarrow M^1S + X^2P)$ | $D(MX \rightarrow M^3P + X^2P)$ |
|----------|----------|---------------------------------|---------------------------------|
| MgF      | 4.3      | 1.6                             | 4.3                             |
| MgCl     | 2.9      | 0.6                             | 3.4                             |
| MgBr     | 2.3      | 0.0                             | 2.8                             |
| CaF      | 3.5      | 3.3                             | 5.2                             |
| CaCl     | 3.5      | 2.3                             | 4.2                             |
| CaBr     | 2.8      | 1.8                             | 3.7                             |

a. Beryllium monohalides. Of the four beryllium monohalides, only BeF and BeCl have been observed by spectroscopic means, although one would expect that both BeBr and BeI would be stable species and observable by standard spectroscopic techniques.

The vibrational analysis of the  $A^2\Pi-X^2\Sigma$  transition has been extended for both the BeF and BeCl molecules.<sup>24,25</sup> Values for  $D(\text{BeF}) = 8.0 \pm 0.5$  eV and  $D(\text{BeCl}) = 5.9 \pm 0.5$  eV were obtained by vibrational extrapolations of these analyses. In light of the work of Blue et al., these values appear to be high.<sup>17</sup>

A new transition of BeCl<sup>25</sup> has been observed at  $2610\text{\AA}$ . It consists of red degraded bands, and although it has not been analyzed probably corresponds to the  $B^2\Sigma-X^2\Sigma$  transition.

b. Magnesium monohalides. A new transition in  $\text{MgCl}_2$  vapor excited by a radio-frequency generator has been discovered at  $21\ 000\ \text{cm}^{-1}$  and ascribed to a  $B^2\Sigma-A^2\Pi$  transition.<sup>22</sup> The upper state lies at  $45\ 000\ \text{cm}^{-1}$  and thus, by comparison with the states of MgF, appears too high to correspond to the  $B^2\Sigma$  or  $C^2\Sigma$  states of MgF. One would expect the corresponding states to lie at energies equal to or lower than  $42\ 000$  or  $37\ 000\ \text{cm}^{-1}$  respectively. Under identical excitation conditions, one might find transitions at approximately  $8\ 000$  to  $10\ 000$  and  $14\ 000$  to  $16\ 000\ \text{cm}^{-1}$ . None of these transitions were seen by the author under conditions of microwave excitation in an electrodeless discharge tube.

Although it is possible that the transitions reported by Harrington<sup>6</sup> (see Sec. IV) correspond to these states, it is highly unlikely because of the unexpected structure these spectra possess. In MgF, well-developed sequences corresponded to transitions from these states, whereas the transitions observed by Harrington are extremely ill defined and diffuse.

Study of the spectra of MgCl under the conditions used by Rao and Rao in the infrared would be helpful in solving this problem.<sup>22</sup>

Similar transitions would be expected in the emission spectra of the MgBr and MgI species under similar conditions.

Rotational analysis of parts of certain bands of the  $A^2\Pi-X^2\Sigma$  transition in the MgCl molecule have confirmed that the  $A^2\Pi$  state is inverted. Since the lowest excited state predicted by molecular orbital theory (see Table I) is also an inverted  $^2\Pi$ , the conclusion that this state is the lowest excited state is supported.

c. Calcium monohalides. Some problems remain in the interpretation of certain phenomena in the spectra of the calcium monohalides. Foremost among these are reported predissociations in the spectra of CaF and CaCl.<sup>26</sup>

In the spectra corresponding to the transition  $A^2\Pi-X^2\Sigma$ , a predissociation was noted in one of the  $A^2\Pi$  components at  $v' = 16$  and an energy of 3.12 eV. In view of the value of 5.44 eV $\pm$ 0.1 eV, obtained by Blue et al.,<sup>17</sup> this predissociation is probably either an extensive perturbation or an instrumental effect.

A predissociation in the  $B^2\Sigma$  state of the CaCl molecule occurs at  $v' = 15$  and would set an upper limit on the dissociation energy of 2.73 eV.<sup>26</sup> The remarks pertaining to the similar predissociation in CaF would apply here also. Further experimental work to clarify these phenomena would be desirable.

On the basis of a very limited rotational analysis, the  $A^2\Pi$  state of CaF was purported to be regular,<sup>27</sup> but on the basis of molecular orbital theory, the lowest state should be inverted. Reinvestigation of the spectrum might settle this question.

The spectrum of CaI, although known, has not been investigated in a systematic manner.

Morgan and Barrow, in rotational analysis of several CaCl bands, have shown that the  $C^2\Pi$  state is regular, in line with expectations from molecular orbital theory.<sup>28</sup>

Two previously unobserved states were seen in the CaCl molecule in emission. The two new states,  $F^2\Pi$  and  $G^2\Delta$ , have the following constants:<sup>29</sup>

|             | $T_e$  | $\omega_e$ | $\omega_e x_e$ |
|-------------|--------|------------|----------------|
| $F^2\Pi$    | 35 700 | 432.5      | 1.1            |
| $G^2\Delta$ | 36 710 | 434.0      | 0.8            |

Vibrational constants for some of the lower states were refined by this analysis.

d. Strontium monohalides. The spectra and states of the strontium monohalides are, with the exception of the iodide, fairly well studied vibrationally and the low-lying states are in order with the predictions of molecular orbital theory.

e. Barium monohalides. In the barium monohalides, due to lowness of d orbitals in the barium atom, there are distinct possibilities of low-lying states from molecular orbital configurations involving d orbitals. However, since the lowest orbitals will still be  $\sigma$  and  $\pi$  orbitals (with the  $\delta$  orbitals at higher energies), the lowest states will not involve electrons in  $\delta$  orbitals.

The barium fluoride and chloride spectra appear to have been fairly thoroughly studied, although there appears to be a missing  $B^2\Sigma$  state in BaCl. The spectra of the BaBr molecule does not include transitions from the expected  $A^2\Pi$  and  $B^2\Sigma$  states that would expectably lie in the near infrared. Very little is known about the BaI spectrum as several transitions have been seen but not analyzed.

B. The IIB-VII Subset

One might initially expect the electronic states of the IIB-VII subset to be quite similar to those of the IIA-VII subset. However further consideration shows that this expectation will not be realized for the lowest lying electronic states. Because of the relatively low energy of the separated ions compared to the separated ground-state atoms, an ionic ground state was probable in IIA-VII molecules. For the IIB-VII compounds, the separated ions lie much higher in energy because of the larger ionization potentials of the IIB metal atoms. Thus the probability of an ionic ground state becomes much smaller.

This argument may be put on a more quantitative basis by considerations presented earlier (Sec. IV.A.). Recapitulating, if  $r_s$  is the internuclear distance at which the coulombic potential energy due to the separated atoms is equal to the negative of the quantity  $IP(M) - EA(X)$ , and  $r_e$  is the equilibrium internuclear distance, then when the ratio  $R = r_s/r_e$  is greater than 2.0, the ground state will be ionic. If  $R$  is less than 1.5, the ground state will be atomic and if  $1.5 < R < 2.0$ , it is difficult to make a decision concerning the character of the ground state. For the IIB chlorides, which present the most favorable possibility for an ionic ground state of all the IIB-VII subset, the following  $R$  values are obtained using the M-X bond length in  $MX_2$  as  $r_e$ :  $R(\text{ZnCl}) = 1.25$ ,  $R(\text{CdCl}) = 1.25$ , and  $R(\text{HgCl}) = 0.99$ . Thus one would not expect the IIB-VII halides to have ionic ground states. By way of comparison, most of the IIA-VII subset members have ratios larger than 2.0.

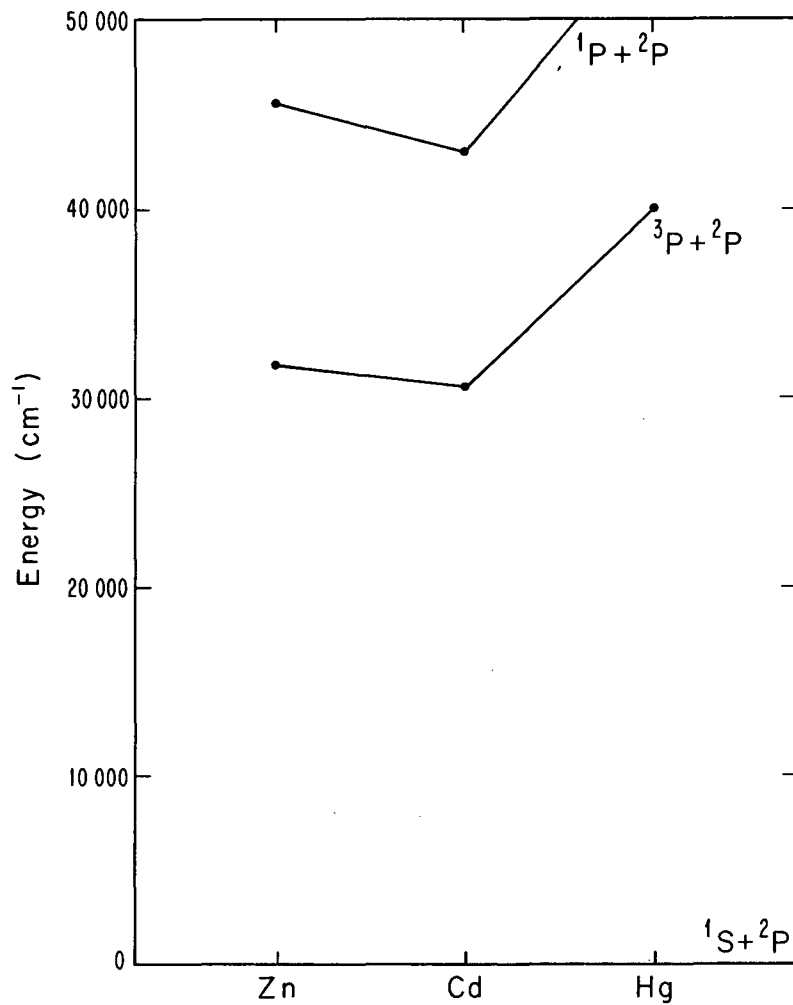
On the other hand, one would expect the first excited state of the IIB monohalides to possess considerable ionic character. If  $r'_s$  is the internuclear distance at which coulombic potential energy is equal to the

negative of the quantity [IP(M)-EA(X)-(energy of first set of excited separated atoms)] and  $r'_e$  is the equilibrium internuclear distance for the lowest excited state, a similar criterion may be obtained for the lowest excited state. Values for  $r'_e$  are not known for the IIB halides, but because of the large value of  $r'_s$ , one may safely conclude that the lowest excited state of these molecules should have a great deal of ionic character.

Studies by Wieland have shown that the first excited states of the IIB monohalides do show great ionic character.<sup>30</sup> In Fig. V is shown a prototype of a potential curve for the Hg molecules taken from the work of Wieland.<sup>31</sup>

Since the ground state of the IIB halides appears to correlate with the ground-state atoms, one would expect the ground state to be, at the most, only slightly stable. However, as Wieland has shown for the mercuric monohalides, the ground state and the lowest lying excited electronic states interact sufficiently to stabilize the ground state considerably.

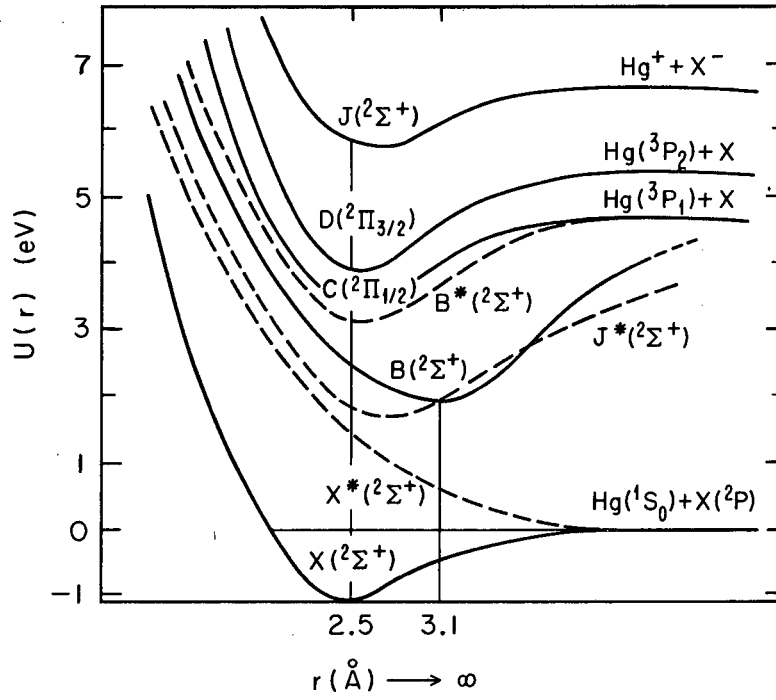
Predictions may be made of the stability of the ground states in the sequence (ZnX--CdX--HgX) by consideration of the energies of the first excited set of separated atoms. As the energy of this first excited set increases, one would expect less stabilizing interaction with the ground state. Since the energies of the first excited states of Zn and Cd are quite comparable (see Fig. IV), the ground states of the monohalides would probably be of the same order of stability. On the same basis, one would expect the mercuric monohalides to be considerably less stable than the monohalides of Zn and Cd.



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Fig. 4





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Fig. 5

From correlations of the ground-state atoms, one would expect a  $^2\Sigma$  and a  $^2\Pi$  state. The  $^2\Sigma$  evidently is the ground state of the molecule, but the  $^2\Pi$  has not been observed for any of the IIB halides. On the basis of observations for some of the IIA monohalides and the relatively small stabilities of the  $^2\Sigma$  state, one would expect it to be either repulsive or only slightly stable. If stable, the  $A^2\Pi-X^2\Sigma$  and  $B^2\Sigma-A^2\Pi$  transitions would be expected to appear in the visible or near infrared regions. Examination of the emission spectra of a number of the IIB monohalides by the author revealed no new transitions in the region between 4000 and 12 000 Å under the excitation conditions used. In the visible region, such a transition would be masked by the  $B^2\Sigma-X^2\Sigma$  emission spectrum.

Several vibrational analyses of spectra belonging to members of the IIB-VII subset have been published, but rotational analysis has not been done for any of IIB monohalide spectra.<sup>8</sup>

### 1. Absorption Continua in IIB-VII Systems

If the absorption spectra of the vapor in equilibrium with the group IIB halides are examined, a number of continua are observed.<sup>32</sup> Although most of them appear to belong to the triatomic species, several may be diatomic absorptions. Because of the interconnection between triatomic dissociative processes and diatomic species production, the triatomic continua are discussed here.

In Table V are given the wavelengths at which the observed continua are bound for the different systems. Among the possible processes that can occur are the following:

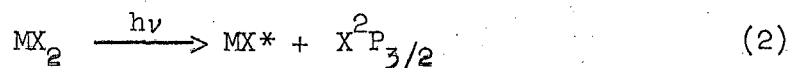
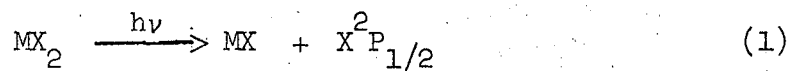
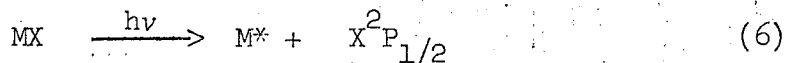
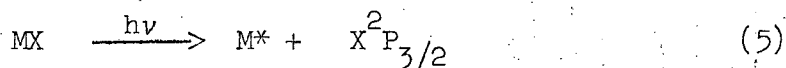
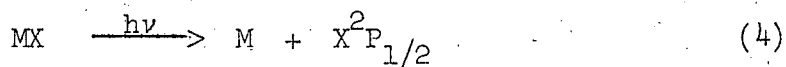
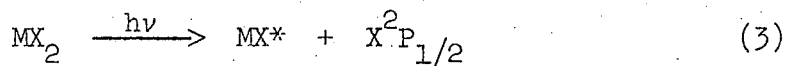


Table V. Absorption continua in the spectra of the molecules of the IIB-VII subset. For the first four molecules listed, the capital letters at the head of the column refer to the processes labeled by similar letters in Fig. 6.

| Molecule          | A(Å)                                    | B(Å) | C(Å) | D(Å) | E(Å) |
|-------------------|---|------|------|------|------|
| HgI <sub>2</sub>  | 2660                                    | 2240 | 1920 | 1730 | 1600 |
| HgBr <sub>2</sub> | 2240                                    | 1850 | 1700 | 1600 |      |
| HgCl <sub>2</sub> | 1850                                    | 1810 | 1600 | 1500 |      |
| CdI <sub>2</sub>  | 2610                                    | 2205 | 2025 |      |      |
| CdBr <sub>2</sub> | Absorption at 1975 and 1580-1710Å       |      |      |      |      |
| CdCl <sub>2</sub> | Absorption below 2070Å                  |      |      |      |      |
| CdF <sub>2</sub>  | Absorption at 2824Å                     |      |      |      |      |
| ZnI <sub>2</sub>  | Absorption at 2280-2380, 1960 and 1720Å |      |      |      |      |
| ZnBr <sub>2</sub> | Absorption at 1570-2050Å                |      |      |      |      |
| ZnCl <sub>2</sub> | Absorption below 2250Å                  |      |      |      |      |
| ZnF <sub>2</sub>  | Absorption at 2110-2180 and 2770-2790Å  |      |      |      |      |

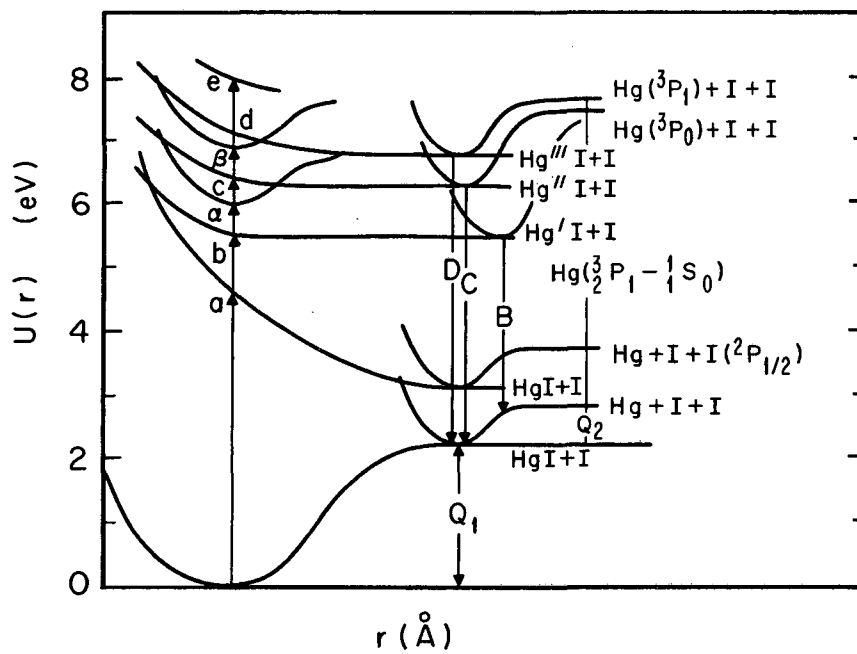


where the asterisk corresponds to an excited state.

At low temperatures and non-reducing conditions, under which the equilibrium concentrations of the diatomic species are low, the continua should correspond to that of the triatomic halides. Thus, if one passes exciting light, with its frequency lying in the absorption region of interest, into the vapor, those absorptions that correspond to dissociation into excited MX molecules will exhibit fluorescence when returning to the ground state. Such behavior is found in the mercuric halides; on the basis of such observations, Wieland was able to establish the process to which each continuum corresponded.<sup>33</sup> The assignments to corresponding processes of each column in Table IV is shown in Fig. 6, again taken from the work of Wieland.<sup>33</sup> The potential curves for the other triatomic and diatomic halides of the group could be expected to be quite similar to the one shown in this figure.

Of the low-temperature continua listed in Table IV, those of  $\text{CdI}_2$  and  $\text{ZnI}_2$  may be assigned rather easily to their analogs in the mercuric compounds. However it is rather difficult to assign processes corresponding to continua in the other halides of zinc and cadmium on the basis of present knowledge. Results of experiments similar to those described above would be valuable for the interpretation of these spectra.

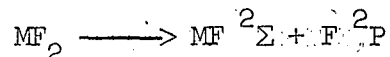
Some possible conclusions concerning the dissociation energies of the  $\text{ZnF}$  and  $\text{CdF}$  molecules may be drawn on the basis of absorption



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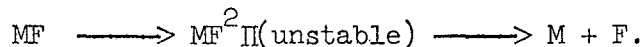
Fig. 6

continua.<sup>21,34</sup> These continua, which only appear at high temperatures, are very narrow. Measurement of the maximum-energy edge gives one a value which is an upper limit on the energy of the corresponding dissociative processes. If the continua belong to the process



then the upper limit on such a process becomes 4.4 eV for the case of  $CdF_2$  and 4.4 eV for the case of  $ZnF_2$ . Knowledge of the heat of atomization of the  $MF_2$  molecule, taken from the compilation by Brewer et al.<sup>8</sup> allows one to place a lower limit on the dissociation energy of the diatomic species. The values thus obtained are  $D(CdF) = 2.2$  eV and  $D(ZnF) = 3.5$  eV.

A less likely possibility is that these continua correspond to the process.



The transition energy in this case gives an upper limit of  $D(ZnF) = 4.4$  eV and  $D(CdF) = 4.4$  eV. Decision as to which of the processes is actually occurring must await further work.

## 2. Further Aspects of IIB Monohalide Spectra

One would expect to find the manifold of low-lying electronic states in the IIB monohalides to be simpler than that of the IIA monohalides for reasons demonstrated in Fig. 4, which shows the manifold of separated atoms. The energies of the lowest three metal atomic states have a much larger spread than the same states of the IIA metals. There are no low-lying atomic states involving electrons in d orbitals; this means that the correlation of low-lying states to separated atoms becomes clearer, providing of course that one has the state type and a vibrational analysis available. Unfortunately such is not the case for most of the observed transitions. The observed transitions and states are surveyed in Rosen.<sup>1</sup>

One reason for the lack of vibrational analyses for the spectra of this group is that each metal possesses a number of stable isotopes that contribute to the complexity of the spectra. However with the present availability of separated isotopes, a number of these systems should become amenable to analysis.

### 3. Considerations Involving Individual Groups of Molecules

- a. Zinc monohalides. No recent work has been reported in the literature on the spectra of the zinc monohalides. The author has found that the spectra of ZnBr and ZnI may be excited in an active nitrogen stream. Several of the known transitions of these molecules were observed, but the sought-after  $A^2\Pi-X^2\Sigma$  transition was not observed.
- b. Cadmium monohalides. The absorption spectrum of the cadmium-cadmium-dichloride system was examined by Bruner and Corbett.<sup>35</sup> They observed the transition attributed to the  $C^2\Pi-X^2\Sigma$ , and on the basis of thermodynamic considerations, were able to establish a dissociation energy of  $D(CdCl) = 2.11 \pm 0.03$  eV.

The spectra of CdBr and CdI were excited by the author in an active nitrogen stream, but again no new systems were observed in the visible or infrared regions.

- c. Mercuric monohalides. The  $B^2\Sigma-X^2\Sigma$  transition of HgCl, HgBr, and HgI has been examined by Wieland under excitation conditions which made possible a much-simplified spectrum. On the basis of his analysis, he was able to find dissociation limits of  $D(HgBr) = .75$  eV,  $D(HgI) = .36$  eV and  $D(HgCl) = 1.04$  eV.<sup>31</sup>

The author has studied the emission spectra of the mercuric monohalides excited in an active nitrogen stream. He found that the  $B^2\Sigma^+ - X^2\Sigma^+$  transition in HgI, HgBr, and HgCl was greatly excited.

When  $\text{HgF}_2$  was placed in the active nitrogen stream and heated, a green glow formed and, upon being photographed under low dispersion, appeared to give a set of bands which might be attributed to the  $B^2\Sigma-X^2\Sigma$  transition. However, the instability of this source did not allow the taking of plates of sufficiently high dispersion to establish a definite identification. A photograph of the bands obtained under low dispersion is given in Fig. 3.

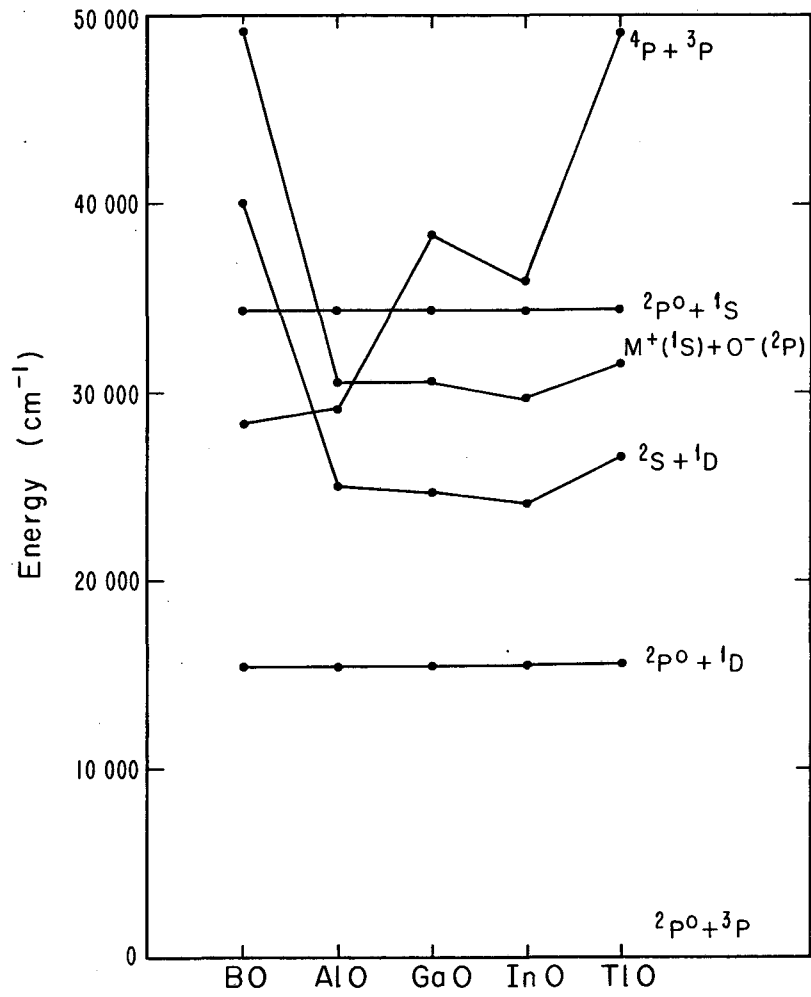
### C. The III-VI Subset

On the basis of molecular orbital theory, the manifold of low-lying electronic states of the III-VI subset would be expected to be quite similar to that of the II-VII molecules. This expectation is realized for the states of those molecules of this group which are known, with the exception of the lowest  $^2\Pi$  state. Although the lowest  $^2\Pi$  state has been seen in some of these molecules, it is as yet unobserved in several others.

The ground states of most of the molecules in the III-VI subset appear to have R values above 1.9. In particular, known data show that  $R(\text{BO}) = 1.97$  and  $R(\text{AlO}) = 2.36$ . On this basis, the ground states of these molecules would be expected to exhibit considerable ionic character. It would seem likely, taking into account the non crossing rule, that the lowest lying electronic states would correlate to the ( $^2P + ^3P$ ) or ( $^2P + ^1D$ ) separated atoms. (See Fig. 7) However, because of the possibility of ionic character in these lower states, it would appear that any linear extrapolation of dissociation limits, in order to correlate molecular states, would not be entirely reliable.

a. Boron compounds. Of the possible boron species, only BO and BS have been observed in spectral sources. In the BO molecules, the discovery of a  $^2\Pi$  state in the vacuum ultraviolet completes the states predicted from





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Fig. 7

the four lowest lying molecular orbital configurations.<sup>36</sup> Boron sulfide has been excited by means of a discharge in  $B_2S_3$ <sup>37</sup> vapor, and a vibrational analysis of a  $C^2\Pi-X^2\Sigma$  and a  $A^2\Pi-X^2\Sigma$  transition has been completed. A further transition in the blue-green region was observed but has not been analyzed; this probably corresponds to the  $B^2\Sigma-A^2\Pi$  transition.

b. Aluminum compounds. Goodlett has examined the spectrum of AlO in a hollow cathode and found two  $^2\Pi$  states, one of which appears to correspond to the  $C^2\Pi$  state belonging to configuration d in Table I.<sup>38</sup> This state lies at  $33175.3 \text{ cm}^{-1}$  above the ground-state energy  $X^2\Sigma^+$  state. Goodlett has also discussed the dissociation energy of the AlO molecule on the basis of his findings his results supported a value of 4.2 eV.

The missing  $A^2\Pi$  state is the main remaining problem for the AlO molecule. Perturbations in the vibrational levels of the  $X^2\Sigma^+$  state indicate that such a state exists and that it lies at least as low as  $8660 \text{ cm}^{-1}$ .<sup>39</sup> Tyte has found emission spectra in the infrared that he attributes to the  $C^2\Pi-B^2\Sigma^+$  transition.<sup>40</sup> However certain discrepancies between the predicted and observed positions of bands suggest that this may be the  $A^2\Pi-X^2\Sigma^+$  transition.

A comprehensive review of the  $B^2\Sigma^+-X^2\Sigma^+$  transition of AlO has been given by Tyte and Nicholls.<sup>41</sup>

The spectra of AlS, AlSe, and AlTe have not yet been observed.

c. Gallium compounds. A partial rotational analysis of the  $B^2\Sigma-X^2\Pi$  transition in GaO was done recently.<sup>44</sup> Confirmation of the existence of a second band system to the red of the B-X transition was mentioned by the same investigators. This second system might correspond to a  $B^2\Sigma-A^2\Pi$  or a  $A^2\Pi-X^2\Sigma$  transition. Analysis of this system would be desirable if sufficient intensity could be obtained. The spectra of GaS, GaSe, and GaTe have not been reported.

- d. Indium compounds. No recent work has been reported on InO. The observed transition is stated to be either  ${}^2\Pi-{}^2\Sigma$  or vice versa.<sup>43</sup> Further work on this spectrum would also be desirable. No other nine-valence-electron indium-containing molecules have been observed.
- e. Thallium compounds. No thallium nine-valence-electron species have been reported, although if the molecule does indeed possess an ionic ground state, one would expect stable species to exist. However, because of the large size of the Tl ion, there is a possibility that an ionic ground state would not occur for this molecule.
- f. General comment. A complicating factor in the search for absorption spectra of the Group III oxides is the great stability of the  $M_2O$  species. In high-temperature equilibrium situations, the stability of this species would be expected to considerably greater than the stability of the MO molecule. Whether the spectra of such species will interfere badly with spectra of the MO species is unknown.

#### D. The IV-V Subset

The observed spectra of the molecules of the IV-V subset have been well analyzed vibrationally and many rotational analyses have been carried out. However, if the possible molecular combinations of this group, only the CN, CP, and SiN molecules have observed spectra.

Douglas and Routly found a number of new band systems due to CN whose upper states appear to come from molecular orbital configurations e (see Table I) or higher.<sup>44</sup> The  ${}^2\Pi$  state correlating with molecular orbital configuration d is still unseen. The states arising from molecular orbital configurations a, b, and c are well characterized.

Although the three lowest states of CP have been observed, the  $C^2\Pi$  state is missing, as are also the states analogous to the higher states

in CN. These would be expected to lie in the ultraviolet region of the spectrum.

The  $A^2\Pi-X^2\Sigma$  transition has not been seen for SiN, although the  $C^2\Pi-A^2\Pi$  and the  $B^2\Sigma-X^2\Sigma$  transitions have been. Thus the outstanding problem for the low-lying states of this molecule is the relative positions of the  $^2\Pi$  and  $^2\Sigma$  states. A recent study of the observed systems of SiN by Broida and Schofield<sup>14</sup> had as one objective the analysis of perturbations in the  $B^2\Sigma-X^2\Sigma$  transition which might allow one to gain information concerning the relative positions of these states. Preliminary investigations by the author indicated that, although SiN systems could be produced in good intensity, no bands definitely attributable to the  $A^2\Pi-X^2\Sigma$  transition could be observed down to 12 000 Å.

#### E. The Ionized Nine-Valence-Electron Molecules

Among the molecules of this group, only  $N_2^+$ ,  $CO^+$ ,  $SiO^+$ , and  $P_2^+$  have been observed. The low-lying  $^2\Pi_u$  state of  $N_2^+$  has been found by observation of the  $A^2\Pi_u-X^2\Sigma_g$  transition in the infrared region of the spectrum.<sup>45,46,47</sup> Several investigators have reported observing bands between 2050 and 3070 Å which evidently correspond to the  $C^2\Pi_g-A^2\Pi_u$  transition, although rotational analysis has not been done.<sup>48,49</sup> Thus, it appears that the states from the lowest lying molecular orbital configurations a,b,c, and d have been observed.

The three lowest lying states of  $CO^+$  have been observed. However the  $C^2\Pi$  has not yet been found. One might expect the transition  $C^2\Pi-X^2\Sigma$  to occur in the vacuum ultraviolet.

Only one band attributed to  $SiO^+$  has been seen and assigned to the (0,0) bands of the  $B^2\Sigma-X^2\Sigma$  transition.<sup>50</sup> Efforts to obtain further spectra of this molecule would be helpful.

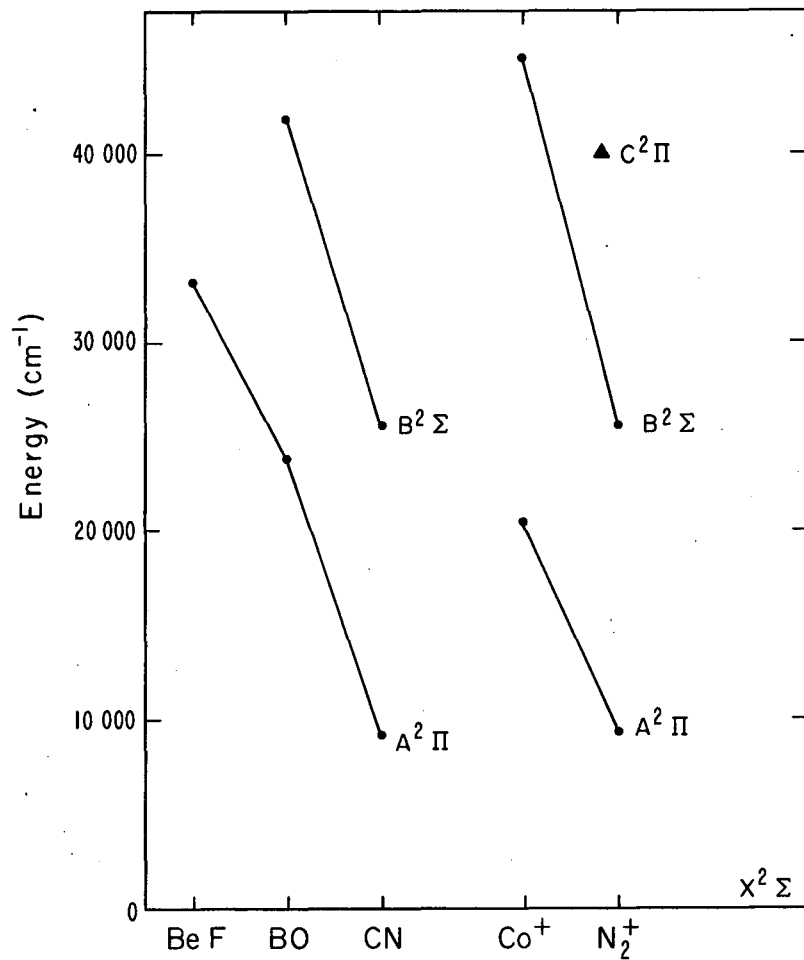
The ion  $P_2^+$  has been observed and the spectra partially analyzed. Thus far a  ${}^2\Pi_g - {}^2\Pi_u$  and a  ${}^2\Sigma_u - {}^2\Sigma_g$  transition have been found. Narasimham mentioned that further spectra were observed in the red where one would hope to find the  $A{}^2\Pi_u - X{}^2\Sigma_g$  spectrum.<sup>51</sup>

## V. SUMMARY AND CONCLUSIONS

We have now answered the questions posed in the Introduction. The first problem concerned the possibility of unobserved low-lying energy levels. Several low-lying states believed to be unobserved in the magnesium monohalide spectra were shown to be unstable. The apparently anomalous behavior of the energy states (of magnesium monohalides) could be explained by (a) the correlation of the molecular states with the separated atoms, and (b) the effects of ionic character entering into the bonding in ground and excited states, as originally proposed by Mulliken<sup>52</sup> and Wieland.<sup>33</sup> A review of the states of the III-VI subset indicated that the  $A^2\Pi$  state in AlO remains unidentified, and that several low-lying states of InO and GaO may still be unobserved.

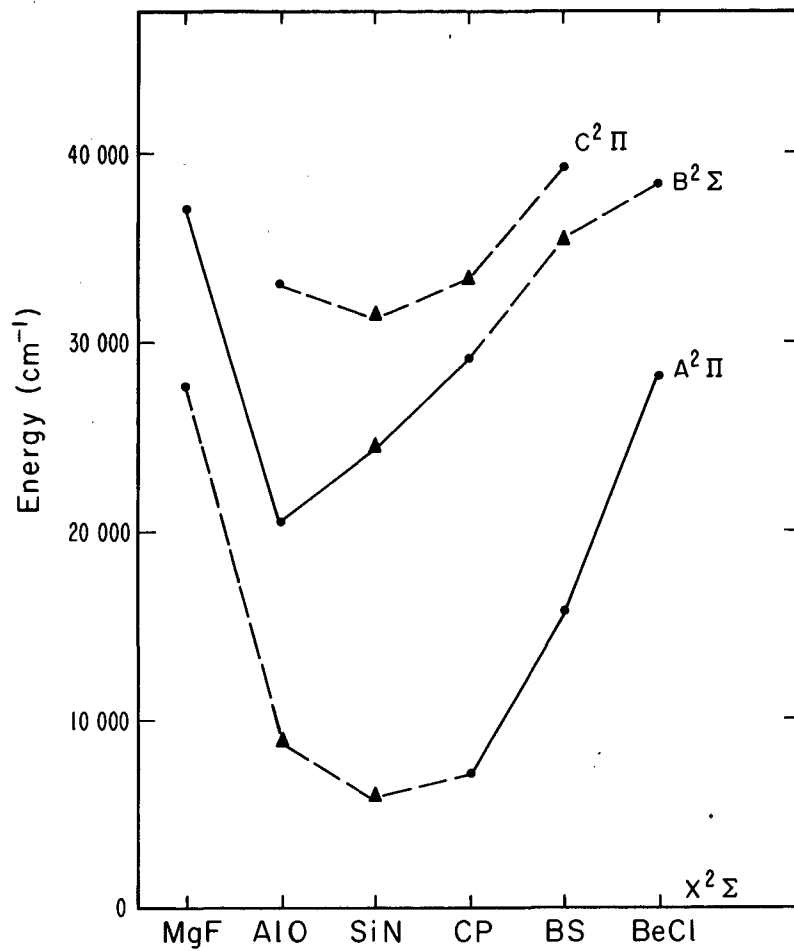
For the IV-V subset, a similar review showed that the  $C^2\Pi$  states in CN and CP have not been observed and that the relative positions of the  $^2\Sigma$  and the  $^2\Pi$  states have not been established for SiN. Of the ionized nine-valence-electron molecules, the four lowest predicted states of  $CO^+$  and  $N_2^+$  have been seen, but further work is needed to establish the relative positions of the  $^2\Pi$  and the  $^2\Sigma$  states in  $P_2^+$  and to discover the unobserved  $^2\Pi$  states in  $SiO^+$ .

The answer to the question "How do corresponding states in an isoelectronic sequence vary in energy with respect to the ground state as one moves from the center of the periodic table toward the edges?" may best be answered by Figs. 8 and 9. Here are shown the energies of corresponding states in isoelectronic sequences for which data are available. Estimated energies are marked by  $\blacktriangle$  but such energies should be reliable within 2000 to 3000  $cm^{-1}$ . The analogous energy levels appear to move up relative to the ground state as one moves from the center to the edges of the



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Fig. 8



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Fig. 9



periodic table. Qualitatively one might correlate this with the circumstance that the excited states of the separated atoms have the least energy spread in the center of the periodic chart. However, in view of the scanty available knowledge of dissociation products, such a correlation would be very hazardous. Although this report has clarified the energy trends of the low-lying states of the diatomic molecules with nine-valence-electrons much work remains to be done before these states are completely understood.

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NOTE ADDED IN PROOF

On the basis of new thermodynamic measurements, the heat of atomization of  $\text{ZnF}_2^1$  has been revised to 191 kcal/mole and that of  $\text{CdF}_2^2$  to 159 kcal/mole. This changes the upper limits on the dissociation limits given in Section IV to  $D(\text{CdF}) = 2.4$  eV and  $D(\text{ZnF}) = 3.7$  eV.

It has been brought to the authors attention that an emission spectrum of AlS has been observed and assigned to a  $^2\Sigma^+ - X^2\Sigma^+$  transition.<sup>3</sup> As the spectrum evidently has not yet been investigated in the infrared region, it would appear hazardous to assign it to the analog of the blue green system of AlO.

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FIGURE CAPTIONS

- Fig. 1 (a) Reaction vessel for examination of spectra arising from reactions of active nitrogen with solids.
- (b) Reaction vessel for examination of spectra excited by reaction of activated gases (i.e., nitrogen, oxygen) with vapors.
- Fig. 2 Spectra excited by
- (a) Active nitrogen: 5-min exposure.
- (b) Active nitrogen with  $\text{HgF}_2$ : 2-min exposure.
- (c) Active nitrogen with  $\text{HgF}_2$ : 4-min exposure.
- (d) Mercury standard.
- Fig. 3 Lowest energy states of alkaline-earth atoms.
- Fig. 4 Lowest energy states of Group IIB atoms.
- Fig. 5 Potential-curve prototype for the IIB monohalides (after Wieland, Ref. 31).
- Fig. 6 Potential curves showing relations between triatomic and diatomic states and dissociative processes (after Wieland, Ref. 33).
- Fig. 7 Energies of lowest-lying separated-atom combinations for the group III oxides.
- Fig. 8 Energy levels in two nine-valence-electron isoelectronic sequences.
- Fig. 9 Energy levels in a nine-valence-electron electronic sequence.

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