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Citation: *J. Chem. Phys.* **3**, 720 (1935); doi: 10.1063/1.1749583

View online: <http://dx.doi.org/10.1063/1.1749583>

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Electronic Structures of Molecules

XIV. Linear Triatomic Molecules, Especially Carbon Dioxide

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(Received August 20, 1935)

Electron configurations of the triatomic linear molecules CO_2 , BO_2^- , N_2O , CS_2 , COS , NO_2^+ , N_3^- , NCO^- , NCS^- , BeF_2 , HgCl_2 , ClCN , ClBO , etc. are given. The electron configurations probably of all of these are formally analogous, or formally identical in the case of isoelectronic molecules, such as CO_2 , N_2O , BeF_2 , etc. The BeH_2 type is also touched on. The relations of the electron configurations to ordinary valence conceptions are discussed, and the importance in practice of cases intermediate between those represented by simple valence formulas is emphasized. The usefulness of the present method in giving a simple description of intermediate cases of all sorts (between double-bonded $\text{A}=\text{B}=\text{C}$ and single-bonded $\text{A}-\text{B}-\text{C}$, between homopolar $\text{A}-\text{B}-\text{C}$, etc., and heteropolar $\text{A}^+\text{B}^{++}\text{C}^-$, etc., between $\text{A}-\text{B}\equiv\text{C}$ and $\text{A}^+=\text{B}=\text{C}^-$, etc.) is brought out. The ionization potentials of CO_2 , CS_2 , N_2O , HgCl_2 are interpreted in relation to their electron configurations. The minimum potentials of CO_2 , of CS_2 , and of HgCl_2 , respectively, correspond to removal of a nearly nonbonding $p\pi$ electron of the O, S, or Cl atom. It is shown that the ultraviolet emission bands of CO_2 probably represent transitions among four electron states of

CO_2^+ which correspond to the four lowest ionization potentials of CO_2 ; if this interpretation of the bands is correct, the CO_2^+ molecule has a linear form in these states. According to this interpretation, the four lowest potentials of CO_2 are probably 13.72, 17.09, 18.00, and about 21.5 volts (or perhaps 14.63, 18.00, 18.91, and about 22.4 volts). These values are based on identification of the CO_2 Rydberg absorption series limit at 18.00 volts with one of the potentials. The minimum potential above obtained (13.72 or perhaps 14.63 volts) differs considerably from the accepted value 14.3 or 14.4 volts based on electron impact. Radicals N_3 , NCO , NCS , and molecules NO_2 and others are also touched on. A reason for the triangular form of NO_2 is found in the fact that linear NO_2^+ (like CO_2 or N_2 or NO^+) is composed of a stable system of closed shells, while the final electron added to make neutral linear NO_2 would have to go into a probably fairly high energy antibonding orbital (as in NO). Evidently the actual NO_2 avoids this by being triangular. Ultraviolet absorption spectra of CO_2 , CS_2 , and COS are also considered.

1. NORMAL STATE OF CO_2

IN X of this series,¹ various molecules containing the $\text{C}=\text{O}$ and $\text{C}=\text{S}$ double bond in compounds $\text{C}=\text{O}$ and $\text{C}=\text{S}$ were considered.

In the present paper, $\text{O}=\text{C}=\text{O}$ and various other linear triatomic molecules and ions whose structures are more or less the same (N_2O , BO_2^- , N_3^- , NO_2^+ , NCO^-) or analogous (CS_2 , COS , NCS^- , etc.) are considered. On comparison with the results of X, it will be found that, although relations can be traced and although here as well as there it is justifiable to speak of

$\text{C}=\text{O}$ and $\text{C}=\text{S}$ double bonds (essentially two pairs of bonding electrons per $\text{C}=\text{O}$ or $\text{C}=\text{S}$ bond), the electronic structures of these bonds are in effect very different here than there. In addition to the double-bonded types, certain other linear triatomic molecules (HgCl_2 , BeF_2 , CNCl , BOCl , and the like) are discussed here, since it is found that their electronic structures are closely related, at least formally, to those of the double-bonded types.

The structure of CO_2 has already been described briefly in I of this series.² The structure there indicated for the normal state (symmetry $D_{\infty d}$ like O_2 or H_2) can be written, omitting 1s electrons, as

$$\begin{array}{l}
 \text{Locn.} \\
 \text{Pred. } I_{\text{uri.}} \\
 \text{Obs. } I
 \end{array}
 \begin{array}{c}
 (2s)^2(2s)^2(\sigma+s+\sigma, \sigma_p)^2(\sigma+\sigma-\sigma, \sigma_u)^2(\pi+\pi+\pi, \pi_u)^4(\pi-\pi, \pi_p)^4, \quad {}^1\Sigma_g^+ \\
 \begin{array}{ccccc}
 \text{O} & \text{O} & \text{O}-\text{C}-\text{O} & \text{O}-\text{C}-\text{O} & \text{O}-\text{C}-\text{O} & \text{O}=\text{O} \\
 & & >19.1 & >14.2 & >14.0 & <15.23
 \end{array} \\
 \begin{array}{ccccc}
 \text{two val-} & & & & & \\
 \text{ues } <32 & & & & & \\
 - & - & 21.5? & 18.0 & 17.1 & 13.7 \\
 & & (\text{or } 22.4?) & (\text{or } 18.9?) & (\text{or } 18.0?) & (\text{or } 14.6?)
 \end{array}
 \end{array}
 \quad (1a)$$

¹ R. S. Mulliken, J. Chem. Phys. 3, 564 (1935): X of this series.

² For a general survey of data and further references on CO_2 , N_2O , CS_2 , HgX_2 , etc., cf. R. de L. Kronig, *The Optical Basis of Chemical Valence*, The Macmillan Co., New York,

1935; and H. Sponer, *Molekülspektren I* (Julius Springer, Berlin, 1935); *Landolt-Börnstein Tabellen*, fifth edition, third Sup. Volume, Part I (J. Springer, 1935); electric moments etc.

³ R. S. Mulliken, Phys. Rev. 40, 60 (1932): I.

That configuration (1a), composed of closed shells, is essentially correct will be shown in section 4 to be extremely probable.

In (1a) the four most loosely bound electrons are in a π_g molecular orbital of LCAO type³ $\alpha(2p\pi_A - 2p\pi_B)$, with $\alpha = 2^{-1}$ approximately (A and B refer to the two O atoms). It will be noted that this $(\pi - \pi)$ orbital involves only the two O atoms (cf. section 4 for derivation of this result), and so gives neither bonding nor antibonding between C and O. Technically, it is $O \leftrightarrow O$ antibonding, but since the two O atoms are relatively far apart, this effect is of little importance, i.e., the orbital is practically nonbonding. Because of the relatively large distance between the O atoms, we have here a case where, unlike the usual case of strongly bonding or antibonding orbitals,³ the LCAO form must represent a good approximation to the true molecular orbital. Here it is $2^{-1}(2p\pi_A - 2p\pi_B)$, with the $2p\pi$ O atom orbitals of about the same size as for neutral O atoms, or better, as for somewhat negatively charged O atoms, because of the C^+O^- polarities within the molecule.

But now since the $(\pi - \pi)$ molecular orbital connects two atoms relatively far apart, should we not get a much better approximation for the total wave function if the four electrons assigned to $(\pi - \pi)$ in (1a) were assigned instead to corresponding atomic orbitals, i.e., to $2p\pi$ O atom orbitals, with two electrons on each O atom? This change would seem to be called for by our usual rule that the use of molecular orbitals gives good approximations only for strongly shared electrons, while atomic orbitals are best for unshared (i.e., nonbonding) electrons. If we make this change, the assignment of the last four electrons is altered so that (1a) is replaced by:

$$\cdots (2p\pi_O^2 2p\pi_O^2), \quad {}^1\Sigma_g^+ \quad (1)$$

In (1) it must be specifically understood that the actual state corresponds to a ${}^1\Sigma_g^+$ wave function built up approximately from determinants (four in number) in which the m_l and m_s values of the last four (i.e., the $2p\pi_O$) electrons appear in various combinations, but only in such ways that there are two $2p\pi$ electrons on each O atom, and that the sum of the m_l 's, and likewise

of the m_s 's, is zero. The fact that CO_2 is diamagnetic gives assurance that a ${}^1\Sigma$ function, which can then hardly be other than ${}^1\Sigma_g^+$, is needed in (1).

In regard to the relative merits of (1) and (1a), obviously (1a) is neater, and also it correctly indicates the fact that there must be only a single I value corresponding to the four π nonbonding O atom electrons, and that removal of one of them gives a ${}^2\Pi_g$ state of CO_2^+ . On the other hand, it would seem that the configuration (1), although rather awkward, should represent a much better approximation according to our usual criteria. It can be shown, however, that when the complete wave functions corresponding to (1) and (1a) are written out, the difference between them is not as great as one might have anticipated.

This is because of certain relations which exist between the $(\pi + \pi + \pi)^4$ and the $(\pi - \pi)^4$ or $(2p\pi_O^2 2p\pi_O^2)$ shells. If $(\pi + \pi + \pi)$ were to lose entirely its C—O bonding properties (i.e., if we had $b'' = 0$ in (2), below), making it of the type $\beta(2p\pi_A + 2p\pi_B)$, with $\beta = 2^{-1}$ nearly, then (1) and (1a), respectively, would become

$$\cdots (2p\pi_A)^4 (2p\pi_B)^4 \text{ and } \cdots (\pi + \pi, \pi_u)^4 (\pi - \pi, \pi_g)^4.$$

Now it can be shown very easily that in this case, if we use the LCAO approximations for $(\pi + \pi)$ and $(\pi - \pi)$, as would be correct here if $b'' = 0$, the complete antisymmetrical wave functions corresponding to (1) and (1a) would be *identical*.

The fact that $b'' \neq 0$ in (2) of course disturbs the foregoing identity of the (1) and (1a) wave functions, but nevertheless leaves them more nearly alike than one would have at first thought. Hence while (1) is probably better than (1a), still (1a) should not be bad, and has certain advantages as already noted.

Turning now to the other orbitals in (1) or (1a), it will be noted that we have used three whole-molecule orbitals each of which gives bonding between the central C atom and both the O atoms simultaneously. Written out in the form of rough LCAO approximations, these three bonding orbitals are as follows (A and B refer to the O atoms):

³ R. S. Mulliken, J. Chem. Phys. 3, 375 (1935): VI.

⁴ R. S. Mulliken, J. Chem. Phys. 1, 492 (1933): V.

$$\begin{aligned}
 & a(2p\sigma)_A + b(2s)_C + a(2p\sigma)_B, \\
 & a'(2p\sigma)_A + b'(2p\sigma)_C - a''(2p\sigma)_B, \quad (2) \\
 \text{and} \quad & a''(2p\pi)_A + b''(2p\pi)_C + a'''(2p\pi)_B.
 \end{aligned}$$

The positive end of each $(2p\sigma)_O$ is taken as directed toward the C atom, the positive end of $(2p\sigma)_C$ toward oxygen atom A; with this convention, all O—C interactions in (2) are bonding, since the overlapping atomic orbitals used are of like sign in regions of strong overlap. The construction of the forms given in (2), and others, including $(\pi-\pi)$ of (1a), will be further discussed in section 4.

Rough estimates can be made of the relative values of coefficients a , b , etc., in (2). These depend partly on symmetry, partly on electronegativity of O relative to C, in a manner discussed in XI, XII of this series.⁵ As electroaffinities of $2s_C$, $2p_C$, and O (i.e., $2p_O$), it will probably be safe for rough qualitative purposes here to use the usual P scale values (cf. XII), even though these are based on single-bonded compounds while here we have double bonds. These values, relative to \bar{P}_H , are $P(2s_C) = 3.04$, $P_O = 1.40$, $P(2p_C) = -0.28$.

If $(2s)_C$ had the same electroaffinity as $(2p\sigma_A + 2p\sigma_B)$, then these would appear with equal coefficients in the first line of (2), assuming the forms $2s_C$ and $(2p\sigma_A + 2p\sigma_B)$ each first separately normalized (cf. XII, section 2). Neglecting the slight lack of orthogonality between $2p\sigma_A$ and $2p\sigma_B$, we should multiply $(2p\sigma_A + 2p\sigma_B)$ by a normalizing factor $2^{-1/2}$, and would thus have $b = 2^{1/2}a$ in the first line of (2).

However, since $2s_C$ is actually considerably more electronegative⁵ (i.e., higher in effective term value) than $(2p\sigma_A + 2p\sigma_B)$,—or what is nearly the same thing, than $2p\sigma_O$,—we must expect b/a to be considerably greater than $2^{1/2}$. In a similar way it can be shown that b'/a' and b''/a'' must each be very considerably less than $2^{1/2}$. We might then proceed further⁵ to determine approximate numerical values of b/a , etc., but this will not be attempted here.

It is of interest to note in the foregoing that as a result of the symmetry of the molecule, just as in CH_4 and CX_4 ,⁴ there is no mixing between $2s_C$ and $2p_C$. In other carbon compounds of

lower symmetry, however,⁶ some mixing occurs, usually of $2s_C$ with $2p\sigma_C$. [In the present case, although mixing of $2s_C$ with $2p\sigma_C$ is absent, mixing of $2s_O$ with $2p\sigma_O$ does occur (see below).]

In addition to the assignments already mentioned, four electrons in (1a) or (1) are assigned to nonbonding O atom $2s$ orbitals. Instead one might assign these electrons to molecular orbitals which may be indicated by $(s+s, \sigma_g)$ and $(s-s, \sigma_u)$. There would then be more or less mixing between these and $(\sigma+s+\sigma, \sigma_g)$ and $(\sigma+\sigma-\sigma, \sigma_u)$, respectively. If this mixing were very pronounced, it would definitely be much better to substitute whole-molecule orbitals for $2s_O$ orbitals in the case of the four electrons in question (cf. section 4).

The nature of the valence bonds in CO_2 is related to configuration (1) or (1a) as follows. Essentially, there are just eight bonding electrons (σ_g, σ_u , and π_u in (1)). Since these, on a time average, are distributed in a symmetrical manner, there are two pairs of bonding electrons per C=O bond. The bonding would be pure homopolar if we had $b/a = b'/a' = b''/a'' = 2^{1/2}$. Actually this is not true, but $b/a > 2^{1/2}$ (favoring the C atom), while b'/a' and $b''/a'' < 2^{1/2}$ (favoring the O atoms), with a net effect decidedly favoring the O atoms, in accordance with their greater electronegativity. That is, the bonding is partially polar with the O atoms decidedly negative.

It may be of interest to give a rough estimate of the relative charges of the C and O atoms in accordance with Eq. (41) of XI of this series,⁵ by using the method of calculation of section 1 of XII.⁵ The mean effective electronegativity of C is $P = 0.55$, that of O is 1.40, hence $P_O - P_C = 0.85$, for C—O single bonds. It is uncertain how nearly correct this will be for double bonds, but we can try it. Substituting in Eq. (41) of XI, we get $Q_C = +0.27e$, per bond. Since there are four bonds, the calculated total Q_C is $+1.08e$, so that CO_2 may be formulated as $O^{-0.54}C^{+1.08}O^{-0.54}$. This would correspond to a bonding 27 percent heteropolar, 73 percent homopolar in character, which appears not unreasonable, but of course represents only a very rough estimate.

In connection with (1) or (1a), vertical I' s have been predicted by the usual methods.⁷ The

⁵ R. S. Mulliken, J. Chem. Phys. 3, 573, 586 (1935): XI, XII.

⁶ R. S. Mulliken, J. Chem. Phys. 3, 517 (1935): IX.

⁷ R. S. Mulliken, J. Chem. Phys. 3, 514 (1935): VIII.

predictions are based on the following valence state I 's, also obtained in the usual way:⁷ C atom I^σ values, in volts: 21 for $2s$, 11.23 for $2p\sigma$, 10.86 for $2p\pi$; O atom I^σ values: 17.17 volts for $2p\sigma$ and $2p\pi$; O atom I^* values: 32 volts for $2s$, 15.23 volts for $2p\pi$.

The predicted I 's involving inequality signs can be made more definite if we estimate the magnitudes of the inequalities. Comparison with CO is helpful in the case of the π_u orbital (not, however, for the σ orbitals, where complications arise in CO). In CO there is a C—O bonding π orbital similar to π_u of CO₂, with predicted $I > 14.0$ just as for the latter. The observed I is known experimentally to be 17.1 volts, assuming the correctness of the electron impact value 14.3 volts for the minimum I of CO.⁸ Hence the inequality sign amounts to about 3 volts for π in CO. A similar or perhaps even larger value would appear reasonable for π_u of CO₂; also a comparable value for σ_u of (1).

For the nonbonding $2p\pi_o$ of (1) or $(\pi-\pi, \pi_o)$ of (1a), the inequality sign corresponds mainly to effects of charge-transfer, whereby I should be lessened because of net negative charges on the O atoms. These net charges may be expected to be less than in such a case¹ as H₂O or H₂CO, since the charges on both O atoms must here be drawn entirely from one C atom. Also, the $2p\pi$ or $(\pi-\pi)$ orbital is strongly subjected to the positive field of the neighboring C atom. On the whole, the inequality between I_{obs} and I^* should be considerably less here than in H₂CO or H₂O. —Similar considerations apply to the nonbonding $2s$ orbitals in (1) or (1a).

Experimentally, we may first consider the electron-impact I of CO₂, which is 14.3 volts according to Mackay.⁹ There can be no doubt, in view of the foregoing predictions, that this must correspond to the removal of one $2p\pi_o$ from (1) or one $(\pi-\pi)$ from (1a), and that it must give the normal state of CO₂⁺, which may be written

$$\cdots(\pi-\pi)^3, {}^2\Pi_g \text{ corresponding to (1a),} \quad (3) \\ \text{or } \cdots(2p\pi 2p\pi^2), {}^2\Pi_g \text{ corresponding to (1).}$$

A second experimental I is obtained from a pair of Rydberg series in the ultraviolet absorption

spectrum of CO₂.¹⁰ These both give $I = 18.00 \pm 0.03$ volts. This I (unless it should prove spurious, as might be remotely possible) must clearly belong either to π_u or to σ_u of (1) and (1a), more probably to the former, as we shall see below.

2. ULTRAVIOLET CO₂⁺ EMISSION BANDS

Further progress can now be attempted by a consideration of the emission band spectrum which is obtained by electrical discharges in CO₂. This spectrum has been shown to contain at least three band systems.¹¹ There has been much discussion as to whether the spectrum is due to CO₂ or to CO₂⁺, but the weight of evidence now seems to favor the latter as emitter of the entire spectrum. In the case of the strong double band near $\lambda 2900$ the direct experimental evidence for CO₂⁺ is nearly conclusive,¹² as is also, independently, the evidence of the band structure.

The $\lambda 2900$ band is apparently composed of two similar but not identical sub-bands each of complex structure, one centered about $\lambda 2883$, the other about $\lambda 2895$. Both sub-bands show marked Zeeman effects.¹¹ No satisfactory analysis of the rotational structure has been made, but there are evidently several branches in each band, and the existence of perturbations has been established. The almost uniform spacings within the discernible series indicate that the moment of inertia is nearly unchanged from the initial to the final electronic state. This situation, in view of the Franck-Condon principle, also affords a reasonable explanation of the isolated occurrence of one double band: it is presumably mainly a 0,0 band, i.e., one starting and ending on vibrationless levels. The main band, however, is pre-

¹⁰ H. J. Henning, Ann. d. Physik [5] **13**, 599 (1932); G. Rathenau, Zeits. f. Physik **87**, 32 (1933).

¹¹ H. D. Smyth, Phys. Rev. **38**, 2000 (1931); **39**, 380 (1932). R. F. Schmid, Phys. Rev. **41**, 732 (1932); Zeits. f. Physik **83**, 711; **84**, 732 (1932). R. S. Mulliken, Phys. Rev. **42**, 364 (1932); in this paper the discussion of the κ selection rule (middle p. 365) is in error, the correct rules being $\Delta\kappa = 0$ if $\Delta\lambda = 0$, $\Delta\kappa = \pm 1$ if $\Delta\lambda = \pm 1$. R. F. Schmid, Zeits. f. Physik **85**, 384 (1933): doublet structures of lines in main band system. R. F. Schmid, Zeits. f. Physik **83**, 711 (1933); $\lambda 2900$ double band. R. F. Schmid, Zeits. f. Physik **84**, 732 (1933); $\lambda 3660$ double band.

¹² P. E. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932).

¹³ A. S. Roy and O. S. Duffendack, Proc. Nat. Acad. Sci. **19**, 497 (1933).

⁸ Cf. R. S. Mulliken, Phys. Rev. **46**, 550 (1934).

⁹ C. A. Mackay, Phys. Rev. **24**, 319 (1924).

sumably overlain by weaker bands starting from upper vibrating states and ending on lower vibrating states but without change of vibrational quantum numbers.¹¹

What is known of the structure appears on the whole to be most consistent with a ${}^2\Pi \rightarrow {}^2\Sigma$ or a ${}^2\Sigma \rightarrow {}^2\Pi$ transition in a linear molecule. In view of the strong experimental evidence¹² that the final state is the normal state of CO_2^+ , the transition should be ${}^2\Sigma^+_{\text{u}} \rightarrow {}^2\Pi_{\text{g}}$. The two parts of the double band should then correspond to the two components of the ${}^2\Pi_{\text{g}}$, and the observed doublet width in the band (about 161 cm^{-1}) should be that of the ${}^2\Pi_{\text{g}}$. This doublet width $\Delta\nu$ should be equal to the spin-orbit coupling coefficient a for a $2p$ electron of the O or O^+ atom, since the ${}^2\Pi_{\text{g}}$ is obtained by removing a $2p\pi_{\text{O}}$ or $(\pi-\pi, \pi_{\text{u}})$ electron.¹³ The coefficient a is 149 cm^{-1} for neutral O and about 270 cm^{-1} for O^+ , and the observed $\Delta\nu$ might be expected to lie between these values. [In this connection, cf. the observed $\Delta\nu = 195 \text{ cm}^{-1}$ for the ${}^2\Pi_{\text{g}}$ normal state of O_2^+ , in which one $(\pi-\pi, \pi_{\text{g}})$ electron is present.] The observed $\Delta\nu = 161 \text{ cm}^{-1}$ in the $\lambda 2900 \text{ CO}_2^+$ band appears to be in reasonable agreement with the prediction.

Although other possible interpretations of the $\lambda 2900$ band cannot be excluded with certainty until it has been analyzed, the foregoing considerations (together with others too numerous and detailed to give here) make it fairly certain that the band is ${}^2\Sigma^+_{\text{u}} \rightarrow {}^2\Pi_{\text{g}}$. The ${}^2\Sigma^+_{\text{u}}$, which from the frequency of the $\lambda 2900$ band must be 4.28 volts above the ${}^2\Pi_{11\text{g}}$ lowest level of CO_2^+ , is then identified as the state expected on removal of one σ_{u} electron from (1). That is, the transition is identified as being from

$$\cdots (\sigma_{\text{u}})^{-1}, \quad {}^2\Sigma^+_{\text{u}} \quad (4)$$

to the ${}^2\Pi_{\text{g}}$ of (3).

The interval 4.28 volts checks fairly well with the interval between the minimum I of CO_2 observed at 14.3 volts (electron impact) and the higher I at 18.0 volts (Rydberg series). It will be seen, however, that the agreement is not accurate. Accepting the spectroscopic value as reliable, one finds that the minimum I of CO_2 must be $18.00 - 4.28 = 13.72$ volts (\pm about 0.03).

¹³ R. S. Mulliken, Rev. Mod. Phys. 4, 34-39 (1932).

This is about 0.6 volts less than the electron impact value. Such a discrepancy is within the usual range of reliability of electron impact I 's determined several years ago, and the direction of the discrepancy is the usual one.

An alternative possibility, however, is that the observed I at 18.00 volts may correspond to removal of a π_{u} electron from (1) to give

$$\cdots (\pi_{\text{u}})^{-1}, \quad {}^2\Pi_{\text{u}}, \quad (5)$$

instead of a σ_{u} to give (4). This possibility will be discussed shortly.

Turning now to the $\lambda 3660$ doublet band,¹¹ there is again a large Zeeman effect in both subbands. The structure seems to be simpler than in the $\lambda 2900$ band. Again there appears to be only an isolated double band, presumably a (0,0) band, although Franck-Condon reasons for this are not evident, since the band structure indicates that the moment of inertia is larger in the upper state. Except for the pronounced Zeeman effects, which tend to favor the interpretation ${}^2\Sigma \leftrightarrow {}^2\Pi$ again, the structure appears consistent with ${}^2\Pi \leftrightarrow {}^2\Pi$. The relatively small observed $\Delta\nu$ (about 58 cm^{-1}) cannot readily be explained in terms of expected low energy states of CO_2^+ if we assume ${}^2\Sigma \leftrightarrow {}^2\Pi$.

Supposing the band is ${}^2\Pi_{\text{u}} \rightarrow {}^2\Pi_{\text{g}}$, starting from (5) and ending on (3), the observed $\Delta\nu$ can be immediately explained as the difference between a $\Delta\nu = 103 \text{ cm}^{-1}$ of the ${}^2\Pi_{\text{u}}$ and the value 161 cm^{-1} already found for the ${}^2\Pi_{\text{g}}$. The bands for a transition ${}^2\Pi_{\text{u}} \rightarrow {}^2\Pi_{\text{g}}$, both ${}^2\Pi$'s being case a and inverted, should contain four main series of lines, namely, two P , R sets each giving one strong head.¹⁴ The observed structure, aside from additional weak series and heads which might be due to superposed bands involving vibrating states, looks like this.

A $\Delta\nu = 103 \text{ cm}^{-1}$ is reasonable for the ${}^2\Pi_{\text{u}}$ state of (5). The π_{u} orbital from which an electron has been removed to get (5) is in LCAO approximation a mixture of $2p\pi_{\text{C}}$ and $2p\pi_{\text{O}}$ (cf. (2)), and should have a spin-orbit coupling coefficient a intermediate between those of $2p$ of C and O (or tending toward something between those of C^+ and O^+). The coefficient a is 28 cm^{-1} for $2p$ of C and 43 cm^{-1} for C^+ . By way of comparison with $\Delta\nu = 103 \text{ cm}^{-1}$ for π_{u} here, the observed

¹⁴ Cf. R. S. Mulliken, Rev. Mod. Phys. 3, 90-155 (1931).

value for the rather similar π orbital in CO^+ (again a mixture of $2p\pi_C$ and $2p\pi_O$) is 125 cm^{-1} . The lower value here would tend to indicate a stronger proportion of $2p\pi_C$, less of $2p\pi_O$, which is not unreasonable.

If the foregoing interpretation of the $\lambda 3660$ band is correct, the ${}^2\Pi_{1/2}$ level of (5) is 3.36 volts above the ${}^2\Pi_{1/2}$ level of (3), and 0.90 volt below the ${}^2\Sigma^+_u$ of (4). This is entirely reasonable according to our predicted I 's for CO_2 . A point supporting this interpretation is that the occurrence of the ${}^2\Pi_u$ level a little below the ${}^2\Sigma^+_u$ affords a reasonable possible explanation of the observed occurrence of perturbations in the $\lambda 2900$ (${}^2\Sigma^+_u \rightarrow {}^2\Pi_g$) band.

If we accept 18.00 volts (see above) as the I required to produce ${}^2\Sigma^+_u$ of (4) from neutral CO_2 , we now get the following system of I 's: 13.72 volts for π_g , 17.09 for π_u , 18.00 for σ_u . Another possibility is that 18.00 volts belongs to π_u , in which case we get 14.63 volts for π_g , 18.00 for π_u , 18.91 for σ_u . This seems less probable, since it makes the minimum I somewhat greater than the reported electron impact value, and makes the inequality signs in the predictions for σ_u and π_u very large (cf. (1)). In any case, it should be borne in mind that the foregoing conclusions based on the $\lambda 3660$ band, while reasonable, are still open to some doubt until the rotational structure has been satisfactorily analyzed. Then again, there might perhaps be a slight possibility that the Rydberg series giving the 18.00 volt potential is illusory.

Finally, the remaining extensive system of red-shaded bands, extending from about $\lambda 3200$ to $\lambda 3800$ and beyond, can probably also be fitted into the CO_2^+ electron level scheme. The structures of these bands were at first found by Schmid to be of a simple $P-R$ branch type like ${}^1\Sigma \rightarrow {}^1\Sigma$ of a diatomic or linear molecule, although certain complications indicated ${}^1\Pi \rightarrow {}^1\Pi$ as more probable.¹¹ Schmid's later discovery that each band line is a very narrow doublet can, however, be understood most simply if the bands are ${}^2\Sigma \rightarrow {}^2\Sigma$. In a diatomic molecule composed of light atoms, this explanation of the doublets would be altogether the most probable: In the present case, however, the doublets might conceivably arise as a result of the presence of

degenerate vibrations,¹⁶ but the ${}^2\Sigma \rightarrow {}^2\Sigma$ explanation nevertheless appears on the whole the most probable. If the bands are ${}^2\Sigma \rightarrow {}^2\Sigma$, they cannot be due to neutral CO_2 but must belong to CO_2^+ . Other evidence bearing on the question of CO_2^+ as against CO_2 appears inconclusive, although the regular appearance of these bands with the $\lambda 3600$ and $\lambda 2900$ bands supports their assignment to a common carrier; moderate differences observed in excitation behavior as compared with $\lambda 3660$, 2900 are obviously explainable by the different initial electronic states.

If the bands are ${}^2\Sigma \rightarrow {}^2\Sigma$, they can immediately be identified as ${}^2\Sigma^+_g \rightarrow {}^2\Sigma^+_u$, coming from

$$\cdots (\sigma_g)^{-1}, \quad {}^2\Sigma^+_g \quad (6)$$

in which a σ_g has been removed from (1), and ending on ${}^2\Sigma^+_u$ of (4). The energy changes corresponding to the observed bands are about 2.6–3.9 volts. The exact energy of the vibrationless transition is unknown, since the vibrational numbering is uncertain. A value of about 3.5 volts may be taken as a reasonable estimate; if correct it makes I about 21.5 volts or 22.4 volts for σ_g of CO_2 , the former if $I=18.00$ volts belongs to σ_u , the latter if it belongs to π_u . Such values are in harmony with what is predicted for I of σ_g (cf. (1)).

Mention should be made of the moments of inertia for the various electronic levels of CO_2^+ , as indicated by the band structures. In terms of the rotational constant B ($B=h/8\pi^2cJ$, J =moment of inertia), the relations are as follows: B about 0.34 cm^{-1} for ${}^2\Sigma^+_g(6)$ and about 0.38 cm^{-1} for ${}^2\Sigma^+_u(4)$, from Schmid's work;¹¹ B probably about the same for ${}^2\Pi_g(3)$ as for ${}^2\Sigma^+_u(4)$, hence about 0.38 cm^{-1} for both; B somewhat less for ${}^2\Pi_u(5)$ than for ${}^2\Pi_g(3)$, hence $<0.38\text{ cm}^{-1}$, if the $\lambda 3660$ band is correctly interpreted above. Finally, for the normal state of neutral CO_2 , $B=0.390$ from data on infrared bands.^{11a} The above value B about 0.38 for the ${}^2\Pi_g$ normal state of CO_2^+ is in agreement with expectation, since the electron removed from neutral CO_2 to produce this state is a nearly

¹⁶ In connection with this question, compare the important paper of R. Renner, *Zeits. f. Physik* **92**, 172 (1934). Renner's work would raise questions particularly in regard to the interpretations given above for the $\lambda 2900$ and $\lambda 3600$ bands, but not in such a way as to make these interpretations improbable in view of the evidence favoring them.

nonbonding one. In the case of the other three CO_2^+ states, (4), (5), and (6), the electron removed is a C—O bonding one, so that we would expect a larger J and smaller B than for neutral CO_2 or than for ${}^2\Pi_u(3)$ of CO_2^+ . The differences, however, should not be great, since in each case only one bonding electron is missing out of the eight which are present in (1). The observed results are in agreement with expectation except in the case of ${}^2\Sigma_u^-(4)$, where the B does not show the expected decrease.

Although the foregoing interpretation of the emission bands obtained in CO_2 must be considered somewhat tentative until the bands have been rather completely analyzed, it seems worth putting forward as being rather probably correct and as furnishing also a guiding scheme for testing by further research. In the latter connection, one notes that a fourth system of CO_2^+ bands, representing the transition ${}^2\Sigma_u^-(6) \rightarrow {}^2\Pi_u(5)$, should be found in the same neighborhood as the other bands.

An interesting feature of the foregoing interpretation is that all the band systems attributed to CO_2^+ are here ascribed to the jumping of an electron from one inner orbital to another, no excited orbitals being involved. In this respect the spectrum would be like an x-ray spectrum, as are all the known spectra of CO^+ , N_2^+ , CN , and BO , except one N_2^+ system. Support for CO_2^+ as emitter of the present bands can be found in the absence of any marked predissociation. As in the bands of CO^+ , N_2^+ , CN , and BO , this can be readily explained by the fact (or probable fact here) that the bands involve mostly electron levels of low energy relative to the normal state of the emitting system.

In the preceding discussion, it has been assumed more or less tacitly that in the various electron states of CO_2^+ considered, the molecule is linear just as in the normal state of CO_2 . While the structures of the $\lambda 2900$ and $\lambda 3600$ bands cannot yet be conclusively cited as support for this, what is known of them appears to agree with it. In the case of the main system of bands, attributed above to ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_u^+$, the structure is definitely that of a linear molecule.¹¹ From the theoretical standpoint, it appears entirely reasonable that the known linear form of neutral CO_2 should be preserved in all the CO_2^+ ion states

(3)–(6). In the normal state (3), the absence of a nonbonding electron should not appreciably alter the forces determining the bond angles. In the other states (4)–(6), where one bonding electron is removed, there appears to be no reason why the remaining bonding electrons should not find a linear form still the most stable.

3. LINEAR MOLECULES ABC

Langmuir¹⁶ introduced the term isostere to designate molecules having the same number of electrons and believed to have essentially the same electronic structure as judged by their properties. As examples of isosteres Langmuir gave, among others, N_2 , CO , CN^- ; CO_2 , N_2O , N_3^- , NCO^- .

It was shown by the writer and by Hund in 1928 that N_2 and CO (and NO^+ and implicitly CN^-) have very similar electronic structures in terms of molecular orbitals.¹⁷ This gave added justification and a more precise meaning to Langmuir's concept of isosterism.

The nature of the isosterism of CO_2 , N_2O , N_3^- , NCO^- , to which may be added NO_2^+ and BO_2^- , can now be made clear. To all of these as well as to the analogous molecules SCN^- , OCS , CS_2 and others, can be assigned electron configurations more or less similar to (1) or (1a) given above for CO_2 , with supplementary descriptions of orbitals similar to those in (2). In this group also perhaps come XBO and XCN ($\text{X} = \text{halogen}$); for example, ClCN and ClBO are isoelectronic with SCN^- . Even BeF_2 , isoelectronic with CO_2 but hardly isosteric, can be described by an at least formally similar configuration, while the other bivalent metal halides MeX_2 have analogous structures ($\text{Me} = \text{Mg}$, Ca , Hg , etc.).

The similarities and the differences among the molecules and ions just mentioned can best be understood by a systematic treatment. In each case, we can safely assume that we are dealing with a linear molecule ABC. In most cases linearity has been satisfactorily proved by evidence from band spectrum, electric moment, electron diffraction, or crystal structure data.^{1a}

¹⁶ I. Langmuir, J. Am. Chem. Soc. **41**, 868, 1543 (1919).

¹⁷ R. S. Mulliken, Phys. Rev. **32**, 186 (1928); F. Hund, Zeits. f. Physik **51**, 759 (1928).

The molecules ABC can be divided into two sets: (a) those of type ABA, where atoms A and C are identical, and the symmetry is $D_{\infty d}$; (b) those where A and C are different, giving symmetry $C_{\infty v}$. The treatment is simpler for the first type, which will be considered in the next section.

All the molecules ABC of both types are alike in having sixteen outer electrons. These all correspond, if ABC is separated into $A+B+C$, to ns and np outer electrons of atoms A, B, and C. For example in $O+C+O$ we have two $2s$ electrons for each atom, and in addition two $2p$ for the C atom and four $2p$ for each O atom. In $S+C+S$ everything is similar except that we have $3s$ and $3p$ instead of $2s$ and $2p$ electrons for the S atoms. When entering into the structure of ABC, ns may be labeled $ns\sigma$, while np splits up into two types $np\sigma$, $np\pi$.

Our problem now is to find the correct orbitals to which these sixteen electrons should be assigned in the normal states of the various molecules ABC. Matters will prove to be simplified if at first we assign them all to molecular orbitals, and afterwards decide whether and how the approximation can be improved by replacing some of these by corresponding atomic orbitals (cf. the case of CO_2 in section 1). In determining the nature of the molecular orbitals, we shall find it convenient to build them up in LCAO approximation out of the various ns , $np\sigma$, and $np\pi$ atomic orbitals.

There are twelve of these, capable, if fully occupied, of holding twenty-four electrons instead of the actual sixteen. They are $ns\sigma_A$, $ns\sigma_B$, $ns\sigma_C$, $np\sigma_A$, $np\sigma_B$, $np\sigma_C$, $np\pi_A$, $np\pi_B$, $np\pi_C$, the last three each embracing two linearly independent forms. Out of these twelve atomic orbitals exactly twelve LCAO molecular orbitals can be constructed (cf. V of this series,⁴ sections 2, 4). The latter can be divided into a set of six σ molecular orbitals constructed from the six σ atomic orbitals, and a set of six $(3 \times 2)\pi$ orbitals constructed from the six $(3 \times 2)\pi$ atomic orbitals. The σ offer more difficulty than the π molecular orbitals.

4. SYMMETRICAL LINEAR MOLECULES ABA

In the case of molecules of symmetry $D_{\infty d}$, the σ and π types of molecular orbitals can be sub-

divided, giving types σ_θ , σ_u , π_u , π_θ . In building up such orbitals, we can proceed in two steps. First we make linear combinations of the normalized atomic orbitals of A and C so as to obtain normalized forms conforming to the types σ_θ , σ_u , π_u , π_θ ; then we combine the resulting forms with the normalized orbitals of atom B, which already belong to these types. Adopting the letters s , σ , π as shorthand for $ns\sigma$, $np\sigma$, and $np\pi$, we now have the following to work with (the normalization factors $2^{-1/2}$ are only approximate):

$$\begin{aligned}\sigma_\theta &: 2^{-1/2}(s_A + s_C), \quad s_B, \quad \text{and} \quad 2^{-1/2}(\sigma_A + \sigma_C) \\ \sigma_u &: 2^{-1/2}(s_A - s_C), \quad s_B, \quad \text{and} \quad 2^{-1/2}(\sigma_A - \sigma_C); \end{aligned} \quad (7)$$

$$\begin{aligned}\pi_u &: 2^{-1/2}(\pi_A + \pi_C), \quad \text{and} \quad \pi_B \\ \pi_\theta &: 2^{-1/2}(\pi_A - \pi_C). \end{aligned} \quad (8)$$

For each s orbital, the outer part is taken as positive in sign; for σ_A and σ_C , the end facing toward the central atom B is taken as positive; for σ_B , the end facing toward atom A is taken as positive.

We now have the problem of finding three new σ_θ and three new σ_u forms by making suitable linear combinations of the forms in (7); and similarly of finding two new π_u forms from those in (8). The π_θ in (8) is all right as it stands.

The three σ_θ molecular orbitals can all be expressed by

$$\sigma_\theta = a2^{-1/2}(s_A + s_C) + b(s_B) + c2^{-1/2}(\sigma_A + \sigma_C); \quad (9)$$

the three different desired orbitals correspond to three different value-sets a , b , c . Similarly the three desired σ_u orbitals can all be described by

$$\sigma_u = a'2^{-1/2}(s_A - s_C) + c'2^{-1/2}(\sigma_A - \sigma_C) + b'(s_B). \quad (10)$$

Assuming that we knew the forms and term values of the three initial orbitals in each case, each problem could be solved systematically by perturbation theory (cf. e.g., XII,⁵ section 2, for a similar problem involving two initial orbitals). We shall not, however, attempt here to do more than to establish certain approximate qualitative relations among the coefficients a , b , c or a' , b' , c' belonging to each solution of (9) or (10).

In attacking either of the two problems, it is well to note certain fixed characteristics of the three initial functions. For definiteness let us first consider (9). Here it is always true that the

initial term value belonging to $2^{-1}(s+s)$ is very considerably larger than that of $2^{-1}(\sigma+\sigma)$, also that these two functions are approximately orthogonal. Both, however, are very far from being orthogonal to the third function s_B , and the largest perturbation effects occur between the latter and each of the former. Sometimes (e.g., N_3^-) the term value of s_B is somewhat larger than that of $(s+s)$, in other more usual cases (e.g., CO_2) it lies between those of $(s+s)$ and $(\sigma+\sigma)$, while in other cases (e.g., BeF_2 and perhaps BO_2^-) it is smaller than that of $(\sigma+\sigma)$.

In the case of (10), the functions $(s-s)$ and $(\sigma-\sigma)$ are always nearly orthogonal, and $(s-s)$ always has the larger term value. Sometimes (e.g., N_3^-) the term value of s_B is a little larger than that of $(\sigma-\sigma)$, more usually it is less, or (e.g., BeF_2) very much less.

A qualitative survey of the approximate relative values of the coefficients in (9) and (10) can profitably be made for each of two special cases: (A), term value of s_B nearly equal to that of $(s+s)$, term value of σ_B nearly equal to that of $(\sigma-\sigma)$; (B), term value of s_B equal to that of $(\sigma+\sigma)$, of σ_B much less than that of $(\sigma-\sigma)$. The qualitative results for other cases can then readily be seen by interpolation or extrapolation. In making this survey, we can conveniently proceed as follows. In (9) for case A, we first solve the problem of the resonance between $2^{-1}(s+s)$ and s_B , neglecting $2^{-1}(\sigma+\sigma)$; then we consider the mutual perturbations between $(\sigma+\sigma)$ and each of the two functions, namely, $\frac{1}{2}\alpha(s+s) + 2^{-1}\alpha s_B$ and $-\frac{1}{2}\beta(s+s) + 2^{-1}\beta s_B$, which resulted from the first step. We can treat (9) for case B and (10) for case A in a similar way.

In following the foregoing procedure, we note from the forms of the orbitals that in every case the energy is lowered (term value increased), and a bonding effect is produced, when the sign of b (or b') is the same as that of a or c (or a' or c'). When the sign of b (or b') is opposite to that of a or c (or a' or c') the energy is raised and an antibonding effect is produced. *Maximum* term value and more or less bonding are secured when a , b , c all have the same sign; *minimum* term value and more or less (usually a strong) antibonding effect when b (or b') is opposite in sign to both a and c (or a' and c'). An *intermediate* term value and more or less of a net bonding or

sometimes antibonding effect are produced when b is like c , but opposite to a , in sign (it can be shown that the reverse case does not occur here). The three cases just mentioned (maximum, intermediate, and minimum term values) correspond to the three solutions of the problem (9), or (10).

The statements just made as to signs of coefficients and their relation to energy and bonding effects are equally valid for case A or B or intermediate cases, but the relative numerical values of the coefficients, and the bonding properties, for the three solutions, of course differ considerably in cases A and B. This can be seen from the following detailed summary of the results; in each case the three solutions of each type are listed *in order of increasing energy* (decreasing term value):

$$\text{Case A, } \sigma_a: (a_1 \approx b_1 > c_1); \\ (-a_2 \approx b_2 > c_2); (a_3 < -b_3 < c_3). \quad (11a)$$

$$\text{Case A, } \sigma_u: (a'_1 > b'_1 > c'_1); \\ (-a'_2 < b'_2 \approx c'_2); (a'_3 < -b'_3 \approx c'_3). \quad (12a)$$

$$\text{Case B, } \sigma_a: (a_1 > b_1 > c_1); \\ (-a_2 < b_2 \approx c_2); (a_3 < -b_3 \approx c_3). \quad (11b)$$

$$\text{Case B, } \sigma_u: (a'_1 > b'_1 > c'_1); \\ (-a'_2 < b'_2 < c'_2); (a'_3 < -b'_3 > c'_3). \quad (12b)$$

The approximate-equality (\approx) or inequality signs refer directly only to the relation between adjacent letters. These approximate-equality signs would become equality signs and simultaneously the third coefficient would vanish, if there were no $s-p\sigma$ hybridization, i.e., no mixing of (s_A+s_C) with $(\sigma_A+\sigma_C)$ and of $(s-s)$ with $(\sigma-\sigma)$. Actually such mixing must occur, but probably always or nearly always only to an extent sufficiently moderate so that the case of no mixing is a better approximation than the case of complete (i.e., 50–50) mixing. As noted earlier, there is never any mixing between s_B and σ_B , for reasons of symmetry. In rare cases, the inequality signs given in (11) and (12), and possibly sometimes the signs of some of the small coefficients in (11) and (12), may be unreliable.

The signs of all the coefficients are (or may be taken as) + or – according as *no* sign, or a minus sign, precedes the coefficient in (11) or (12). [Of course for any given orbital the signs of all coefficients can be reversed simultaneously,

if desired.] Signs and magnitudes of bonding effects for the various cases included in (11), (12) can be read from the relative signs and magnitudes of the coefficients. Likeness of sign between b and a or c gives bonding, unlikeness antibonding; equality of magnitude between b and a or c tends to give maximum strength of bonding (or antibonding). In extreme cases, b (or both a and c) may be nearly zero, and such orbitals are nearly nonbonding. [Throughout this discussion, we have neglected the small and unimportant bonding or antibonding effects between end-atoms A and C, involved in the forms $(s \pm s)$ and $(\sigma \pm \sigma)$.]

To the foregoing results for the σ_g and σ_u orbitals may now be added those for the π_u orbitals. The two π_u orbitals can both be covered by

$$\pi_u = b''(\pi_B) + c''2^{-1/2}(\pi_A + \pi_C). \quad (13)$$

For the above-discussed cases A and B one finds:

$$\text{Case A, } \pi_u: (b_1'' = c_1''), \quad (-b_2'' = c_2''). \quad (14a)$$

$$\text{Case B, } \pi_u: (b_1'' < c_1''), \quad (-b_2'' > c_2''). \quad (14b)$$

Finally, for the type π_g , at least if we consider only the original twelve s and p atomic orbitals of the outer shells of the atoms A, B, and C, we have only the single representative $(\pi - \pi)$ given in (8). This, if we neglect the slight $A \leftrightarrow C$ antibonding, should be essentially nonbonding.

As noted earlier, we now have twelve molecular orbitals (counting each π orbital double) of which only eight are needed to hold the sixteen available electrons. For the normal state of each molecule, the eight lowest energy orbitals out of (11), (12), (14), and π_g of (8) will be filled up, leaving the four highest energy orbitals as excited orbitals. Examination of the twelve available orbitals indicates without reasonable doubt that the two lowest σ_g , the two lowest σ_u , the lower π_u , and the π_g will be filled, leaving the highest σ_g , the highest σ_u , and the higher π_u as excited orbitals in both the cases A and B and in intermediate cases and in all other, outside, cases which we meet in this paper. Of the filled orbitals, there seems to be no reasonable doubt that the nonbonding π_g should be the most loosely bound (last to be filled) in all the cases. These conclusions show that all the sixteen-outer-electron linear molecules here considered should be at

least formally analogous in outer-electron structure.

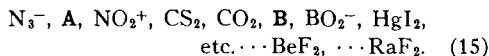
Of the excited orbitals, it appears that all or most should be high in energy above the last filled (π_g) orbital. The only excited orbital which seems likely ever to come rather low in energy is the excited σ_g in or beyond case A. In this case (cf. (11a)), the excited σ_g is of the form

$$\sigma_g = c_3 2^{-1/2}(\sigma_A + \sigma_C) - b_3(s_B) + \dots,$$

with $b_3 < c_3$. For $b_3 = 0$, this σ_g would be approximately equal in term value to the filled orbital π_g and so would begin to compete with the latter. Actually b is still probably large enough, however, even in case A and for some distance beyond (in the direction away from case B), to keep the σ_g well above the π_g . In going *toward* case B and on beyond it, the energy of this σ_g should become very considerably higher.

Roughly speaking, the filled orbitals include all the bonding and nonbonding orbitals of (11), (12), (14), and (8), while the excited orbitals include the antibonding orbitals of (11), (12), and (14). This situation shows how it is that the sixteen-outer-electron linear molecules under consideration represent a particularly stable diamagnetic type with properties characteristic of closed-shell electronic structures (cf. the somewhat similar diatomic closed-shell molecules N_2 , CO, CN^- , NO^+).

It should be possible to arrange the various molecules under consideration in a series with respect to their relation to the cases A and B discussed above. In this way the differences in their outer-electronic structures can be expressed in terms of variations in the coefficients a , b , c , etc., of (11), (12), (14). It is not difficult to see that the series must run about as follows:



Here N_3^- , NO_2^+ , and CS_2 are probably near case A, with N_3^- somewhat to the left of it; CO_2 is probably well between cases A and B, BO_2^- is probably near case B, HgI_2 considerably to the right of B, with other salts MeX_2 , especially the fluorides, extending much farther to the right with RaF_2 probably the most extreme case.

Electron configurations for the normal states of typical molecules of the series (15) can now

be given (see (16a)). As already pointed out, these are all identical except for variations in relative values of a , b , and c in the orbitals used. Over the range covered by (15), however, these variations are large, and suffice to account for the change from molecules classed as double-bonded to those classed as single bonded homopolar and finally to single-bonded heteropolar.

In obtaining the orbital symbols used in the configurations (16a), the following procedure was used. In (11), (12), (14), the smallest of the three coefficients, which is usually small enough to be roughly negligible, was first dropped; or in extreme cases, all coefficients but one were dropped as negligible. Referring then to (9), (10), (13), the usual LCAO shorthand symbol, corresponding to the remaining non-negligible

coefficients, was written down for each orbital. In deciding which coefficients might properly be neglected, (15) was used. Naturally the results are not exact, but are intended to give a survey of the essential features of the electron configurations in the various cases. A more exact understanding can be obtained by referring back to (11), (12), (14). It should always be borne in mind, in any case, that even the rather complicated LCAO forms represented by (11), (12), (14) constitute only crude approximations to the real forms of the actual best molecular orbitals. Further, the molecular orbital symbols in (16a) and elsewhere, even though given in LCAO shorthand, should always be thought of as really referring fundamentally to the actual best molecular orbitals.³

$$\begin{aligned}
 \text{FMeF: } & (s+s, \sigma_\theta)^2 (s-s, \sigma_u)^2 (\sigma+s+\sigma, \sigma_\theta)^2 (\sigma-\sigma, \sigma_u)^2 (\pi+\pi, \pi_u)^4 (\pi-\pi, \pi_\theta)^4 \\
 \text{IMeI: } & (s+s, \sigma_\theta)^2 (s-s, \sigma_u)^2 (\sigma+s+\sigma, \sigma_\theta)^2 (\sigma+\sigma-\sigma, \sigma_u)^2 (\pi+\pi, \pi_u)^4 (\pi-\pi, \pi_\theta)^4 \\
 \text{OCO: } & (s+s+s, \sigma_\theta)^2 (s-s, \sigma_u)^2 (\sigma+s+\sigma, \sigma_\theta)^2 (\sigma+\sigma-\sigma, \sigma_u)^2 (\pi+\pi+\pi, \pi_u)^4 (\pi-\pi, \pi_\theta)^4 \\
 \text{(NNN)-: } & (s+s+s, \sigma_\theta)^2 (s+\sigma-s, \sigma_u)^2 (s-s+s, \sigma_\theta)^2 (\sigma+\sigma-\sigma, \sigma_u)^2 (\pi+\pi+\pi, \pi_u)^4 (\pi-\pi, \pi_\theta)^4 \\
 \text{ABA in general: } & \sigma_\theta^2 \sigma_u^2 \sigma_\theta^2 \sigma_u^2 \pi_u^4 \pi_\theta^4, \text{ with forms given by (9), (10), (13), (8).}
 \end{aligned} \tag{16a}$$

In all cases the resultant state is of course ${}^1\Sigma^+$. In every case, inner-shell electrons are omitted.

The excited molecular orbitals derivable from (7), (8) and included in (9)–(14) are

$$\begin{aligned}
 \text{MeF}_2: & (\sigma-s+\sigma, \sigma_\theta); \quad (np\sigma_u)_{\text{Me}}; \quad (np\pi_u)_{\text{Me}} \\
 \text{MeI}_2: & (\sigma-s+\sigma, \sigma_\theta); \quad (\sigma-\sigma-\sigma, \sigma_u); \quad (np\pi_u)_{\text{Me}} \\
 \text{CO}_2: & (\sigma-s+\sigma, \sigma_\theta); \quad (\sigma-\sigma-\sigma, \sigma_u); \quad (\pi-\pi+\pi, \pi_u) \\
 \text{N}_3^-: & (\sigma-s+\sigma, \sigma_\theta); \quad (\sigma-\sigma-\sigma, \sigma_u); \quad (\pi-\pi+\pi, \pi_u).
 \end{aligned} \tag{17}$$

In (16a) and (17), two sizes of type are used to indicate varying relative magnitudes of the coefficients with which the various atomic orbitals appear in each LCAO approximate molecular orbital. In estimating the relative sizes of the coefficients, allowance has been made for the factors 2^{-1} which appear in (9), (10), and (13). For instance, the N_3^- orbital written as $(s+s+s, \sigma_\theta)$ in (16a) is obtained by putting $a=b$ and neglecting c in (9),—cf. (11a). The resulting orbital is then approximately of the form

$$\alpha(\frac{1}{2}s_A + 2^{-1}s_B + \frac{1}{2}s_C),$$

so that s_B is considerably more prominent than s_A and s_C . In (16a) and (17), wherever just one atomic orbital symbol appears, it belongs to the

central atom B (cf. e.g., $np\pi_u$ in (17)). Where two symbols appear, they belong to the end atoms A and C (cf. e.g., $(s+s)$ for MeI_2 in (16)). Where three atomic symbols appear, they refer to atoms A, B, C in that order (cf. e.g., $(s+s+s)$ for N_3^- in (16a)).

Since those orbitals in (16a) which involve only the two end atoms A and C are really practically nonbonding, the approximation may be improved if these orbitals are replaced by corresponding atomic orbitals (cf. discussion of $(\pi-\pi)$ of CO_2 given in section 1 in connection with (1) and (1a)). [Exception: when bonding and corresponding antibonding shells of this type are both filled up, e.g., $(s+s)^2(s-s)^2$ of MeF_2 , MeI_2 , CO_2 , or $(\pi+\pi)^4(\pi-\pi)^4$ of MeF_2 or MeI_2 , in (16), then there is no real improvement in the

wave function on substituting atomic orbitals (cf. section 1). Nevertheless the use of the latter perhaps gives a somewhat clearer idea of the

nature of the electronic structure.] Making the changes indicated, we have instead of (16a) the following:

$$\begin{aligned} \text{MeF}_2: & 2s_F^2 2s_F^2 (\sigma + s + \sigma, \sigma_\sigma)^2 (2p\sigma_F 2p\sigma_F) 2p\pi_F^4 2p\pi_F^4 \\ \text{MeI}_2: & 5s_I^2 5s_I^2 (\sigma + s + \sigma, \sigma_\sigma)^2 (\sigma + \sigma - \sigma, \sigma_u)^2 5p\pi_I^4 5p\pi_I^4 \\ \text{CO}_2: & (s + s + s, \sigma_\sigma)^2 (2s_O 2s_O) (\sigma + s + \sigma, \sigma_\sigma)^2 (\sigma + \sigma - \sigma, \sigma_u)^2 (\pi + \pi + \pi, \pi_u)^4 (2p\pi_O^2 2p\pi_O^2) \\ \text{N}_3^-: & (s + s + s, \sigma_\sigma)^2 (s + \sigma - s, \sigma_u)^2 (s - s + s, \sigma_\sigma)^2 (\sigma + \sigma - \sigma, \sigma_u)^2 (\pi + \pi + \pi, \pi_u)^4 (2p\pi_N^2 2p\pi_N^2). \end{aligned} \quad (16)$$

In arriving at the configurations (16a) and (16), and in interpreting them in relation to ordinary valence theory, a knowledge of the distribution of charge between the three atoms A, B, C would be helpful. For this purpose it is sufficient to determine the net charge on atom B, which can be done if it can be ascertained how many of the sixteen outer electrons belong, on the average, to atom B. Aside from the inherent arbitrariness involved in trying to draw boundaries for "atom B" inside the molecule ABC, this can be done in a fairly sensible way, insofar as the LCAO approximation is valid (cf. XI of this series, section 7).

From a knowledge of the various coefficients a, b, c in (11), (12), (14), it is possible to compute how much of the charge $-2e$ of each electron-pair belongs, on the average, to atom B. By summing over the eight outer-electron pairs, and subtracting this sum from the number of outer (ns, np) electrons in the neutral atom B, the mean charge on atom B is obtained.

For one electron-pair, proceeding in analogy to Eq. (38) of XI, one writes

$$-2e = -2e \int (\phi_{ABC})^2 dv = -2e[a^2 + b^2 + c^2 + 2b(aS_{XB} + cS_{YB})],$$

where $S_{XB} = \int \phi_X H \phi_B dv$. The final result on the right of the equation is obtained after dropping a term $2ac \int \phi_X \phi_Y dv$ which should be negligibly small. [Note that ϕ_X is of the form $2^{-1}(s_A \pm s_C)$ and ϕ_Y is of the form $2^{-1}(s_A \pm s_C)$ or $2^{-1}(\pi_A + \pi_C)$; also note that $a=0$ in the case of π_u , cf. (14).] Of the total charge $-2e$, the portion

$$-q_B = -2e[b^2 + b(aS_{XB} + cS_{YB})] \quad (18)$$

may reasonably be allotted to atom B (cf. XI, section 7 just after Eq. (38)). Making use of the normalization condition implicit in the preceding

equation just given above, Eq. (18) can be reduced to

$$n_B = -q_B/e = (1 + b^2 - a^2 - c^2),$$

which will be seen to yield $q_B = -2e$, as it should, if $a=c=0, b=1$.

Now summing over the two σ_σ , two σ_u , and two π_u electron pairs (the two π_σ pairs have $q_B=0$), we have for the (average) number of outer electrons assignable to atom B,

$$N_B = \Sigma n_B = \Sigma(1 + b^2 - a^2 - c^2) = 6 + \Sigma(b^2 - a^2 - c^2), \quad (19)$$

the summation being taken over all the orbitals appearing in (16a), with coefficients a, b, c as in (11), (12), and (14), and with the π_u orbital taken twice. For the net (mean positive) charge Q_B on atom B, we have

$$Q_B/e = N^\circ_B - N_B, \quad (20)$$

where N°_B is the number of outer electrons on atom B in the free neutral state ($N^\circ_B = 5, 4, 3, 2$ for atoms N, C, B, Me, respectively).

The quantity N_B is of course expected to run more or less parallel to N°_B . Now it will be found on examination of (11), (12), (14) in connection with (19) that N_B decreases in the direction from case A to case B, i.e., from left to right in (15). For case A, we find, to the approximation that (11a) and (12a) with equality signs instead of near-equality signs \approx are correct,

$$N_B = 6 - c_1^2 - a_1'^2 + b_1'^2 - c_1'^2 - c_2^2 - a_2'^2. \quad (21)$$

In practice, this gives N_B somewhat less than 5. If there were no mixing at all between orbitals of the types ϕ_X and ϕ_Y , nor between σ_B and $(\sigma_A - \sigma_C)$, i.e., no $s-p\sigma$ hybridization, we would have $c_1 = b_1' = c_2 = a_2' = 0$ and $a_1' = 1$ in Eq. (21), which would hold exactly, and would then give $N_B = 5$.

For case B, N_B is clearly less than for case A. For a case so far to the right that it is a good approximation to put $a_1 = a_1' = c'' = 1$, $b_1 = c_1 = b_1' = c_1' = b_1'' = 0$, we get $N_B < 2$ (cf. MeI_2 , MeF_2 in (16)). For a case $N_B = 2$, it is clear that there would be considerable departures from the relations $a_1 = a_1' = c'' = 1$, $b_1 = c_1 = b_1' = c_1' = b_1'' = 0$.

The case $N_B = 4$, $Q_B = 0$ would evidently correspond to the usual chemical conception of an ideal homopolar double-bonded type $A=B=A$; $N_B = 2$, $Q_B = 0$ to an ideal homopolar single-bonded type $A-B-A$; and $N_B = 0$, $Q_B = +2$ to an ideal heteropolar type $A^+B^{++}A^-$. Actual molecules never conform exactly to these ideal cases. When approximate conformity exists, an approximately valid classification can be made in accordance with ordinary valence theory. In intermediate cases, which are rather common in practice, ordinary valence theory is somewhat at a loss, and arbitrary attempts are often made to force molecules into one of the simple ideal categories. In such cases, disputes have been frequent as to which ideal category is the proper one. It is, however, often but not yet universally realized now that the admission of intermediate or mixed cases affords the only correct way of settling such disputes (cf. especially Pauling's papers on "resonance" of molecules between different valence states).

The present method shows particularly clearly the "naturalness" of the intermediate cases and the relative improbability of the pure ideal cases. It also shows the possibility of a great variety of types of intermediacy, particularly when we consider molecules and ions ABC (see below) as well as ABA. We can illustrate here by a discussion of some of the important examples of the types ABA, as listed in (15) and described in (16) and (16a).

We may well begin with N_3^- , at the extreme left in (15). A structure $N^-=N^+=N^-$ is frequently assigned to this molecule. Such a structure would imply $Q_B/e = +1$, $N_B = 4$. As will be shown, however, $N_B = 5$ is in all probability much more nearly correct, so that $N^-=N^+=N^-$ is probably a very poor approximation to the real structure.

If (I) we knew the exact location of N_3^- in (15), the various a , b , c 's would be more or less

definitely determined, so that, using (19), N_B would be more or less definitely determined. On the other hand (II) if we knew N_B , this would suffice to determine approximately the relative term values of the three N atoms in N_3^- and so to locate N_3^- in (15). The two distinct conditions (I) and (II), taken jointly, evidently impose a condition of *self-consistency* on N_B . This is similar to the condition of self-consistency met in using the Hartree method for determining the forms of atomic or molecular orbitals.

In seeking to determine the true value of N_B for N_3^- , we may proceed by a trial and error or variation method until consistency is obtained as regards conditions (I) and (II). As an initial trial assumption, let us suppose that N_3^- in (15) comes just at case A, and let us first apply condition (I). N_B is then given, very nearly, by Eq. (21). Although an exact result cannot be obtained without calculation, a survey of the coefficients a , b , c in Eq. (21) shows that N_B is somewhat less than 5, but in all probability nearer 5 than 4. The value $N_B = 5$ represents approximately an upper limit, which would hold for the case of no mixing of $(s+s)$ with $(\sigma+\sigma)$ nor of $(s-s)$ or σ_B with $(\sigma-\sigma)$; for this case, $c_1 = b_1' = c_1' = c_2 = a_2' = 0$ and $a_1' = 1$, giving $N_B = 5$. Since there is actually some mixing, we see that $N_B < 5$.

But now if $N_B < 5$, it is easily shown, on applying condition (II), that N_3^- cannot belong to case A, but must lie rather far to the left of A in (15), thus contradicting our initial trial assumption. The proof that, if $N_B < 5$, N_3^- must be to the left of case A in (15), is as follows. Suppose we had $N_B = 5\frac{1}{3}$ (equal distribution of charge among the three N atoms, which may be formulated $N^{-1}N^{-1}N^{-1}$). In this case, roughly, one might expect corresponding term values of the three atoms to be equal, fulfilling case A. More accurately, however, N_3^- would fall to the left of case A in (15) for $N_B = 5\frac{1}{3}$, since for a given orbital, an electron of the central atom B surely would move on the average in regions of lower potential than for the same orbital in one of the outer two atoms; thus B would have somewhat higher term values than the other atoms, so placing the molecule to the left of case A. Now for $N_B < 5$, the term values of atom B would be still further increased, placing N_3^- still further

to the left of case A in (15). Hence our initial trial assumption of case A for N_3^- is not consistent with itself, since by (I) it requires an N_B which by (II) would put N_3^- far to the left of case A.

Hence our initial assumption must be altered considerably, and it is readily seen that, to get self-consistency, N_3^- must actually be located well to the left of case A in (15) and N_B must be considerably greater than is given by the relation $N_B < 5$ required by case A. While the exact value of N_B cannot be determined by this qualitative argument, it becomes very probable that it is in the neighborhood of 5, quite possibly even somewhat greater than 5, and practically certainly much greater than 4. The charge distribution then corresponds in all probability not to $N^+N^+N^-$, but probably much more nearly to N^+NN^- or possibly even $N^+N^+N^-$. [The whole argument is subject of course to some uncertainty insofar as it depends on the use of LCAO forms for molecular orbitals; but it at least tends to cast very grave doubt on the formulation $N^+ = N^+ = N^-$.]

The structure thus indicated for N_3^- is one which cannot very well be described by an ordinary chemical formula, at least by no single formula; it is a highly intermediate case. Nevertheless, on examination of (16) and (16a), one sees that the internal electronic structure of N_3^- is very similar to that of CO_2 , having, in particular, similar bonding electrons. It is also readily seen that NO_2^+ and CS_2 should be intermediate in these respects between N_3^- and CO_2 (cf. (15)).

In comparing the configurations of N_3^- and CO_2 , the most noticeable difference is that there is a partial shift of bonding power from lower- to higher-energy σ orbitals in going from N_3^- to CO_2 . In N_3^- the lowest σ_g is strongly bonding, the second one probably mildly antibonding; in CO_2 the first σ_g is weakly bonding, the second strongly bonding; the net total bonding power of the two σ_g may, however, be somewhat the same in the two molecules. In N_3^- the lowest σ_u is weakly bonding, the second one moderately bonding; in CO_2 the lowest σ_u is probably nearly nonbonding, the second one strongly bonding, but the total bonding power of the two σ_u may be somewhat the same in the two molecules.

For the π_u orbitals, we have $b_1'' = c_1''$, nearly, in N_3^- , but $c_1'' > b_1''$ in CO_2 (cf. (14)). This tends to make the π_u homopolar bonding stronger in N_3^- than in CO_2 . Similar differences exist also in the σ orbitals.

In the various molecules N_3^- , NO_2^+ , CS_2 , CO_2 , the bonding may be described as partially heteropolar, partially homopolar, the homopolar part then being described as double-bonded, single-bonded, or some mixture. In CO_2 , for instance, it was estimated in section 1 that the charge distribution within the molecule is roughly $O^{-1}C^{+1}O^{-1}$, i.e., $Q_B/e = +1$, or $N_B = 3$. In terms of ordinary chemical bonds, this would correspond to a condition about half-way between $O=C=O$ (neutral atoms, two covalent double bonds) and $O^--C^{++}-O^-$ (two covalent single bonds, and two ionic bonds like those in $F^-Ba^{++}F^-$). Or one might say that there are two, approximately half polar, double bonds.

In the present method the amount of heteropolar bonding may be judged from the estimated Q_B values, while the amount of homopolar bonding may be qualitatively read out of the signs and magnitudes of the LCAO coefficients a, b, c involved in the molecular orbitals in (16a) or (16). In the present method, there is no very definite way in general of expressing the number of chemical bonds, as ordinarily assigned, in terms of *numbers of bonding electrons*. In simple cases, as was pointed out by Herzberg for homopolar diatomic molecules, the number of ordinary chemical bonds is equal to the number of pairs of (strongly) bonding electrons minus the number of pairs of (strongly) antibonding electrons. Roughly, we can say (cf. (16a), (16)) that there are four pairs of bonding electrons in the molecules CO_2 , CS_2 , NO_2^+ , N_3^- ; this would agree with ordinary chemical ideas. More accurately, however, it will be seen that the total bonding power is not precisely confined to just eight bonding electrons, but spreads more or less over the other electrons. Strictly speaking, some bonding power (positive or negative) must be attributed to all the electrons, as was pointed out for diatomic molecules in the writer's 1928 paper on the use of electron configurations built from molecular orbitals.

In the present case, it will be seen from the comparison of N_3^- and CO_2 orbitals given above

that eight σ and four π_u electrons participate more or less actively in the bonding, although the total bonding effect is about the same as if only four σ and the four π_u electrons participated strongly, so that we may speak with reasonable justification of the presence of two double bonds. Intermediate cases often arise, however, where it becomes purely arbitrary to decide how many bonding electron pairs there are which are *strongly enough* bonding to be counted as chemical bonds. Since bonding power can vary continuously, no sharp line can be drawn between bonding and nonbonding electrons. As will be seen from (16a) and (16), the bonding power of the two pairs of π_u electrons, which entitles them to be called bonding electrons in CS_2 or CO_2 , becomes small enough to be neglected in HgCl_2 or MeX_2 , so that "double bonds" in CO_2 fade into "single bonds" in HgCl_2 .

An interesting intermediate case should exist in BO_2^- . One might seek to formulate this chemically either as $\text{O}=\text{B}^-=\text{O}$ like $\text{O}=\text{C}=\text{O}$, with four bonding electron pairs, or as $\text{O}^--\text{B}^+-\text{O}^-$ like $\text{Cl}-\text{Hg}-\text{Cl}$, with two bonding electron pairs. Probably the second is the more nearly correct, but a better answer is that we have an intermediate case. BO_2^- can be interpolated between CO_2 and MeI_2 in (15) and (16a). Clearly there are two strongly bonding electron pairs (one σ_g , one σ_u , as in CO_2 and MeI_2) which correspond to the two bonds of the formulation $\text{O}^--\text{B}^+-\text{O}^-$. In addition, there can be no doubt that the four π_u electrons have an amount of bonding power which is not negligible, although surely much smaller than for the π_u electrons in CO_2 , CS_2 , or N_3^- . Thus the two π_u electron pairs are intermediate in character between bonding and nonbonding, although here probably somewhat nearer the latter, if such a description makes sense. They represent the second bonds of two double bonds which are here well on the way toward becoming single bonds.

Digressing for a moment from the discussion of the series of cases in (15), reference may be made to the interpretation of the observed ionization potential I of CS_2 in relation to electron configurations (16), (16a). The observed I is 10.4 ± 0.2 volts by electron-impact methods,¹⁸

¹⁸ H. D. Smyth and J. P. Blewett, *Phys. Rev.* **46**, 276 (1934). W. C. Price, unpublished work, kindly communicated to the writer.

while a value of 10.1 volts from Rydberg absorption series is given by Price.¹⁸ These values are in reasonable agreement with the predicted I , i.e., $I^*(3p\pi)$ of the S atom, which has the value 11.13 volts. The fact that the observed I is somewhat less than the predicted suggests the presence of some net negative charge⁷ on the S atoms. This would be contradictory to the fact that sulfur is slightly less electronegative than carbon on Pauling's scale; however, the scale was developed only for single bonds and may not hold very well for double bonds.

Turning to $(\text{NNN})^-$, it will be noted that the minimum I (belonging to the $2p\pi_N$ orbital, according to (16)) represents the *electron affinity* of linear N_3 . It can be estimated that this electron affinity is fairly large,—comparable with that of CN or Cl,—since the structure of N_3^- consists of a set of very stable closed shells rather like those of CN^- , which resembles Cl^- .

The molecules MeX_2 (e.g., BeF_2 , CaF_2 , CaBr_2 , HgF_2 , HgI_2) are of course very different from the others in (16), being intermediate between $\text{X}^-\text{Me}^+\text{X}^-$ and $\text{X}-\text{Me}-\text{X}$ in character, with hardly any tendency toward $\text{X}^+=\text{Me}^-=\text{X}^+$. A linear structure is fairly well assured for most if not all these molecules in the vapor state. In the most nearly homopolar types HgX_2 , this is evident from the zero dipole moment.^{1a} In the more heteropolar types it is to be expected because of the electrostatic repulsion between the two X^- ions, taking into account also the absence of any considerable polarizability of the central Me^{++} ion which might make possible (cf. H_2O) a triangular form.

The electron configurations of these molecules are then describable as in (16a) or as in (16). The formulations (16a) show that the structures may be regarded as formally like those of CO_2 and the other $\text{A}=\text{B}=\text{C}$ types. However, the π_u orbitals which give two of the homopolar bonds in the latter now lose nearly all homopolar bonding power because $n p \pi$ of X is so much more electronegative than $n p \pi$ of Me. Hence ($n p \pi - n p \pi$, π_u) of $\text{X}+\text{X}$ and $n p \pi_u$ of Me occur nearly unmixed, the former in (16a), the latter as an excited orbital in (17). In MeF_2 a similar situation exists also for the σ_u orbitals, where nearly unmixed ($n p \sigma - n p \sigma$, σ_u) of $\text{F}+\text{F}$ occurs in (16a) and $m p \sigma_u$ of Me in (17). In MeI_2 , how-

ever (except for the most electropositive Me atoms like Ca), it appears very probable that the σ_u in (16a) gives rather strong I—Me—I homopolar bonding, and so should be formulated ($\sigma + \sigma - \sigma, \sigma_u$).

The foregoing conclusions are based on considerations of relative electronegativity and of overlapping. By using the writer's electroaffinity scale (M scale),⁵ estimates of M values have here been made for the $2s$ and $2p$ orbitals of Be and the $6s$, $6p$ orbitals of Hg. The difference in M between iodine ($5p$) and np of Be (about 1.92) or of Hg (about 2.12) is found to be about the same as the difference (2.05) between F ($2p$) and H ($1s$), so that, with comparable overlapping, the degree of homopolar bonding might be comparable. Now in HF the bonding orbital, which in LCAO approximation is $a(2p\sigma_F) + b(1s_H)$, has b/a very considerably less than 1, but large enough to correspond to a very considerable amount of homopolar bonding. A somewhat similar relation may then reasonably be expected for the σ_u orbitals of MeI₂, given in LCAO approximation essentially by

$$2^{-1/2}c_2'(5p\sigma_1) + b_2'(mp\sigma_{Me}) - 2^{-1/2}c_2'(5p\sigma_1),$$

since there should be strong overlapping of $(mp\sigma_u)_{Me}$ with each $5p\sigma_1$. For the π_u orbitals of MeI₂ in (16a), however, the overlapping is so much less, hence H_{AB} so much less,⁵ that the ratio b_2'/c_2' is probably negligibly small.⁵ In MeF₂, the electronegativity difference between fluorine ($2p$) and mp_{Me} is much larger than between iodine ($5p$) and mp_{Me} , so that the ratios b/c are probably negligible even for σ_u and certainly for π_u . Various intermediate cases should occur for molecules MeCl₂ and MeBr₂, although both of these types (in agreement with experimental data) should resemble the iodides more closely than the fluorides.

In the case of the σ_g orbital in (16a) which is built up in LCAO approximation mainly from ms_{Me} and $np\sigma_X$, there can be no doubt that there is a considerable X—Me—X homopolar bonding except perhaps in the most extreme heteropolar cases like CaF₂. In the least heteropolar case (probably HgI₂), the ratio b_2/c_2 in

$$[2^{-1/2}c_2(5p\sigma_1) + b_2(6s)_{Hg} + 2^{-1/2}c_2(5p\sigma_1)], \sigma_g$$

is probably close to unity, since the s (i.e., $6s$) electroaffinity of Hg is estimated to be $M = +0.19$, nearly the same as the ($5p$) electroaffinity $M = +0.41$ of iodine.

Summarizing, we find for the molecules MeX₂ a range of types from the most nearly heteropolar cases like CaF₂ in which one σ_g pair of electrons gives a little homopolar bonding, to the most nearly homopolar cases like HgI₂ where the σ_g pair gives essentially homopolar bonding while a second, σ_u , pair gives bonding which is partially (perhaps half) homopolar. The net total bonding may be described as perhaps nearly pure heteropolar in the one extreme and perhaps about three-fourths homopolar in the other. (The meaning of the present discussion will be made clearer by comparison with the more detailed considerations concerning molecules MA₂ in XII of this series.) The present discussion illustrates well the possibility in the present method of describing the electronic structures of molecules of varying polarity from a single standpoint in a way which is hardly possible in terms of ordinary chemical valence concepts.

The descriptions (16) and excited orbitals (17) should be of value in interpreting the electronic bands of molecules MeX₂, which are especially well known in the case of the HgX₂ absorption spectra.^{1a} This subject will not be entered upon here. Mention may be made, however, of the observed electron-impact ionization potentials^{1a} of ZnCl₂ (12.9 volts) and HgCl₂ (12.1 volts). According to (16), modified to fit MeCl₂, each of these observed potentials should correspond to removal of a nonbonding $3p\pi_{Cl}$ electron from the molecule. The predicted I for this process, according to VIII of this series,⁷ is <13.62 volts, the inequality sign representing 1 or 2 volts and corresponding to the effect of the net negative charge on the Cl atoms. The observed potentials for HgCl₂ and ZnCl₂, especially the former, are in excellent agreement with this prediction. The higher value for ZnCl₂ than for HgCl₂ is very likely due to experimental error: since the net negative charge on the Cl atoms should be larger in ZnCl₂ than in HgCl₂, the I ought to be somewhat less.

The structures and low excited orbitals of molecules MeH₂ should be essentially similar to those of MeI₂ in (16) and (17) if one omits all

ns_X and $np\pi_X$ electrons from (16) and (17), and replaces $\pm np\sigma_X$ by $1s_H$ in the LCAO forms. The normal state of BeH_2 has already been formulated in V of this series,⁴ Table I.

5. UNSYMMETRICAL LINEAR MOLECULES ABC

In the unsymmetrical molecules NNO , OCS , $(\text{NCO})^-$, $(\text{NCS})^-$, also NCCl , OBCl , etc., the σ_u classification of the states and orbitals is lost and as a result the LCAO forms become less simple. Roughly speaking, the configurations are like (16) or (16a) but with mixing between σ types corresponding to σ_u , σ_g and again between π types corresponding to π_u , π_g of (16a). Or in other words, instead of having four distinct and

relatively simple secular problems as in (7), (8), we have two more complicated problems, one for the six σ molecular orbitals, one for the 3×2 π orbitals. Under these circumstances, a qualitative treatment becomes more difficult than before. Somewhat helpful in the case of NNO is the fact that it forms a sort of mean between $(\text{ONO})^+$ and $(\text{NNN})^-$, which are both rather near to but on opposite sides of case A (cf. (15)). Similarly, OCS is a sort of mean between OCO and SCS ; and CIBO between OCO and ClBeCl .

The following represents a very tentative description of the electron configuration of N_2O using molecular orbitals for the sixteen outer electrons:

$$(s+s+s, \sigma)^2(s+\sigma-s, \sigma)^2(s-s+s, \sigma)^2(\sigma+\sigma-\sigma, \sigma)^2(\pi+\pi+\pi, \pi)^4(\pi+\pi-\pi, \pi)^4, \quad {}^1\Sigma^+ \quad (22a)$$

$$\text{N}-\text{N}-\text{O} \quad \text{N}-\text{N} \leftrightarrow \text{O} \quad \text{N} \leftrightarrow \text{N} \leftrightarrow \text{O} \quad \text{N}-\text{N}-\text{O} \quad \text{N}-\text{N}-\text{O} \quad \text{N}-\text{N} \leftrightarrow \text{O}.$$

Here bonding and antibonding effects between atoms are indicated by $-$ and \leftrightarrow , respectively; the antibonding effects in (22a) are probably all relatively weak. In each LCAO molecular orbital, the coefficients of the three atomic orbitals used are more or less unequal, as roughly indicated by the sizes of the type used. The minimum I should be that of the very likely nearly non-bonding orbital denoted $(\pi+\pi-\pi)$. The I of $(\pi+\pi-\pi)$ may reasonably be compared with $I^*(2p\pi)$ of N or O, probably more nearly of N. The observed I of N_2O is given as about 12.9 volts (electron-impact¹⁹), which may be compared with $I^*=12.7$ or 15.23 volts for $2p\pi$ of N or O.

The structure of N_2O (cf. discussion of N_3^- in section 3) is probably not very close to $\text{N}^-=\text{N}^+=\text{O}$, but may be intermediate between this and

various other structures such as $\text{N} \equiv \text{N}^+-\text{O}^-$, $-\text{N}=\text{N}-\text{O}-$, etc.^{19a}

The structures of OCS , OCN^- , and SCN^- are doubtless intermediate between the structures $\text{O}=\text{C}=\text{S}$, $\text{O}=\text{C}=\text{N}^-$, $\text{S}=\text{C}=\text{N}^-$ and other structures analogous to those just mentioned for N_2O . Especially for SCN^- , there might be a considerable tendency toward $\text{S}^--\text{C} \equiv \text{N}$, but chemical evidence, and the fact that normally N is considerably more electronegative than S, indicate that this tendency is not predominant. The linear molecule NCCl , however, although isoelectronic with NCS^- , doubtless has a structure which is predominantly $\text{N} \equiv \text{C}-\text{Cl}$, but with appreciable tendencies toward $\text{N}^-=\text{C}=\text{Cl}^+$.

If the structure of CNCl is predominantly $\text{C} \equiv \text{N}-\text{Cl}$, it might be described tentatively more or less as follows:

$$(s_{\text{Cl}}, \sigma)^2(s_{\text{N}}+s_{\text{C}}, \sigma)^2(s_{\text{C}}-s_{\text{N}}, \sigma)^2(\sigma_{\text{Cl}}+\sigma_{\text{C}}, \sigma)^2(\pi_{\text{N}}+\pi_{\text{C}}, \pi)^4(\pi_{\text{Cl}})^4, \quad {}^1\Sigma^+. \quad (23)$$

Here we have more or less arbitrarily used orbitals localized within the Cl atom and the CN radical. Only one orbital, $(\sigma_{\text{Cl}}+\sigma_{\text{C}})$, has been used to represent bonding between the Cl and the CN. Such localization is, at least to a large extent, allowable in the sense that the corre-

sponding wave function should represent a good approximation.

The relation of (23) to (22a) and others in this paper is made clearer by giving up this localization and using whole-molecule orbitals; it can be shown that the corresponding wave function is

¹⁹ H. D. Smyth and E. C. G. Stueckelberg, Phys. Rev. **36**, 478 (1930).

^{19a} L. Pauling, Proc. Nat. Acad. Sci. **18**, 498 (1932) considers that the structure of N_2O is a mixture of $\text{N}^-=\text{N}^+=\text{O}$ and $\text{N} \equiv \text{O}^-$.

not very much altered thereby. We then have, very tentatively,

$$(s+s+s, \sigma)^2(s+s-s, \sigma)^2(s-s+s, \sigma)^2(\sigma+\sigma-\sigma, \sigma)^2(\pi+\pi+\pi, \pi)^4(\pi-\pi-\pi, \pi)^4, \quad {}^1\Sigma^+. \quad (24)$$

$$\text{Cl}-\text{C}\equiv\text{N} \quad \text{Cl}-\text{C}\leftrightarrow\text{N} \quad \text{Cl}\leftrightarrow\text{C}\leftrightarrow\text{N} \quad \text{Cl}-\text{C}-\text{N} \quad \text{Cl}-\text{C}-\text{N} \quad \text{Cl}\leftrightarrow\text{C}-\text{N}$$

The formulas (23) and (24), although very tentative, illustrate the possibility of getting a net bonding effect equivalent to the structure $\text{Cl}-\text{C}\equiv\text{N}$, even though using an electron configuration which, if the LCAO coefficients were properly readjusted, would correspond to $\text{Cl}^+ \equiv \text{C} = \text{N}^-$. This is another illustration (cf. the cases of BO_2^- and MeX_2 in section 3) of how formal analogies of chemically quite dissimilar molecules are revealed by the present method, and of how molecules belonging to types intermediate between the orthodox chemical bond types can be simply described and understood.

Another interesting case is that of BOCl . According to ordinary valence theory, this would have a structure intermediate between the homopolar form $\text{O}=\text{B}-\text{Cl}$ and the heteropolar form $\text{O}=\text{B}^{++}\text{Cl}^-$ or perhaps $\text{O}^--\text{B}^{++}\text{Cl}^-$. According to the present method, the structure would be similar to that of CNCl as given by (23) or (24). [It will be recalled that the electronic structure and low excited levels of BO according to the present method are very similar to those of CN .] The LCAO coefficients would, however, be considerably altered, in such a way as to give, on the whole, increased weight to the O and decreased weight to the B atom, as compared with the respective corresponding atoms N and C in NCCl .

In the molecules SCN^- and OCN^- , like NNN^- , the electron affinity should be fairly large (cf. CN^-), since the electron removed is from a stable group of closed shells. It would appear also from the foregoing electron configurations that each of the free radicals SCN , OCN , and NNN should be a fairly stable physical structure, rather like CN , and like the latter should have some low energy x-ray-like excited states obtained by shifting the missing electron from one to another of the orbitals in (16a) or (22a). Another similar radical would be OBO .

6. NO_2 AND OTHER MOLECULES. ULTRAVIOLET ABSORPTION OF CO_2 , COS , CS_2 AND N_2O

In the various molecules $\text{A}=\text{B}=\text{C}$ just considered, the electronic structure of the normal

state consists in a set of firmly bound closed shells of electrons, giving a chemically saturated structure. The orbitals represented are of two kinds (a) types which give strong bonding between the central atom B and one or both of the two outer atoms; (b) types which are essentially nonbonding. No types with pronounced net antibonding properties are present, or at most one, of high I . This situation is closely similar to that which is met in the diatomic molecules N_2 , CO , CN^- , NO^+ , etc. The situation is evidently responsible for the resemblance of the neutral molecules of these various types (N_2 , CO , CO_2 , N_2O) to rare gases (most closely to argon), and of the negative and positive ions to atom-ions with rare gas shells (most closely to Cl^- and perhaps K^+).

Our knowledge of these types forms an interesting point of departure for the study of other molecular types having more or fewer electrons. Types having one less electron are physically stable but chemically unsaturated free radicals (CN , BO , OCN , SCN , NNN) or positive ions (N_2^+ , CO^+ , CO_2^+ , N_2O^+ , etc.) possessing various low energy electron levels permitting the ready occurrence of easily observable band spectra. Types with two less electrons, e.g., C_2 , also occur and give band spectra.

Types having one or more additional electrons form a quite different class of molecules (NO , NO_2 , OO_2 or SO_2 , ClO_2 , etc.) or ions (O_2^+ , SO_2^+ , etc.). The case of NO is typical for the diatomic examples. Since all the available low energy bonding (and nonbonding) orbitals are filled up with NO^+ , the last electron has to go into a strongly antibonding and relatively high energy orbital.²⁰

Now it appears very probable that an analogous situation exists in linear NO_2 . Linear NO_2^+ is a stable closed-shell arrangement like CO_2 (cf. (16)), but if another electron is added, the lowest energy available orbital is of one of the three types given by (17). From their forms, it is evident that these give an antibonding action between the central atom and the two outer

²⁰ Cf. R. S. Mulliken, *Rev. Mod. Phys.* **4**, 1 (1932).

atoms. Moreover, what is more important, it is probable that these three orbitals of (17) are all of high energy. This is immediately evident in the cases of σ_u and π_u of (17), but in the case of σ_g of (17),—cf. second paragraph preceding (15),—it is less clear. We may, however, reasonably postulate that the σ_g of (17) is of at least moderately high energy for linear NO_2 . Empirical evidence in support of this postulate is to be found in the absence of evidence for low energy excited electron levels in CO_2 , COS , and CS_2 (see below).

Now NO_2 differs from NO in that it has a means of avoiding acceptance for its last electron of a loosely bound antibonding orbital; namely, by an alteration in the shape of the molecule, the forms, energies, and properties of the various orbitals of (16) and (17) may be radically altered. From the fact that NO_2 is empirically known to have a triangular shape, we may fairly safely conclude empirically that the high energy of the last electron of linear NO_2 is actually lowered, and more than enough to make up for any net increase in the energies of the other electrons, when the molecule takes on a triangular form. The observed minimum ionization potential I_{\min} of NO_2 (11 volts)^{1a} presumably corresponds to removal of an electron from what would be the σ_g orbital of (17) if NO_2 were linear. It will be noted that this I , in spite of the fact that it is presumably considerably larger, according to the foregoing argument, than if NO_2 were linear, is still about 3 volts less than I_{\min} of CO_2 .

Similar considerations apply to O_3 , SO_2 , ClO_2 , and others. A detailed consideration, showing how the observed spectra and other properties of such molecules, including NO_2 , can be understood along these lines, will be reserved for another paper.

We may next consider the ultraviolet absorption spectra of CO_2 and CS_2 . Experimentally,²¹ CO_2 is practically transparent to below $\lambda 1800$, and shows a very weak system of red-degraded bands from about $\lambda 1712$. The maximum intensity for this system is near $\lambda 1600$ or below. At shorter wave-lengths, other stronger band systems occur.¹⁰ Very roughly, we may take $\lambda 1600$ or even less as corresponding to the

vertical excitation energy of the first CO_2 absorption system. This then amounts to about 8 volts. Subtracting from the observed I of CO_2 (about 14 volts), we get about 6 volts, or perhaps less, as the I of the excited orbital involved.

This may be identified with one of the three orbitals σ_g , σ_u , π_u of (17). Since the electron excited surely comes out of π_g of (1), the transition is then from (1) to one or more of the states

$$(\pi_g)^{-1}\sigma_g, {}^1, {}^3\Pi_g \text{ or } (\pi_g)^{-1}(\sigma_u), {}^1, {}^3\Pi_u \\ \text{or } (\pi_g)^{-1}(\pi_u), {}^1, {}^3\Sigma^+_{u, \Sigma}{}^-, \Delta_u. \quad (25)$$

Although theoretical considerations indicate (cf. second paragraph preceding (15)) that the ${}^1, {}^3\Pi_g$ should be lowest in energy of the states of (25), identification of the ${}^1\Pi_g$ as the upper level of the observed bands is rendered somewhat doubtful by the fact that transitions from the normal state to it are forbidden by the electronic selection rules for symmetry $D_{\infty d}$ (linear molecule). Low intensity violations of these rules are possible,²² however, if suitable allowed transitions occur in the neighborhood, as seems to be the case here (occurrence of stronger bands at shorter wave-lengths). Another factor which might help here in allowing otherwise forbidden bands to occur weakly is that the equilibrium form of the molecule in the upper level of the observed bands might be triangular. For since a triangular form minimizes the energy of NO_2 , the same might well be true of the excited states of CO_2 given by (25). Although the Franck-Condon principle would still preclude the occurrence of any *strong* transitions violating the selection rules characteristic of the symmetry $D_{\infty d}$ of the initial state, nevertheless *weak* transitions could occur if allowed, as would be true in the present case, by the selection rules for a triangular molecule (symmetry C_{2v}). On the whole, it seems very likely that the observed weak system of bands with which the CO_2 absorption begins does represent transitions to the $(\pi_g)^{-1}\sigma_g, {}^1\Pi_g$ state (accompanied by much fainter transitions to the ${}^3\Pi_g$). This would make I about 6 volts for the σ_g excited orbital in CO_2 . In case, however, the observed bands involve a π_u or σ_u excited orbital, then the I of σ_g may be less or greater than 6 volts. the former is unlikely, while the latter

²¹ S. W. Leifson, *Astrophys. J.* **63**, 73 (1926).

²² G. Herzberg and E. Teller, *Zeits. f. physik. Chemie* **B21**, 410 (1933); cf. also discussion in reference 1.

(i.e., $I > 6$ volts) would be possible only in case the electronic selection rules operate so rigorously that transitions to the ${}^1\Pi_g$ of (25) have an intensity too weak to have been observed. Further work will be needed to clear up this question with certainty, but it seems fairly probable, especially in view of the evidence from CS_2 and COS now to be presented, that the result $I \approx 6$ volts for the excited σ_g is correct.

The first, moderately intense, electronic absorption band system²³ of CS_2 , occurring at $\lambda\lambda 2900\text{--}3800$, with maximum intensity near $\lambda 3200$ (3.9 volts), shows a large number of more or less sharp bands. Some of these are reported by Jenkins to show indications of having a simple structure like that for a linear molecule. The complicated and irregular arrangement of the bands, however, suggests that the equilibrium form of the molecule may be triangular for the upper electron level; but without more complete analysis, this must be considered uncertain. The vertical I of the excited orbital involved in the CS_2 bands is found to be about $10.2 - 3.9 = 6.3$ volts, nearly the same as for the lowest excited orbital in CO_2 .

In seeking to determine the nature of the excited orbital involved in the CS_2 bands, we have the same kinds of possibilities as in CO_2 . As compared with CO_2 , however, the bands are apparently more intense, also they are apparently more widely separated from the next ultraviolet system, so that it is rather hard to believe that they can represent a transition forbidden by the selection rules of $D_{\infty d}$, unless it be that the equilibrium form of the molecule in the upper electron level is triangular. It should be noted that the I of the excited orbital here in CS_2 ,

although nearly the same as that from the first bands of CO_2 , is *relatively* considerably higher than in CO_2 . In CO_2 , $I \approx 6$ volts for the excited orbital, about 14 for the π_g , giving a ratio of $6/14 = 0.43$; in CS_2 , $I \approx 6.3$ volts for the excited orbital, about 10.2 for the π_g , giving a ratio of 0.62, much higher than in CO_2 . This behavior is what would be expected if the excited orbital is σ_g (cf. second paragraph preceding (15)), but is not so readily explained if it is σ_u or π_u . On the whole, considering also the evidence from COS given below, it appears rather probable that the excited orbital involved in the CS_2 bands near $\lambda 3200$ is the σ_g orbital.

The absorption spectrum of COS is continuous,²⁴ beginning near $\lambda 2550$. The absence of longer wave-length absorption indicates that the three excited orbitals analogous to those in (17) here definitely are all of high energy, since in COS there is no g, u electronic selection rule to restrain transitions to any of the three. This result for COS leaves little doubt that the three excited orbitals (17) are all of fairly high energy also in CO_2 and CS_2 , and probably in NO_2 , thus furnishing a reasonable basis for the explanation given above for the instability of linear NO_2 . To be sure, the excited σ_g (probably; or possibly it is the π_u or σ_u) is only 3.9 volts above the π_g in CS_2 , and may be no higher in NO_2 (cf. second paragraph preceding (15)), so that it would seem that the instability of linear NO_2 relative to triangular NO_2 may be not so very pronounced.

The electronic absorption spectrum of N_2O begins with continuous absorption near $\lambda 2000$.^{21, 25} Taking into consideration the probably somewhat lower $I_{\min.}$ for N_2O than for CO_2 ,¹⁹ this indicates that the lowest excited orbital has an I about the same as in the case of CO_2 .

²³ E. D. Wilson, *Astrophys. J.* **69**, 34 (1929); F. A. Jenkins, *Astrophys. J.* **70**, 191 (1929); V. Henri, *Leipziger Vorträge*, 1931; W. W. Watson and A. E. Parker, *Phys. Rev.* **37**, 1013A (1931); R. K. Asundi and R. Samuel, *Proc. Acad. Sci. U.P., India* **4**, 203 (1934).

²⁴ W. Lochte-Holtgreven and C. E. H. Baun, *Trans. Faraday Soc.* **28**, 698 (1932).

²⁵ G. Herzberg, *Zeits. f. physik. Chemie* **B17**, 68 (1932); CO_2 and N_2O , including a discussion of dissociation products and predissociation. O. R. Wulf and E. H. Melvin, *Phys. Rev.* **39**, 180 (1932); N_2O absorption.