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THE ASSIGNMENT OF QUANTUM NUMBERS FOR ELECTRONS IN MOLECULES. II. CORRELATION OF MOLECULAR AND ATOMIC ELECTRON STATES

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Abstract

A few revisions, suggested by recent results of Herzberg on N_2^+, are made in Table III of I, for N_2^+, CN, and O_2^+. These revisions involve dissociation of unexcited molecules to give one excited atom or ion. With these revisions, and a revised heat of dissociation for N_2, the quantum number assignments previously made are found to be all consistent with Hund's rule of σ_l and s sums, and, except for one or two states of F_2, with the σ_{l_τ} *conservation rule* given in I. This result gives needed support to the latter rule. The probable atomic *dissociation products* are determined for most of the molecular states given in Table III of I. In the cases of N_2 and N_2^+ the probable dissociation products and energies are given in Table I. An interpretation is given of the dissociation processes involved in Hogness and Lunn's NO ionization potentials at 21 and 22 volts, and of their 24 volt N_2^+ potential. Evidence is brought forward for a revision of Birge and Sponer's values of the *heats of dissociation* for the normal states of several molecules, in particular N_2. Suggested new or revised values are, in volts, N_2, 9.5; N_2^+, 7.1; NO, 7.3; CO^+, 8.3; NO^+, 11.2. The alkali and hydrogen halides are briefly discussed with reference to their electronic states and dissociation products.

Introduction

In a previous paper, which in the following will be referred to as I,[1] tentative electronic quantum number assignments were made for a number of molecular states. In the present paper an attempt is made to determine so far as possible the electronic states of the atomic products which would result by dissociation from each such molecular state. The conclusions in regard to this correlation have already been summarized in Table III of I. A few changes in these conclusions are given below for N_2^+, CN, and O_2^+.

Hund[2] has previously discussed briefly the correlation of atomic and molecular states for the molecules BO, CN, CO^+, N_2^+, and CO, making use of the rule that σ_l and s of the molecule must be obtainable from σ_l and s of the atoms by algebraic or vector addition, and that there is a one to one correspondence between molecular states and atomic states.[3] In addition to these rules of Hund, we may often or perhaps usually expect σ_{l_τ} for each electron to be preserved in the formation of the molecule (σ_{l_τ} conservation rule). Reference should be made to the section in I entitled "Correlation of molecular quantum numbers with those of separate atoms" for further details in regard to the meaning and method of application of these rules.

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[1] R. S. Mulliken, Phys. Rev. **32**, 186 (1928).

[2] F. Hund, Zeits. f. Physik **42**, 93 (1927).

[3] As Hund remarks, some of the predicted molecular states may be very unstable, but it seems hardly justifiable to say, as Heitler and London appear to do, that these are not real molecular states.

The specific problem here considered is as follows: given a molecular state of known type and configuration, into what states of atoms or ions would it dissociate on increasing the vibrational quantum number? The solution of this problem in any individual case suffers from difficulties of various kinds. (1) In the first place, the molecular configurations given in Table III of I are all more or less uncertain, while in many cases even the molecular state (as ^2D) is not sure. For this reason one of the *objects* of the present paper is to investigate whether the assignments made in Table III of I are consistent with the dissociation products which are called for by the rules discussed in the preceding paragraph. (2) Another difficulty is that one of these rules, the $\sigma_{l\tau}$ conservation rule, has no sure theoretical basis; hence another of the *objects* of the present paper is to investigate the extent to which this rule is consistent with known data; the result of this investigation, it may be well to state at once, is that there seem to be only two examples (^1S states of F_2) which definitely conflict with this rule. (3) A further difficulty in testing the theory is that in most cases not just *one* but a considerable number of molecular states of a given type and configuration class are to be expected from the union of normal or slightly excited atoms; e.g., $s^{10}p^4$, ^3S states of N_2 should be formed as follows from N atoms[3,4]: one from $N(^4S)+N(^4S)$; one from $^4S+^2D$; one from $^4S+^2P$; three from $^2D+^2D$; three from $^2D+^2P$; one from $^2P+^2P$. To make possible the definite correlation of a particular observed $s^{10}p^4$, ^3S state with its dissociation products, supplementary evidence is needed. An accurate knowledge of relative energy levels and dissociation energies (D^v) for observed states, together with a definite knowledge of the dissociation products of at least one state of N_2, would evidently serve this purpose, and it is in fact to such data that we chiefly turn for empirical evidence here and in the matters just mentioned in (1) and (2). Unfortunately, however, the D^v values are for the most part rather uncertain. (For exact definitions of D and D^v, cf. Table III of I, note 7.)

A helpful principle in combating the difficulties just mentioned is that, in a general way, the lowest states of a molecule may be expected to be derived from the lowest states of the atoms. For example, if one had to determine the dissociation products of the *lowest* $s^{10}p^4$, ^3S state of N_2, the most likely guess, in the absence of other evidence, would be that it is derived from two ^4S atoms; similarly, for the next higher $s^{10}p^4$, ^3S state the best guess would probably be a ^4S plus a ^2D atom (cf. above). The usefulness of this method is, however, obviously weakened by the fact that in practise our empirical knowledge of the energy levels of molecules is very incomplete; thus in the present instance, conclusions in regard to *observed* $s^{10}p^4$, ^3S levels would be uncertain if other undiscovered levels of this kind might exist.

Furthermore, the method is also on theoretical grounds an uncertain one, since the energy curves $E(r)$ for two molecular levels of a given type may sometimes cross or tend to cross. As a result, the energy order of the *molecu-*

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[4] These results can be deduced by means of Table II of I.

lar levels (at $r=r_0$) may be different from the order of the correlated *atomic* levels ($r=\infty$); or else, as Hund as shown,[5] the correlation of the molecule with the separate atoms may be ambiguous, i.e., a molecule in a particular state may dissociate with a certain probability in each of two or more ways. The possibilities of reversal of energy order and of ambiguous correlation may be illustrated by considering the normal state of HF. This is a ^1S state with probably a Ne-like electron configuration of the s^6p^4 class. Such a state would be expected from the union of an H atom (^2S, s^1 class) and an F atom ($^2S^P$, s^5p^4 class, cf. Table II of I), but another state of the same kind would be expected from the union of an H^+ ion and an F^- ion ($F^- = {}^1S$, s^6p^4). Although $H^+ + F^-$ represents a higher energy than $H+F$, it is nevertheless likely that the normal state of HF is derived from $H^+ + F^-$, according to Pauling[6]; in this case the s^6p^4, ^1S state of HF which is derived from the atoms must be an *excited* (possibly unstable) state. Or it may be that in HF we have an example of ambiguous correlation, so that *each* of the two ^1S states mentioned dissociates with a certain probability into either atoms or ions. Questions of this kind have been discussed in recent papers by Hund,[5] London,[6] and Pauling.[6]—Similar ambiguities of correlation and reversals of energy order are also expected in other cases where the choice is not between atoms and ions, but between different states of the same atoms. For example, the normal, s^9p^4, ^2S, state of N_2^+ probably gives an N^+ ion and an *excited* N atom on dissociation, while the first excited s^9p^4, ^2S state probably gives an *unexcited* atom and ion (see below).

DISCUSSION OF EXAMPLES

The discussion of individual examples given in the following paragraphs is subject to the limitations and uncertainties described in the preceding section, and the conclusions reached are in most cases more or less tentative. The general procedure is to make a list of the molecular states, derived from each possible combination of low-lying atomic states, making use of Table II of I for this purpose, then to compare this list of predicted states with the list of observed molecular states; then to make identifications between the two lists, so far as is possible with the help of the criteria already discussed.

Li_2. Two unexcited Li atoms (each s^3, $^2S^S$) should give an s^6, ^1S and an s^6, ^3S Li_2 molecule. The lowest possible s^6, ^1S state of Li_2 must almost certainly be a $(1s^s)^2(2s^p)^2(2s^s)^2$ state, as assumed in Table III of I, and this is doubtless the normal state of Li_2. (Such a state is not yet known experimentally for Li_2, but a corresponding state is known for the analogous Na_2.) For the lowest possible s^6, ^3S state of Li_2 one of the $2s^s$ electrons of the ^1S state just mentioned must evidently be promoted to a $3s^p$ or $3s^s$ (or possibly $3s^d$) orbit (cf. BeO and C_2, Table III of I). This ^3S state must then be one with a small D^v, and it may be related to the ^1S state much as the 2^3S state of H_2 formed by two normal H atoms is related to the 1^1S normal state of H_2

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[5] F. Hund, Zeits. f. Physik **40**, 742 (1927).

[6] F. London, Zeits. f. Physik **46**, 455 (1928); L. Pauling, Proc. Nat. Acad. Sci. **14**, 359 (1928).

(cf. "discussion of Heitler and London's work" in I). Heitler, approaching the matter from a different viewpoint, has reached essentially this conclusion.[8]

LiF, BeO, *alkali halides*, BeF. From unexcited Li+F we expect the following states of LiF: ^3S and ^1S, both s^8p^4, from Li(s^3; $^2S^S$)+F(s^5p^4, $^2S^P$), and ^3P_i and ^1P, both s^9p^3, from Li(s^3, $^2S^S$)+F(s^6p^3, $^2P^P$). From normal $Li^+ + F^-$ we expect only a ^1S, s^8p^4 molecule of LiF, since we have Li^+(s^2, ^1S) $+F^-$(s^6p^4, ^1S). Normal LiF (s^8p^4, ^1S according to Table III of I) is probably derived from $Li^+ + F^-$ (cf. discussion of NaCl and other alkali halides by Hund[5] and London[6]), while the four states derived from unexcited Li+F are probably excited states of LiF.

The relations for LiF are probably typical for the alkali halides. The continuous absorption spectra shown by these molecules in the ultra-violet[6a] probably represent jumps from the normal, ionic, state to the dissociation continua associated with these four excited states and with others involving an excited alkali atom as a dissociation product. These excited states are evidently all relatively unstable, since the continuous character of the absorption shows, according to Franck's theory, that the most probable jump is that to a condition of dissociation.

Of the two observed, presumably low-lying, ^1S states of BeO (cf. Table III of I) one may perhaps be derived from $Be^{++} + O^{--}$ and be analogous to the s^8p^4, ^1S state of LiF from $Li^+ + F^-$, and the other may be derived from $Be^+ + O^-$ and be analogous, except for greater stability, to the ^1S of LiF derived from Li+F. Probably neither one is derived from neutral Be+O, especially since one or both atoms would have to be excited in order to yield a ^1S molecule (cf. Table II of I).

The supposed ^2S normal state of BeF (Table III of I) may perhaps be derived from Be^+ (like Li) and F^- (like Ne).

C_2 *molecule*. For the Swan band emitter C_2 two ^3P states are known, both of an s^9p^3 class according to Table III of I. Two normal (^3P) carbon atoms are capable of yielding one ^3P molecular state of this class, while for the other ^3P we must assume at least one excited atom (^1D or ^1S). The possible correlations are numerous; the most plausible guess is given in Table III of I.

BO, CO^+, CN, N_2^+. Hund has already discussed these molecules,[2] and has concluded that all of the three known states (s^9p^4, ^2S; $s^{10}p^3$, ^2P_i; s^9p^4, ^2S, in order) of BO and C^+O may be formed from normal atoms. For the analogous states of CN and N_2^+ he reached similar conclusions, except that one ^2S state should have D at least 2.39 volts higher (corresponding to excitation of an N atom from ^4S to ^2D) than the ^2P_i and the other ^2S state. Hund, of course, did not consider the question of configuration class. In many cases this factor would affect the results, but as will be seen from the following, its consideration does not alter his conclusions here.

Normal B (or C^+) plus normal O gives the following possibilities (cf. discussion of B+O in I, preceding Table II): $s^{11}p^2$, ^4S, ^2S; $s^{10}p^3$, ^4P, ^2P, ^4P, ^2P;

[6a] Cf. H. Sponer, Ergebnisse der exakten Naturwissenschaften **6**, 97 (1928). J. Springer.

s^9p^4, ^4D, ^2D, ^4S, ^2S, ^4S, ^2S. All three states of BO (or CO^+) may be identified with members of this group, although the possibility exists that one or more of them (in particular, the excited ^2S state) should be identified with states correlated with a slightly excited O atom.

It is possible that some or all of the states of CO^+ should be correlated with $C+O^+$ (analogous to $C+N$), but the correlation with C^++O seems more likely, since, as Mecke has emphasized,[9] the CO^+ electron levels parallel those of BO rather than CN. Birge and Sponer,[7] however, using the relation $D^+=D+I_a-I_m$, where D^+ is D for CO^+, D is that for CO, and I_a and I_m are the respective ionization potentials of atom (C or O) and molecule (CO), have concluded that the observed D^+ values (9.3 to 9.8 volts, according to extrapolations made by Birge and Sponer for the three states of CO) support the correlation $C+O^+$. Assuming $CO\rightarrow CO^+\rightarrow C+O^+$, we have $D^+=11.2+13.6-14.2=10.6$ volts; while if $CO^+\rightarrow C^++O, D^+=11.2+11.3-14.2=8.3$ volts; here the value $D=11.2$ is used (cf. discussion of CO below), while $I_m=14.2$, and $I_a=11.3$ for C and 13.6 for O.[10] Since the observed D^+ values (9.3–9.8 volts)[7] lie between the calculated values for C^++O and $C+O^+$, they evidently do not suffice to decide between the two possibilities.

Normal C (or N^+) plus normal N yields only $s^{10}p^3$, ^6P, ^4P, ^2P, and s^9p^4, ^6S, ^4S, and ^2S. This is capable of accounting for *one* of the two (s^9p^4, ^2S) states of CN (or N_2^+), and for the $s^{10}p^3$, ^2P state of CN. The *other* s^9p^4, ^2S state of CN (or N_2^+) must then involve at least one excited atom; very likely it is derived from a normal C (or N^+) atom, and a ^2D, or possibly a ^2P, excited N atom. According to recent conclusions of Herzberg[11] on the D^v values for the two ^2S states of N_2^+, it appears that it is the *normal* state which dissociates to give an ion and ^2D excited atom, while the *excited* ^2S state dissociates to give the normal atom and ion (cf. Table I below). There is also evidence for similar relations in the case of CN.[11a]

The above empirical evidence that the lowest electron level of N_2^+ is not derived from the lowest levels of the dissociation products N^++N is important in giving us warning that similar reversals of energy order may occur in other cases.

Nitrogen. In their work on heats of dissociation, Birge and Sponer,[7] by linear extrapolation from the vibrational levels for the lowest electronic state (X) of N_2, obtained the value 11.75 volts[12] for the heat of dissociation (D_X) of this state. The similar value (11.9 volts) obtained for state A gave

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[7] R. T. Birge and H. Sponer, Phys. Rev. **28**, 259 (1926).

[8] W. Heitler, Zeits. f. Physik **46**, 47 (1927).

[9] R. Mecke, Naturwiss. **13**, 698 (1925); Zeits. f. Physik **36**, 797 (1926).

[10] Ionization potentials, oxygen, cf. J. J. Hopfield, Astrophys. J. **59**, 114 (1924); carbon, I. S. Bowen, Phys. Rev. **29**, 231 (1927).

[11] G. Herzberg, Ann. d. Physik **86**, 189 (1928).

[11a] Herzberg, ref. 11, p. 206, footnote 2. According to recent data of Jenkins on the violet CN bands, it appears that D^v and D for the excited ^2S state of CN should be considerably reduced as compared with the values given in Table III of I.

[12] H. Sponer, Proc. Nat. Acad. Sci. **13**, 100 (1927).

support to this value. Thus 11.8 volts would seem to be a reasonable estimate for D_X. There are, however, several facts which point to a lower value, in the neighborhood of 9.5 volts. The evidence for each of these values will now be considered in a study of the known electron levels of N_2 and N_2^+. These levels, with the configuration class of each, are listed in Table I, together with their probable D values and dissociation products according to each of the two assumptions (1) $D_X=11.8$ volts, (2) $D_X=9.5$ volts. In connection with this discussion, the writer is greatly indebted to Professor Birge for information, suggestions, and criticism. Independently of the writer, Birge has also concluded that $D_X=9.5$ is probably correct.

TABLE I. N_2 *and* N_2^+ *levels and possible dissociation products.*

Level	Probable electron configuration	Electron energy	D(obs.)	D(calc. 1)	D(calc. 1) $-D$(obs.)	D(calc. 2)	D(calc. 2) $-D$(obs.)
$X={}^1S$	$s^{10}p^4$	0	11.75	$11.8({}^4S+{}^4S)$	+0.0	$9.5({}^4S+{}^4S)$	−2.2
$A={}^3D$ or ${}^3S$	$s^{10}p^4$	8.2	11.9 (>10.3)	$11.8({}^4S+{}^4S)$	−0.1	$11.9\ ({}^4S+{}^2D)$	−0.0
$a={}^1P$	s^9p^5	8.5	14.24 (>10.1)	$16.6({}^2D+{}^2D)$	+2.4	$14.3\ ({}^2D+{}^2D)$	+0.1
$B={}^3P$	s^9p^5	9.35	14.6 (>12.9)	$14.2({}^4S+{}^2D)$	−0.4	$14.3\ ({}^2D+{}^2D)$	−0.3
$C={}^3P$	s^9p^5	13.0	14.6 (>13.94)	$16.6({}^2D+{}^2D)$	+2.0	$15.45({}^2D+{}^2P?)$	+0.85
$D={}^3D$ or ${}^3S$	$s^{10}p^4?$	14.8	>14.8	—	—	$16.6?({}^2P?+{}^2P)$	—
$X'={}^2S$	s^9p^4	16.9	26.0	$\{23.7({}^2D+{}^3P)$or $26.3({}^4S+{}^3P)$	−2.7or −0.3	$26.4({}^2D+{}^3P)$	−0.4
${}^2P$	$s^{10}p^3$	17?	—	$26.3({}^4S+{}^3P)$	—	$24.0({}^4S+{}^3P)$	—
$A'={}^2S$	s^9p^4	20.1	23.6	$\{28.7({}^2D+{}^3P)$or $26.3({}^4S+{}^3P)$	{−5.1or −2.7	$24.0({}^4S+{}^3P)$	−0.4
${}^2S?$	s^9p^4	24	>24	$28.7({}^2D+{}^3P)$	See below	$26.4({}^2D+{}^3P)$, or higher	See below

Notes (*a*) The electronic energies (E) and "observed" D values are all referred to the normal state of N_2 as a zero of energy. Further details, and additional states, will be found in Table III of I (cf. also ref. 61 of I). The "observed" D values ($D=E+D^v$) are those given by Birge and Sponer, [7,12,13] or (N_2^+) by Herzberg.[11] The parenthetical inequalities given in the D(obs.) column set extreme lower limits for the correct values of D; the value given in each case (e.g. 10.3 for state A) is the energy value for the highest yet observed vibrational state of the electron level in question. (*b*) In the fifth column the calculated heats of dissociation and probable dissociation products are given on the assumption $D_X=11.8$, and the observed and calculated D values are compared in the sixth column. In the seventh and eighth columns, a similar correlation and comparison is given for the assumption $D_X=9.5$. In calculating D values for dissociations giving ${}^2D$ or ${}^2P$ atoms, the value 2.39 volts is used for the energy (above ${}^4S$) of the ${}^2D$ state, and 3.56 volts for that of the ${}^2P$ state.[14] (*c*) The D(calc.) values for N_2^+ make use of the value 14.5 volts for the ionization potential I_a of the unexcited (${}^4S$) N atom;[14] $D(\text{calc.})=D_X+I_a$ for dissociation into $N^+({}^3P)+N({}^4S)$, or $D_X+I_a+2.39$ when dissociation yields $N^+({}^3P)+N({}^2D)$.

Let us first consider levels X and A. Two unexcited (${}^4S$) nitrogen atoms (each ${}^4S^S$, s^5p^2) should give four states of N_2, namely a ${}^1S$, a ${}^3S$, a ${}^5S$, and a ${}^7S$ state, all belonging to the $s^{10}p^4$ configuration class. We may identify the normal, ${}^1S$, state X of N_2 with the predicted ${}^1S$ state, and if $D_X=11.8$, we may identify the lowest excited state A with the predicted ${}^3S$ state. In agreement with this, both these molecular states have $s^{10}p^4$ configurations, and extrapolated D values which are nearly equal. The metastability of state A (cf. I, p. 216) also supports this identification. Heitler has recently reached similar conclusions,[15] showing that $N({}^4S)+N({}^4S)$ should yield two

[13] The observed D value given for state a is a revised recent value of Birge (private communication).

[14] According to Hopfield (Phys. Rev. **27**, 801, 1926), the two largest term values for the neutral nitrogen atom are at 14.49 and 12.10 volts; these are presumably ${}^4S$ and ${}^2D$ respectively in accordance with the Hund theory; hence 2.39 volts probably represents the energy of ${}^2D$. The probable value 3.56 volts for ${}^2P$ is a result of unpublished work of Compton and Boyce (private communication).

[15] W. Heitler, Zeits. f. Physik **47**, 857 (1928).

states (^1S and ^3S) of N_2,—the upper one metastable,—with D^V values similar to those observed for states X and A. The other two (^5S and ^7S) states, Heitler shows, should correspond to states of "repulsion" (i.e., r_0 very large, D^V very small).

If we assume $D_X=9.5$, instead of 11.8, no change is needed in the interpretation of state X; the discrepancy between Birge and Sponer's extrapolated $D_X=11.75$ and the assumed $D_X=9.5$ is, however, surprisingly large; but the extrapolation is a very long one here. With $D_X=9.5$ for state X, we can no longer assume dissociation of state A into unexcited N atoms, since we are sure $D>10.3$ for state A (cf. Table I); the best assumption now is that A is an $s^{10}p^4$, ^3D_z state which gives $^4S+^2D$ on dissociation. A ^3D_z state is to be expected (cf. Tables I and III of I) from the same electron configuration which gives a ^3S state of the kind assumed for state A in the preceding paragraphs; the as yet incompletely known structure of the first positive nitrogen bands ($B\rightarrow A$) appears to be compatible with either a $^3P\rightarrow{}^3S$ or a $^3P\rightarrow{}^3D_z$ transition. Also, such a ^3D_z state should be metastable like the ^3S state.

An argument in favor of the identification of state A with ^3S of $N(^4S)+N(^4S)$, in agreement with $D_X=11.8$, is that if we do not do this, it seems necessary to postulate the existence of an as yet undiscovered additional $s^{10}p^4$ state of this kind; and if such an additional state exists, it is surprising that it does not combine, to give visible or ultra-violet bands, with one of the known states B or C.

Thus for states X and A of N_2, the weight of evidence and plausibility favors $D_X=11.8$. Turning now, however, to state a, we find evidence which strongly favors $D_X=9.5$. From the fact that the N_2 bands $a\leftrightarrow X$ are of high intensity and apparently simple structure, it seems extremely probable that state a is a singlet state; if so, it is necessarily (because of the selection rule for σ_l) either ^1S or ^1P, since X is ^1S. Birge has assumed it to be ^1P, in analogy with CO. Now except for the one ^1S state from $^4S+^4S$ which we have identified with X of N_2, *all* singlet states of N_2 are necessarily derived from *two excited atoms*,—as can be seen from a study of Table II of I. Of ^1P states of N_2, two s^9p^5 states should be obtained from $N(^2D)+N(^2D)$, one s^9p^5 state from $^2D+^2P$, and one $s^{11}p^3$ state from $^2P+^2P$. State a of N_2 should then probably be correlated with $^2D+^2D$ (this would also be reasonable even if a is a ^1S state). As will be seen from Table I, the calculated and observed D values are then in good agreement for state a if $D_X=9.5$ is assumed, but the observed D is too low, by an amount probably exceeding any possible error in the extrapolation, if $D_X=11.8$. This is strong evidence for $D_X=9.5$.

According to Table III of I, the ^3P states B and C of N_2 both have s^9p^5 configurations. By means of Table II of I we find that one s^9p^5, ^3P state should be obtained from $^4S+^2D$, two from $^2D+^2D$, and one from $^2D+^2P$. The most likely correlations for each of the two assumptions $D_X=9.5$ and 11.8 are given in Table I. The agreements are better for $D_X=9.5$.

Data on N_2^+ afford strong evidence for $D_X=9.5$. On the basis of Herzberg's recent revision[11] of the observed D^V values for the 17 and 20 volt

^2S levels of N_2^+ (cf. discussion of N_2^+, above), there appears to be no way of getting reasonable agreement between D (obs.) and D (calc.) for both these states, except to assume $D_X = 9.5$ and at the same time to assume that the dissociation products are $N_2^+(17) \rightarrow N^+(^3P) + N(^2D)$ and $N_2^+(20) \rightarrow N^+(^3P) + N(^4S)$. The justification for this statement will be evident from an examination of the observed D values as compared in Table I with D values calculated for various assumptions.

Besides the 17 and 20 volt ^2S states of N_2^+ there is another, probably also ^2S, level at 24 volts, which is unstable on collision (Smyth, Hogness and Lunn[16]; cf. I, Table III and p. 208). This state of N_2^+ must on *adiabatic* dissociation give at least one excited particle, since the ^2S from unexcited $N^+ + N$ is already accounted for. The possibility of lowest energy is $N^+(^3P) + N(^2D)$. This makes D at least 26.4 or 28.7 volts (according as $D_X = 9.5$ or 11.8) for this state.[11] But Hogness and Lunn in their positive ray experiments have shown that 24-volt N_2^+ is completely dissociated by *collisions* if sufficient opportunity for these is given (high pressure). From this we must conclude either that the ions acquire additional kinetic energy, to the extent of 2 or 4 volts, before colliding, or else that 24 volts is enough energy for dissociation. But Hogness and Lunn explicitly mention the first alternative and give evidence that possession of kinetic energy does *not* promote dissociation of 24 volt N_2^+ (ref. 16, bottom p. 790). The most reasonable explanation seems then to be the following: the collisions which produce dissociation are "collisions of the second kind" in which the energy, although inadequate for *adiabatic* dissociation to $N^+(^3P) + N(^2D)$, becomes available for dissociation into $^3P + ^4S$. But even this process, unless the ions acquire kinetic energy contrary to Hogness and Lunn's conclusions, would require 26.3 volts if $D_X = 11.8$; if $D_X = 9.5$, however, the required energy is reduced to 24.0 volts (cf. Table I), a value which is consistent with the observed dissociation of 24 volt N_2^+ ions on collision. Thus we have another argument in favor of $D_X = 9.5$ volts for N_2.—Incidentally, the value 24.0, after subtraction of the ionization potential of N_2 (16.9 volts) gives a new value $D_X = 7.1$ volts for N_2^+, as compared with Birge and Sponer's value of 9 volts.

The fact that the energy transferred by active nitrogen to other molecules is usually limited to about 9.4 volts (cf. I, discussion and ref. 64) also tends to support $D_X = 9.5$, since active nitrogen is probably atomic nitrogen mixed with products formed by the union of the N atoms.[17]—An argument in favor of $D_X = 11.8$ rather than 9.5 for N_2 is the fact that the high value $D_X = 11.2$ is well assured for the chemically less stable molecule CO.—On the whole, the evidence appears strongly to favor $D_X = 9.5$ volts for N_2, but it is not yet conclusive.[17a]

Carbon monoxide. From the application of his σ_l and s addition rules to CO, Hund has tentatively concluded that the states X, A, B, a and b of CO should all be derived from two normal atoms. This conclusion seems

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[16] Hogness and Lunn, cf. ref. 39 of I.

[17] J. Kaplan and G. Cario, Nature, June 9, 1928.

[17a] For additional evidence in favor of $D_X = 9.5$, cf. E. Gaviola, Nature **122**, 313 (1928).

to be in the main verified by the experimental D values (cf. Table III of I). The correlation of atomic and molecular states is quite different than for N_2, in spite of the marked analogies between the molecular levels of CO and N_2.—Let us now consider in detail the correlation of C+O with CO.

Two unexcited atoms, $C(^3P)+O(^3P)$, should give the following molecular states: $s^{11}p^3$, ^5P, ^3P, ^1P; $s^{10}p^4$, ^5D, ^3D, ^1D, ^5S, ^3S, ^1S, ^5S, ^3S, ^1S, ^5S, ^3S, ^1S; s^9p^5, ^5P, ^3P, ^1P. The $s^{10}p^4$ states X and a' (^1S and ^3S?) of CO may probably be identified with two of the above group of states, and the s^9p^5 states a and A (^3P and ^1P) with two more of this group; the experimental D values are about equal for all four of these states, as they should be if this identification is correct. The extrapolated value $D_X=11.2$ volts is apparently not far wrong in this case, especially since it is confirmed[7] by the value 10.8 obtained from chemical data, assuming only the (probably reliable) value $D_X=7.0$ for O_2. It is probable that the $s^{10}p^4$, ^3S state b also dissociates into normal atoms: only one b vibrational state ($n=0$) is known with certainty, thus indicating a very low value of D^V.[18] It may be that the $s^{10}p^4$, ^1S state B also dissociates into normal atoms, although the experimental D value (based on Birge, Int. Crit. Tables, from work of Hopfield and Birge[19]) is too large.

The more highly excited states of CO beginning with state C *must* give at least one excited atom on dissociation, since the electronic energy *alone* now exceeds the heat of dissociation into normal atoms. In the case of *singlet* states of CO not formed from the normal atoms, *both* atoms must be in excited states on dissociation (cf. Table II of I).

Some general considerations on predicted and observed levels. Although eighteen different molecular states are predicted as capable of being formed by the union of two unexcited atoms (C+O), not more than five have as yet been identified. Probably many or most of the remaining states correspond, like the 2^3S state of H_2 formed from two normal H atoms (cf. section in I on Heitler and London's work) and like the ^5S and ^7S states of N_2 formed from two normal N atoms (cf. above), to very unstable molecules, i.e., molecules whose r_0 is very large and D^V very small because of a rapid increase in promotion energy with decreasing r. This must especially be true of such states as ^5D, ^5P, ^5S, since a quintet state ($s=2$) requires the presence of at least four electrons in shells which are not closed, and therefore, as compared with the normal state of CO, requires the excitation of at least two electrons from two different closed shells. If r_0 for such states had values comparable with those of the observed states of CO, the excitation energy for such a process would probably be at least 18 or 20 volts, which would be incompatible with dissociation into normal atoms ($D=11$ volts).

It is possible however, that at least a few comparatively stable excited states of CO capable of dissociating into unexcited atoms remain to be discovered; among the likely possibilities are $s^{10}p^4$, ^3D and ^1D, and perhaps $s^{11}p^3$, ^3P. It is not unlikely that the hitherto unassigned "triplet carbon bands,"

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[18] Cf. R. T. Birge, Phys. Rev. **28**, 1173 (1926); third positive carbon bands ($b\rightarrow a$); also the fact (Birge, private communication), that only the $0\rightarrow 0$ band is known for $X\rightarrow b$.

[19] Cf. ref. 37 of I.

with $\omega_0'=1105$, $\omega_0''=(1714)$, and $\Delta v\sim 160$ (Birge, private communication) are $^3S\rightarrow{}^3P$ or $^3P\rightarrow{}^3S$ and involve an $s^{11}p^3$, ^3P_i state of CO, perhaps the expected state which should dissociate into normal atoms.

Considerations similar to those just given for CO, bearing on the question of observed and predicted states, also apply to the other molecules treated in this paper. In the case of most of them, many reasonably stable excited levels probably remain to be discovered.

Nitric oxide (NO). For the normal, $s^{10}p^5$, ^2P, state of NO, the "observed" D (6.8 volts[19a]) may be compared with the more reliable value calculated indirectly making use of chemical data and D_X values of N_2 and O_2; this indirect value, here recalculated, is $D_X=7.3$, or 8.4, according as $D_X=9.5$, or 11.8, for N_2; the observed value 6.8 evidently agrees better with the calculated value 7.3 and so supports $D_X=9.5$ for N_2. Dissociation into unexcited atoms is in harmony with the theory, since $N(^4S)+O(^3P)$ should give $s^{11}p^4$, ^6S, ^4S, ^2S, and $s^{10}p^5$, ^6P, ^4P, ^2P, the last of these being here identified with unexcited NO. The first excited, ^2S, state of NO has already been discussed in the section on NO in I, and shown to involve a *highly* excited N or O atom. Since unexcited N+O should give only one ^2P state, according to Table II of I, and since this is already accounted for, we must conclude that the *excited* $s^{10}p^5$, ^2P state of NO dissociates to give at least one excited atom. The union of $N(^2D)$ and $O(^3P)$ is capable of giving an $s^{10}p^5$, ^2P state; D for this, assuming $D_X=9.5$ for N_2, should be $7.3+2.4=9.7$ volts, in agreement with the observed (but very uncertain) extrapolated $D=10$ volts. The two remaining known excited states of NO probably correspond to moderately excited atoms, but the data are incomplete.

We next consider NO^+. The molecular states formed by union of unexcited $N(^4S)+O^+(^4S)$ should be ^7S, ^5S, ^3S, ^1S, $s^{10}p^4$, as in the case of $N(^4S)+N(^4S)$; unexcited $N^+(^3P)+O(^3P)$ should give a variety of states like those of $C(^3P)+O(^3P)$. Unexcited NO^+ may reasonably be correlated with ^1S of $N(^4S)+O^+(^4S)$, or perhaps with $N^+(^3P)+O(^3P)$. Assuming $N+O^+$, and using $D_X=7.3$ for NO, we can calculate D_X for NO^+: $D_X{}^+=D_X+I_a-I_m=7.3+13.6-9.4=11.2$ volts. If the dissociation products are N^++O, $D_X=7.3+14.5-9.4=12.4$ volts.

As already pointed out in the section on NO in I, each of Hogness and Lunn's potentials, 21 volts ($N+O^+$) and 22 volts (N^++O), agrees closely with the calculated D value for ionization and dissociation of NO into the respective unexcited atom and ion.[20] The 21 volt state, being correlated with $N(^4S)+O^+(^4S)$, must then be an S state. Probably it is a ^3S state analogous to the lowest ^3S state of N_2 (i.e., to state A, if $D_X=11.8$); or, if

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[19a] F. A. Jenkins, H. A. Barton, and R. S. Mulliken, Phys. Rev. **30**, 172 (1927).

[20] At each of the potentials 21 and 22 volts, a large fraction of the NO molecules is dissociated directly, according to the data of Hogness and Lunn, while the remainder give NO^+ molecules capable of being dissociated in subsequent collisions.[21] As interpreted by Birge and Sponer,[7] this means that there is a large probability, but not a certainty, that the impinging electron will give the molecule enough vibrational energy to cause dissociation, in addition to the energy of removal of an electron. The observed potentials then probably include, strictly speaking, 1 or 2 volts of vibrational energy.

the normal state of NO^+ gives $N^+ + O$ on dissociation, the 21 volt state may be a ^1S corresponding to X of N_2. The 22 volt state may reasonably be identified with an s^9p^5, ^3P or ^1P state derived from $N^+(^3P)+O(^3P)$, like state a or A of CO. The three ionization potentials of NO then correspond (cf. Table III of I) respectively to removal of a $3p^p$, a $2p^p$, and a $3s^s$ electron from neutral NO.[22]

Oxygen. Two unexcited (^3P) O atoms should give the following states of O_2 (cf. Table II of I): $s^{10}p^6$, ^5D, ^3D, ^1D, ^5S, ^3S, ^1S, ^5S, ^3S, ^1S; $s^{11}p^5$, ^5P, ^3P, ^1P, ^5P, ^3P, ^1P; $s^{12}p^4$, ^5S, ^3S, ^1S. The two $s^{10}p^6$, ^3S states of Table II, both of which probably dissociate into normal atoms,[7] may evidently be identified with the two predicted $s^{10}p^6$, ^3S states. The 1.6 volt state of O_2, which is a ^1S state according to recent work of the writer,[22a] may correspond to one of the other $s^{10}p^6$ states.

The two $s^{10}p^5$, ^2P states involved in the ultra-violet O_2^+ bands are supposedly analogous (cf. I) to the two states involved in the B bands of NO. The same might then be expected of their dissociation products; that is to say (cf. NO, above), we might expect the lower ^2P to dissociate into unexcited $O^+ + O$ ($^4S+^3P$) and the upper ^2P into $O^+(^2D)+O(^3P)$. (Other excited states of O^+ or O are of course not entirely excluded as possible dissociation products.) Or perhaps, unlike NO, the excited ^2P might give unexcited $O^+ + O$, and vice versa. As a matter of fact, as we shall see, the empirical data indicate dissociation into unexcited $O^+ + O$ for *both* ^2P states; the evidence is strong in the case of the lower state, and practically conclusive for the upper state. But since this is quite impossible according to the theory (cf. NO, above), we must apparently conclude that this evidence is unreliable for one of the two states, in all probability the lower, since it is weaker there. We have then probably a reversal of energy order during molecule formation, as in the case of N_2^+ discussed above.

For the process $O_2 \rightarrow O^+(^4S)+O(^3P)$, the total energy D' can be calculated from the known D_X of O_2 and the ionization potential I_a of the O atom: $D'=D_X+I_a=7.02+13.56=20.58$ volts. For $O_2 \rightarrow O^+(^2D)+O(^3P)$, the total energy is 3.32 volts higher[23]: $D'=20.58+3.32=23.9$ volts.

For each of the two ^2P states of O_2^+, D' is known empirically as the sum of the three quantities I_m (ionization potential of O_2), E^e (electronic energy above the normal ^2P state), and D^V. For the upper ^2P level, the value $D^V=$ 1.76 volts is known from Birge and Sponer's work, and is probably reliable within a few tenths of a volt. For the lower ^2P level, the value of D^V depends on the uncertainly known value of E^e of the upper level; assuming $E^e=5.2$ volts, Birge and Sponer's method gives $D^V=6.9$ volts. Assuming $I_m=13.5$ (this, like E^e, is uncertain within a volt—cf. I), we find for the lower ^2P

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[21] Cf. note 43 of I.

[22] For the 21 volt potential at least, the possibility is excluded that it is a $2s^s$ or a $3s^p$ electron which is removed, since such removal would give a P state of the molecule, which would be incompatible with $N(^4S)+O^+(^4S)$.

[22a] R. S. Mulliken, Phys. Rev., Dec., 1928: interpretation of atmospheric oxygen bands.

[23] 3.32 volts is the energy required to excite O^+ from ^4S to ^2D: cf. I. S. Bowen, Phys. Rev. **29**, 231 (1927); H. N. Russell, Phys. Rev. **31**, 27 (1928).

state, $D'=13.5+0+6.9=20.4$ volts, and for the upper ^2P state, $D'=13.5+5.2+1.8=20.5$ volts. Both agree well with the calculated value 20.58 volts for dissociation into unexcited atoms. For the upper state, the value of D' is also supported by independent evidence, for as shown in I (p. 212), Hogness and Lunn's ionization potential at 20 volts, at which simultaneous dissociation and ionization occur, in all probability corresponds to the convergence limit of the vibrational levels of the upper ^2P state.[24] Because of this evidence, and in view of the much longer extrapolation involved for D^V in the lower than in the upper state, the value of D' is clearly more probably reliable for the upper than for the lower state. We therefore accept the agreement of the observed and calculated D' for the upper state and so conclude that this state dissociates into unexcited $O^+ + O$, but reject on theoretical grounds (cf. above) the agreement for the lower state—in spite of the fact that the discrepancy between the theoretical value $D'=23.9$ which we must now assign to it and the empirical $D'=20.4$ is unaccountably large. —As a possible escape from this discrepancy, it is of course true that errors may exist in the classification of the O_2^+ levels, since our knowledge of the O_2^+ bands is very incomplete (cf. I).

Fluorine. For two fluorine atoms, we need consider only the normal state of each; there are no excited states of low energy. Two such atoms should give: $s^{12}p^6$, ^3D, ^1D, ^3S, ^1S, ^3S, ^1S; $s^{11}p^7$, ^3P, ^1P, ^3P, ^1P; $s^{10}p^8$, ^3S, ^1S. The two observed ^1S, $s^{10}p^8$ states, both of which dissociate into normal atoms,[25] must probably be correlated with the two expected ^1S, $s^{12}p^6$ states, in spite of the fact that this involves a violation of the $\sigma_{l\tau}$ conservation rule.[26]

General conclusions. With two possible exceptions (state a of N_2, if $D_X=11.8$, and one state of O_2^+), all the assignments made in Table III of I are in conformity with Hund's rule that σ_l and s for the molecule should be obtained from the atomic σ_l and s values by addition. A further conclusion is that, with the exception of the two states of F_2 and possibly also of the two states (of N_2 and O_2^+) just mentioned, no contradiction is found to the applicability of the (non-detailed) $\sigma_{l\tau}$ conservation rule during molecule formation. This empirical result is especially valuable because no strict theoretical basis has been obtained for the rule.

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July, 1928.

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[24] Recent work of Smyth and Stückelberg (Phys. Rev. **32,** 779 (1928) gives new evidence, in agreement with Hogness and Lunn's results, that $O^+ + O$ is formed by electron impact at 20 volts.

[25] The normal ^1S state of F_2, judging by analogy with Cl_2, Br_2, and I_2, gives $F(^2P_{1\frac{1}{2}})+F(^2P_{1\frac{1}{2}})$ on dissociation, while the excited ^1S state gives $F(^2P_{1\frac{1}{2}})+F(^2P_{\frac{1}{2}})$: cf. J. Franck, Trans. Far. Soc. 21, Part 3, 1925, and H. Kuhn, Zeits. f. Physik **39,** 77 (1927). Such differences are, however, unimportant for present purposes, since $\Delta\nu$ is small for light atoms. Similar differences must exist in other cases where multiple atomic levels are involved (e.g. ^3P of oxygen).

[26] The possibility that one or both of the observed ^1S states may really be of an $s^{12}p^6$ type seems relatively small, in view of the evidence given in I for the configurations there assigned.