

ON A CLASS OF ONE-VALENCE-ELECTRON EMITTERS  
OF BAND SPECTRA

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## ABSTRACT

**Bands emitted by one-valence-electron molecules.**—*Series A:*  $\text{BeF}$ ,  $\text{BO}$ ,  $\text{CO}^+$ ,  $\text{CN}$ ,  $\text{N}_2^+$ . These molecules each contain, like the Na atom, 8+1 electrons outside the nuclei and K electrons. The bands of  $\text{CO}^+$  (the comet-tail, negative Deslandres and new quadruple-headed bands reported by Baldet and Johnson) are particularly discussed and analogies to the bands of  $\text{BO}$  and of  $\text{CN}$  are pointed out, as well as analogies between the bands of  $\text{N}_2^+$  and of  $\text{CN}$ . The data for  $\text{BeF}$  bands are less complete. The lines of the known band systems of all these molecules can in each case be expressed as combinations of three electronic terms (each of course with a variety of vibrational and rotational states). These are a singlet term  $N$  probably belonging to the normal state, a doublet term  $A$  corresponding to the first excited state, and a singlet term  $B$  corresponding to the second excited state. There is evidence that the average angular momentum of the emitting electron—which is presumably the odd ninth electron—is the same for the  $N$  and  $B$  states, but different for the doublet  $A$  state; presumably the former resemble  $s$  states, the latter resemble (inverted doublet)  $p$  states. In the cases of  $\text{BO}$  and  $\text{CO}^+$ , all of the three conceivable combinations between  $N$ ,  $A$ , and  $B$  are known; two are known in the case of  $\text{CN}$ , and one in that of  $\text{N}_2^+$ ; the systems not yet observed probably lie in the infrared. There is a remarkable parallelism between the spectra of the several molecules mentioned in respect to structure of analogous band systems and to molecular constants of corresponding electronic states (cf Table I). *Series B:*  $\text{MgF}$ ,  $\text{AlO}$ ,  $\text{SiN}$ . These molecules contain an additional electron shell. They are the probable emitters of band spectra which show marked analogies to those of  $\text{BeF}$ ,  $\text{BO}$  and  $\text{CN}$ . *Additional series* of emitters are represented by  $\text{CaCl}$ ,  $\text{SrBr}$ , etc.

**Suggested grouping of bands according to the number of valence electrons of the emitters.**—Molecules with no unused valence electrons— $\text{HF}$ ,  $\text{LiF}$ ,  $\text{BN}$ ,  $\text{NaCl}$ , etc.—show analogy to the rare gases; they do not emit electronic band spectra. Molecules with two excess electrons— $\text{CO}$ ,  $\text{NO}^+$ ,  $\text{N}_2$ ,  $\text{SiO}$ —should show analogies to alkaline earth metals. The odd multiplicity of  $\text{N}_2$  agrees with this suggestion. Molecules with three excess electrons, e.g.,  $\text{NO}$ , should resemble  $\text{Al}$ ; in fact the bands probably due to  $\text{NO}$  show even multiplicity.

**Nature of multiplicity in band spectra.**—Two causes of multiplicity are suggested: (a) connected with the interaction of the emitting electron with the rest of the molecule, and (b) attributed by Kratzer to the interaction of the angular momentum of the emitting and other electrons with that of the nuclei. Examples of each are discussed.

**Emitters of certain bands.**—*Second negative  $\text{N}_2$  bands of Duffendack* may be due to neutral nitrogen molecules in each of which two electrons are initially excited. Evidence is presented for attributing the familiar *aluminum bands* to  $\text{AlO}$ .

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IN previous papers<sup>1,2</sup> attention has been called to a class of alkali-metal-like diatomic "odd molecules" containing one easily excited electron, and giving rise to conspicuous band spectra. These molecules do not appear in ordinary chemistry, doubtless on account of the activity of this odd electron. Except for the odd electron, these molecules have just enough electrons to form one or more rare gas shells. From the elements of the first and second series of the periodic system the following two series of such molecules are possible:

Series A:	Li	BeF	BO	CN
Series B:	Na	MgF	AlO	SiN

In each case the positive valence of the more electropositive atom exceeds by one the negative valence of the other atom, thus leaving one of the former's valence electrons free as in an alkali metal atom. Numerous additional examples of this type are possible with homologous elements of higher atomic weight; some of these (of which CaCl is typical) have been previously discussed.<sup>2</sup> Such ionized molecules as CO<sup>+</sup> and N<sub>2</sub><sup>+</sup> also belong with series A. The spectra of the compounds of this type, like those of the alkali metals, show the presence of electronic doublets. Series A differs from B or other possible series in that the total number of electrons is sufficient only for one group of eight, so that, as was suggested previously,<sup>1</sup> it may be that the two nuclei share an octet and that, at least when the nuclear charges are nearly equal, the molecule as a whole specifically resembles a Na atom. The electropositive atoms in the molecules of series A and B and similar series might also be considered, at least for the earlier members of each series, as "stripped atoms" whose lost electrons, however, now attached to the electronegative atom, still exert a considerable screening effect.

The chief object of the present paper is to bring together evidence that the molecules of series A and B are indeed all ready emitters of band spectra, and to show from these spectra, so far as is possible with the data available, that these molecules are closely similar to one another in many respects. This will be preceded by a brief discussion of the question of multiplets in band spectra.

#### MULTIPLICITY IN BAND SPECTRA

Mecke<sup>3</sup> has recently discussed the question of multiplets in band spectra and has attempted to set up a formal analogy to the relations

<sup>1</sup> R. S. Mulliken, *Phys. Rev.* **25**, 259-294 (1925), especially pp. 290-1.

<sup>2</sup> R. S. Mulliken, *Phys. Rev.* **26**, 1-32 (1925), especially pp. 29-32.

<sup>3</sup> R. Mecke, *Zeits. f. Phys.* **28**, 261-77 (1924).

which hold in line spectra. He assumes the angular momentum of the emitting electron and of the nuclei, in molecules, to be respectively analogous, in determining multiplet structure, to the angular momentum of core and of emitting electron in atoms. But it seems to the present writer that the real situation must be more complicated, and that there should be two distinct causes of multiplicity in band spectra, (a) one connected with the interaction of the emitting electron with the rest of the molecule, as in the case of excited electron and atom-core in line spectra, and (b) another which has been attributed by Kratzer<sup>4</sup> to the interaction of the angular momentum of the emitting and other electrons with that of the nuclei. Cause (a) gives the most obvious explanation of the occurrence of systems of bands having true multiple origins and two or more widely-spaced heads for each band, separated by a frequency-interval which remains constant or nearly so throughout the spectrum. In the following this will be called multiplicity of class *a*. Examples of this are the doublet *a* bands of BO ( $\Delta\nu = 126$ ), the interesting doublet alkaline earth halide bands,<sup>2</sup> the doublet  $\beta$  ( $\Delta\nu = 87$ ) and  $\gamma$  ( $\Delta\nu =$  about 111) bands of NO, the red CN bands ( $\Delta\nu =$  about 54) and, particularly striking because the structure has been analyzed in detail, the doublet bands of CO<sup>+</sup> ( $\Delta\nu = 126$ ). Except in the  $\beta$  bands of NO, each doublet component or sub-band has two heads ( $\Delta\nu = 13$  for BO and about 13 for CO<sup>+</sup> and 19 for NO $\gamma$ ), giving an apparent quadruplet structure. But Baldet's work<sup>5</sup> on the comet-tail bands of CO<sup>+</sup> shows that here the two heads belong to a Q and an R branch, respectively, and it is probable (contrary to the assumption made in previous papers<sup>1,2</sup> in the cases of BO and the alkaline earth halides) that the *small*  $\Delta\nu$  is not an electronic doublet in any of the above cases. The cuprous halides<sup>2</sup> show possible further examples of class (a), differing, however, from the above cases, as might be expected from the much larger  $\Delta\nu$  values, in that the molecular constants (vibration frequency, etc.) differ considerably for the various initial electronic states comprising the multiplet.

An apparently distinct type of multiplicity in band spectra, which will here be called *b*, is the "fine structure," according to the nature of which bands have been classed by Heurlinger as singlet, doublet, and triplet bands.<sup>6</sup> Singlet bands may consist of single lines or of doublets whose separation increases steadily with the rotational quantum number, from

<sup>4</sup> A. Kratzer, (a) *Ann. der Phys.* **71**, 72 (1923); (b) *Zeit. f. Phys.* **16**, 353 (1923); (c) **23**, 298 (1924); (d) *Naturwissenschaften* **27**, 581 (1923).

<sup>5</sup> F. Baldet, *Compt. Rend.* **180**, 820 (1925).

<sup>6</sup> T. Heurlinger, *Dissertation*, Lund 1918. Cf also review by R. Mecke,<sup>23</sup> who gives an excellent description and diagrams of the various types of fine-structure multiplets.

zero or nearly so at the origin; the violet CN bands are an example of the latter type. Heurlinger doublet and triplet bands have relatively wide separations near the origin, but the components approach each other with increase in the rotational quantum number; each component may in addition show doublet structure of the violet CN type. The structure of Heurlinger singlet and doublet bands has been explained by Kratzer in terms of cause *b*; but there are difficulties,<sup>7</sup> especially in the case of triplet bands,<sup>3</sup> and it may be that class *a* and class *b* multiplicity are not wholly distinct except as limiting cases. Causes *a* and *b* should in general both operate, it would seem, to produce whatever complexity is observed.

#### ANALOGY BETWEEN THE BANDS OF CO<sup>+</sup>, BO, CN AND N<sub>2</sub><sup>+</sup>

Let us now turn to a detailed consideration of the molecules of series A and B. The so-called comet tail bands and the first negative carbon bands of Deslandres are always obtained together and have been attributed to CO by nearly all who have studied them;<sup>8,9,10,11</sup> in particular, Baldet has obtained them in pure CO.<sup>11</sup> Recently it has been found<sup>12,13</sup> that these two systems of bands have a common final electronic state. They are obtained at very low pressures, or near the cathode at somewhat higher pressures<sup>9</sup>—conditions where ionization is to be expected. Under similar conditions Baldet<sup>11</sup> obtains the N<sub>2</sub><sup>+</sup> (negative nitrogen) bands when a little N<sub>2</sub> is introduced. They are also obtained when traces of carbon compounds are added to helium at 20 mm pressure; perhaps here the excitation occurs in impacts with metastable excited He atoms whose energy (about 20 volts) is approximately that required to simultaneously ionize and excite the CO molecule so as to give rise to the emission of these bands. Under similar conditions,<sup>10</sup> traces of N<sub>2</sub> give the N<sub>2</sub><sup>+</sup> bands. The above facts, together with the extraordinary analogy which these systems of bands present to the  $\alpha$  and  $\beta$  bands of BO,<sup>1</sup> make it practically certain that they are due to the CO<sup>+</sup> molecule, which has

<sup>7</sup> R. T. Birge, *Phys. Rev.* **25**, 240 (1925) (abstract No. 21).

<sup>8</sup> A. Fowler, *Month. Not. Roy. Astron. Soc.* **70**, 176 (1909); **70**, 484 (1910); *Astrophys. J.* **35**, 85 (1912); and earlier work of Deslandres.

<sup>9</sup> P. R. Merton, and R. C. Johnson, *Proc. Roy. Soc.* **103A**, 383 (1923).

H. B. Lemon, *Proc. Nat. Acad. Sci.* **11**, 41 (1925). Cf also W. Jevons, *Phil. Mag.* (6), **47**, 586 (1924), in regard to the Deslandres bands.

<sup>10</sup> R. C. Johnson, *Proc. Roy. Soc.* **108A**, 343 (1925).

<sup>11</sup> F. Baldet, *Compt. Rend.* **178**, 1525 (1924); **180**, 271, 1201 (1925).

<sup>12</sup> C. M. Blackburn, *Phys. Rev.* **25**, 888, 1925 (abstract); other preliminary results, *Proc. Nat. Acad. Sci.* **11**, 28 (1925); and unpublished work.

<sup>13</sup> R. T. Birge, *Nature*, **116**, 171 (Aug. 1, 1925)

the same number of electrons as BO, presumably arranged in a very similar manner.

*Analogy of CO<sup>+</sup> to BO bands.* The quadruple-headed comet-tail bands in the visible are clearly analogous to the  $\alpha$  bands of BO; the identical values of  $\Delta\nu$  (cf above) in the two cases are particularly striking. Preliminary results of an analysis of these bands have been given by Blackburn<sup>12</sup> and by Baldet<sup>5</sup>; they show that each comet-tail band consists of two closely similar sub-bands which are nearly superposable by a translation of about 126 units along the wave-number axis, thus clearly constituting a class ( $a$ ) doublet. Blackburn's analysis of the CO<sup>+</sup> bands, which he has kindly rendered available to the writer before publication, shows that the lines can all be expressed as the difference of two sets of terms of the form:

Initial:  $F_i'(n', m') = \nu_i^e + F'(n') + B_i'^n m'^2 + \dots$  ( $m'$  = nearly integral).  
 Final:  $F''(n'', m'') = F''(n'') + B''^n m''^2 + \dots$  ( $m''$  = half-integral).  
 Here  $F(n) = an - bn^2 + \dots$ ,  $n$  being the vibrational quantum number, while  $m$  is the nuclear rotational quantum number. For the two sub-bands,  $\nu_i^e$  differs as already indicated,  $F'(n')$  is nearly if not quite identical, while  $B_i'$  differs slightly. As shown by Baldet,<sup>5</sup> each sub-band consists of a P, a Q, and an R branch, the latter two giving the two observed heads. Baldet also finds a second intense Q branch (Q' branch), which is apparently absent under the conditions used by Blackburn. If in the latter case the direct excitation of the CO is by excited He atoms, the situation may parallel that of the  $\beta$  bands of BO as excited in the arc and in active nitrogen.<sup>1</sup> In the arc the  $\beta$  bands show a doublet structure, while in active nitrogen one component of each doublet is missing.

The single-headed ultraviolet first negative Deslandres' bands, as studied by Blackburn, show marked analogy to the  $\beta$  bands of BO. The data on these bands are not such as to permit a wholly independent analysis, but on the very probable assumption that, in view of the identity of  $F''(n)$  for the two systems,<sup>10,11</sup>  $F''(n'', m'')$  is identical for the two, the analysis shows that  $\Delta m = \pm 1$ , hence that  $m'$ , like  $m''$ , has half-integral values—all quite as in the violet CN bands. Hence the Deslandres' bands probably consist of normal P and R branches of the violet CN type, except for the apparent absence of the class ( $b$ ) doublets which are characteristic of the latter.

In addition to the two systems of CO<sup>+</sup> bands above discussed, which, like the  $\alpha$  and  $\beta$  systems of BO, are both shaded toward the red, some additional quadruple-headed bands which are shaded toward the violet

have been reported by Baldet<sup>11</sup> and by Johnson.<sup>10</sup> They have the same major doublet separation ( $\Delta\nu = 126$ ) as the comet-tail bands, although the minor doublet separation ( $\Delta\nu = 25$ , according to Johnson) is different. A study of the data shows that they form a system having for their initial electronic state the initial state of the negative Deslandres' bands, and for their *final* electronic state the *initial* state of the comet-tail bands; on this basis the bands observed by Baldet have the vibrational quantum numbers  $(n', n'') = (0, 1)$ ,  $(0, 0)$ , and  $(1, 0)$ , while the bands observed by Johnson correspond to  $(0, 1)$ ,  $(1, 2)$ ,  $(0, 0)$ ,  $(1, 0)$ ,  $(2, 0)$ , and  $(3, 0)$ —except that the absolute  $n''$  values are subject to the same uncertainty which is present in the  $n'$  values for the comet-tail bands (cf note to Table I). The fact that the bands are shaded toward the violet follows at once from the analysis of the other two systems as discussed in the preceding paragraphs, for according to this  $B$  is greater (see Table I) for the initial state of the Deslandres' bands than for that of the comet-tail bands, hence  $C (= B' - B'')$  is here positive. The different minor doublet separation is also to be expected; the structure of the bands is presumably of the P, Q, R type, like the comet-tail bands, but with the P and Q, instead of the Q and R branches, forming heads. This third system of  $\text{CO}^+$  bands is evidently completely analogous to the "combination system" of BO bands,<sup>1</sup> except for the probably superficial difference that only the Q heads are conspicuous in the latter.

Table I summarizes the molecular constants determined by the analysis of the  $\text{CO}^+$  bands. Comparative data are also given on BO. From the close analogy to  $\text{CO}^+$  it is now probable that the four heads ( $A_1, A_2, B_1, B_2$ ) of the  $\alpha$  bands of BO are R and Q heads ( $R_A, Q_A, R_B, Q_B$ , respectively) corresponding to a double electronic level, and not R heads corresponding to a quadruple level, as previously<sup>1</sup> assumed. Considerable independent support is given to this conclusion by the previously somewhat mysterious fact that the combination bands of BO (ref. 1, pp. 284-7) each show only two strong heads instead of four. These strong heads are no doubt the beginnings of Q branches (it may be noted that the Q heads are more intense than the R heads in the  $\alpha$  bands); P and R branches may well also be present, the former giving rise to heads, but evidently of low intensity since their presence was not detected except perhaps in one or two cases. The positions of the heads of the combination bands can furthermore be correctly calculated, as should be possible on the above basis, by subtracting observed positions of  $Q_A$  and  $Q_B$   $\alpha$  heads from calculated positions of suitable  $\beta$  band-origins. In spite of the changed interpretation of the bands, no change is required in the values of  $B'$  and  $B''$  previously given, nor in the interpretation of the  $\beta$

bands, nor in other essential results (such as the existence of half-integral vibrational quantum numbers) of the discussion previously given.

*Analogy to CN bands.* It is probable that there is a more or less complete analogy between the comet tail and Deslandres' bands of  $\text{CO}^+$ , the  $\alpha$  and  $\beta$  bands of BO, and the red and violet CN bands. The doublet structure and quadruple heads of the comet tail bands and the  $\alpha$  bands of BO again appear in the red CN bands; in all three cases the doublet component of longer wave-length is the more intense, as if due to an *inverted* pair of  $p$ -terms for the initial state. In each case the larger doublet separation is more or less variable; in BO, slight variability was reported by Jevons, although not noted by the present writer<sup>1</sup>; in  $\text{CO}^+$ , Baldet reports a change from  $\Delta\nu =$  about 17 at  $\nu = 18,000$  to about 10 near  $\nu = 31,000$ ; in CN (for data cf Kayser-Konen, Handbuch der Spektroskopie, Vol. VII), the smaller  $\Delta\nu$  changes for the low-frequency pair of heads in each band from about 18 near 14700 to 15 near 21000, and from about 28 to about 21 in the same range for the high-frequency pair, the head of highest frequency also being unusually weak (probably because it corresponds to a relatively high rotational quantum number). This evidence points strongly to a close resemblance in structure for the  $\alpha$  BO and the red CN bands to the P, Q, R comet-tail type, with its true doublets (large, constant  $\Delta\nu$ ), and its false doublets (small, variable  $\Delta\nu$ ) corresponding to the separation between a Q and an R head; the marked inequality of the two small  $\Delta\nu$ 's in CN may be attributed to an unusually large difference in the values of  $B'$  for the two components of the true doublet, combined with a relatively small value of  $C$  ( $C = B' - B''$ ).

*Discussion of electronic states of the molecules.* The above analogies are present to a marked degree in the  $F(n')$  and  $F''(n'')$  coefficients and in the values of  $\nu^e$ , as is shown in Table I, which summarizes the available data from the band spectra of the molecules of series A and B. These coefficients, it may also be noted, vary in a more or less systematic manner with the atomic number or weight. The values of the vibration frequency ( $a'$ ) and of the moment of inertia (equal to  $h/8\pi^2B'$ ) suggest in each case a markedly lesser stability of the molecule for the *first* than for the *second excited state* of the molecule in spite of the smaller energy of electronic excitation in the former. Apparently the motion of the excited electron is of a quite different type for the two excited states, and furthermore differs less in the second than in the first excited state from that in the common final, probably normal, state. This is understandable in terms of Kratzer's interpretation<sup>4</sup> of bands for which  $\Delta m \neq \pm 1$  or 0. Such bands are explained by postulating that the resultant electronic angular momentum changes in such a way that  $\Delta j = \pm 1$  or 0,

where  $j$  is the quantum number corresponding to the *total* angular momentum (analogous to the inner quantum number in line spectra), and here equal to the vector sum of the electronic and nuclear rotational quantum numbers  $\rho$  and  $m$ . In case the latter two are parallel,  $\Delta j = \Delta m + \Delta \rho = \pm 1$  or 0. In the comet tail bands, where  $\Delta m$  is not equal to 0 or  $\pm 1$  (and presumably by analogy in the red CN and  $\alpha$  BO bands)  $\Delta \rho$  must certainly differ from zero if  $\Delta j = \pm 1, 0$ , whereas in the Deslandres and violet CN bands—and presumably in the  $\beta$  BO bands—with  $\Delta m = \pm 1$ , the simplest assumption is  $\Delta \rho = 0$ . The simplest explanation of the latter ( $\Delta \rho = 0$ ) is that the average angular momentum of the *emitting electron*—which in the case of odd molecules of the CN type is presumably the “odd” electron and presumably is the *only* electron whose quantum numbers here change—does *not* change during emission (cf Kratzer,<sup>14</sup> p. 83) but that in the former ( $\Delta \rho \neq 0$ ) its angular momentum *does* change in direction if not in magnitude. The relations mentioned above between the characteristics of the molecule in its different electronic states may then be correlated with the average angular momentum (and perhaps with an azimuthal quantum number) of the emitting electron. Furthermore, the presence of class *a* doublets for the *first excited* state in these molecules, and their absence in the *normal* and in the *second excited* state, are now explained if the two latter, which have *the same*  $\rho$ , are of the nature of *s* states, while the former, which has a *different*  $\rho$ , is of the nature of an inverted doublet *p*-state. (This is of course contrary to a suggestion made in a previous paper<sup>1</sup> as to a possible analogy of the two excited states to the  $2p$  and  $3p$  states of the Na atom.)

*Analogy between bands of  $N_2^+$  and CN.* The very close resemblance of the  $CO^+$  spectrum to that of BO is probably paralleled by a similar analogy between the spectra of  $N_2^+$  and CN. The “negative nitrogen” bands, which are definitely known to be due to  $N_2^+$ , resemble the violet CN bands extremely closely in structure (including the appearance of the CN type doublets)<sup>14</sup>, in position in the spectrum, and in the relative values of the coefficients of  $n'$  and  $n''$ . Although no second system of  $N_2^+$  bands has been found analogous to the red CN bands, it may well be that these lie in the near infrared so as to have escaped observation. The fact that the negative nitrogen bands have been obtained by Duffendack<sup>15</sup> in the low-voltage arc at a potential just about enough above the ionizing potential to correspond to  $\nu^e$  (3.2 volts), indicates that their final

<sup>14</sup> M. Fassbender, *Zeits. f. Phys.* **30**, 73 (1924).

<sup>15</sup> O. S. Duffendack, *Phys. Rev.* **20**, 665 (1922); *Astrophys. J.* **61**, 221 (1925).

<sup>16</sup> R. S. Mulliken, *Cf Nature*, Dec. 13, 1924.

<sup>17</sup> O. S. Duffendack, and D. C. Duncan, *Phys. Rev.* **23**, 295 (1924).



state must be the normal state of the  $N_2^+$  molecule, again in analogy to the CN bands<sup>16</sup> and the BO bands.<sup>1</sup>

Simultaneously with the negative nitrogen bands, according to Duffendack and Duncan,<sup>17</sup> a new system appears further in the ultraviolet; these Duffendack<sup>15</sup> has called the *second negative bands*. Since  $\nu^*$  here considerably exceeds the value which it has for the first negative bands, according to Duffendack,<sup>15</sup> it seems probable, however, that these bands are not emitted by the  $N_2^+$  molecule but by a neutral molecule in which both of the final pair of electrons (whose analogy to the pair of valence electrons of such a metal as Mg has been suggested above) are excited.

The negative nitrogen bands differ from the other bands of their class in showing a peculiar alternating intensity in each branch which has led Dieke<sup>18</sup> to propose a subdivision of each branch into two. This peculiarity, however, seems to be characteristic of homopolar molecules,<sup>9</sup> and the proposed change, as first pointed out by Birge (private communication), would involve a conflict in the calculated moment of inertia and internuclear distance (cf Table I) with the remarkably consistent and reasonable values obtained by the usual interpretation for all the members of this class of emitters (and for related molecules such as  $N_2$  and CO). Dieke's interpretation would halve the value of  $r_0$  given in the table for  $N_2^+$ .

#### OTHER ONE-VALENCE-ELECTRON BANDS

Of the members of series A and B above, BO and CN, and their analogues  $CO^+$  and  $N_2^+$ , have now been discussed; BeF and MgF are the probable emitters of the known<sup>20</sup> beryllium and magnesium fluoride bands (cf Table I and notes); there remain SiN and AlO. The SiN bands, first described by Jevons<sup>21</sup> and recently studied by the writer,<sup>22</sup> show close analogy to the violet CN bands.<sup>22</sup> From this one might expect in the red or near infrared a system of SiN bands analogous to the red CN bands. Although no such bands have been detected, a new double-headed system ( $\Delta\nu = 27$ ) has been found<sup>22</sup> whose final state may possibly be the same as the initial state of the hypothetical red SiN bands.

*Bands of AlO.* The last member of series A and B is accounted for if the familiar *aluminum bands* centering in the green are attributed to AlO.

<sup>18</sup> G. H. Dieke, *Zeits. f. Phys.* **31**, 326 (1925).

<sup>19</sup> R. Mecke, *Zeits. f. Phys.* **31**, 709 (1925). This characteristic of homopolar molecules was also independently pointed out (private communication) by R. T. Birge.

<sup>20</sup> S. Datta, *Proc. Roy. Soc.* **99A**, 436 (1921 ; **101A**, 187 (1922).

<sup>21</sup> W. Jevons, *Proc. Roy. Soc.* **89A**, 187 (1913).

<sup>22</sup> R. S. Mulliken, *Nature*, (March 22, 1924) and (July 4, 1925); *Phys. Rev.* **26**, 319 (September 1925).

The question has long been in dispute<sup>23</sup> as to whether these bands are due to the metal or to the oxide. Since the structure of the bands is that of a diatomic emitter, the alternatives are  $\text{Al}_2$  and  $\text{AlO}$ . The isotope effect is unfortunately not available as a criterion, on account of the absence of Al isotopes. The vibration frequencies in the initial and final states<sup>24</sup> (cf Table I) for the bands in question are of the same order of magnitude as for  $\text{SiN}$ , and are more in accord with the undoubtedly tightly-bound  $\text{AlO}$  than with a loosely-bound compound such as  $\text{Al}_2$  whose bands would presumably resemble the  $\text{Na}_2$  bands. Also Mörikofer has shown that the bands are emitted in all parts of the Al arc, indicating that, although easily excited, their emitter is also stable under more violent conditions.<sup>25</sup> Furthermore, the results of an unpublished calculation from measurements on structure lines, made by W. C. Pomeroy and R. T. Birge and kindly rendered available to the writer, give for  $\text{AlO}$  an internuclear distance  $1.615 \times 10^{-8}$  cm, not far from that of  $\text{SiN}$ . The corresponding calculated value  $1.38 \times 10^{-8}$  for  $\text{Al}_2$  seems too small for a loosely-bound molecule composed of two atoms with complete shells and with three additional outer electrons in fairly large orbits. The larger values of  $r_0$  for  $\text{AlO}$  and  $\text{SiN}$  than for  $\text{BO}$  and  $\text{CN}$  are in accord with expectation, on account of the extra electron shell present in the positive ions of the former. Also, the structure of the bands is of the violet  $\text{CN}$  doublet type.

The great affinity of aluminum for oxygen, and the analogy to  $\text{BO}$ , also favor  $\text{AlO}$ . Experiments by the writer show that the bands are obtained in active nitrogen under the same conditions as are required for the  $\text{BO}$  bands.  $\text{AlCl}_3$  vapor was introduced into active nitrogen containing varying amounts of oxygen. With no oxygen, a weak continuous spectrum in the visible resulted. When enough oxygen was added so that the  $\beta$  bands of active nitrogen ( $\text{NO}$  bands) exceeded in intensity the  $\alpha$  bands ( $\text{N}_2$  bands), the bands which are here attributed to  $\text{AlO}$  became faintly visible; the strongest heads were identified both visually and photographically.<sup>26</sup>

#### ANALOGIES IN OTHER SERIES OF BANDS

*Two-valence-electron bands.* If the molecules of series A and B resemble alkali metal atoms, molecules having one more electron, such as  $\text{CO}$ ,  $\text{NO}^+$ ,  $\text{N}_2$ , and  $\text{SiO}$ , should show analogies to the alkaline earth metals,

<sup>23</sup> H. Kayser and H. Konen, *Handbuch der Spektroskopie*, Vol. 7, section on Al.

<sup>24</sup> R. Mecke (*Phys. Zeit.* **26**, 235, 1925) gives the equation for the heads.

<sup>25</sup> R. Mörikofer, *Dissertation*, Basel, 1925.

<sup>26</sup> It cannot be stated positively that the bands were not weakly present (and obscured by continuous background) when the nitrogen was free from oxygen; but there is no evidence for this.

e.g., in degree of multiplicity of electron levels and (cf above under  $N_2^+$  in regard to simultaneous excitation of electrons in  $N_2$ ) in occurrence of double electron jumps. The change from odd to even multiplicity shown

TABLE I  
Constants of emitters of the CN type

Emitter	$\nu^e$	Excited states				Probable normal state			
		$a'$	$b'$	$B_0'$	$r_0(10)^8$	$a''$	$b''$	$B_0''$	$r_0(10)^8$
BeF	{ 33180-33215	1157	8	....	....	1250	12	....	....
	{ Below $\lambda$ 2200?	....	....	....	....				
B <sup>11</sup> O	{ 23522-23648	1248	10.6	1.92	1.20	1873	11.8	2.30	1.09
	{ 42881	1269	10.0	2.03	1.16				
CO <sup>+</sup>	{ 20346-20472?	1550?	14.1?	{ 1.56 1.28	{ 1.60 1.26	2199	15.5	1.97	1.14
	{ 45637	1701	26	1.80	1.19				
CN	{ 14376-14430	1728	13.5	<1.89>	1.17	2056	13.5	1.89	1.17
	{ 25800	2244	20.3	1.96	1.13				
N <sub>2</sub> <sup>+</sup>	{ Near infra-red?	....	....	....	....	2187	16.1	1.92	1.12
	{ 25547	2398	26.2	2.07	1.08				
SiN	{ Near infra-red?	....	....	....	....	1145	6.6	0.74	1.55
	{ 24234	1016	17.8	0.73	1.56				
AlO	{ Near infra-red?	....	....	....	....	971	7.2	0.64	1.62
	{ 20646	866	4.0	0.61	1.65				

Notes for Table I. General: the values of  $\nu^e$ ,  $a$ , and  $b$  are for *heads*, except in the cases of SiN, the violet CN bands, and the high-frequency CO<sup>+</sup> bands, and serve merely to give an approximate idea of the true values, except that in the doublet bands, the heads given are Q heads and should nearly coincide with the true  $\nu^e$  values; also, the values given would be somewhat changed if half-integral vibrational quantum numbers were adopted, as they probably should be.<sup>1,2</sup>—The constants for BeF are from an analysis of Datta's results (ref. 20); Datta reported only three heads for each band (at 33218, 33215, and 33180 for the 0,0 band), but it is possible that a weak fourth head (the third head is weak) may have escaped notice among the numerous structure lines; although some data are given on structure lines, and the region of the null-line can apparently be located approximately, reliable values of  $B'$  and  $B''$  could not be obtained. The formulation of the heads requires a relatively large term in  $n'n''$  (about  $-5 n'n''$ ), which must be due to variation with  $n'$  and  $n''$  of the (evidently rather large) distance from head to origin;<sup>27</sup> the fact that the mutual separation of the three observed heads is not constant may be ascribed to this fact combined with the existence of appreciable differences in the values of  $B$  for the different heads.—For the low-frequency CO<sup>+</sup> bands (comet tail bands) the constants  $\nu^e$ ,  $a$ , and  $b$  are as given by Birge,<sup>13</sup> although the true values may be considerably different, due to uncertainty as to the correct assignment of vibrational quantum numbers; the values of  $\nu^e$ ,  $a$ , and  $b$  for the other CO<sup>+</sup> bands are from Blackburn's published equations;<sup>12</sup> the  $B_0'$  and  $B_0''$  values are preliminary values from unpublished work of Blackburn, and involving a revision of his published values. For CN, N<sub>2</sub><sup>+</sup>, SiN, AlO, respectively, see refs. 24, 14, etc.; 15; 22; 24 and text.

<sup>27</sup> R. S. Mulliken, Phys. Rev. **25**, 119-38 (1925).

in passing from the spectrum of  $N_2$  to that of  $N_2^+$  (this change being analogous to that expressed by the alternation law in line spectra) has been discussed by Mecke, who has also discussed the application of the displacement law of line spectra to the emitters of band spectra, in particular to hydrides.<sup>3</sup>

*Three-valence-electron bands.* Further, odd molecules like NO, with one more electron than for the  $N_2$  type, should resemble atoms of the aluminum family; the probable spectra of NO ( $\beta$  and  $\gamma$  bands of active nitrogen, the latter being the same as the third positive nitrogen bands)<sup>1</sup> show electronic doublets (see above), in accord with the expected even multiplicity. Nitric oxide, it may be recalled, is one of the very few substances composed of odd molecules whose chemical activity is sufficiently low to permit its existence in quantity under ordinary conditions.

*No-valence-electron bands.* Again, going backward from series A and B, molecules of the type of LiF (and HF, NaCl, etc.), BeO, BN, containing no unused valence electrons, should have an analogy with the rare gases; this is indeed borne out by the complete absence<sup>2</sup> of electronic band spectra in the case of the halides (and apparently for BN), but is seemingly contradicted in the case of the alkaline earth oxides by the occurrence of characteristic band spectra (but see discussion in a previous paper<sup>2</sup>).

*Note added in proof.* Since the above was written, a part of the relations noted have been pointed out independently by R. T. Birge (Nature, August 8, discussion of the combination bands of  $CO^+$ ) and R. Mecke (Naturwissenschaften, August 7, combination bands of  $CO^+$  and analogies between BO and  $CO^+$ ; CN and  $N_2^+$ ).

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