467. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part II.* Non-hydride AB_2 and BAC Molecules.*

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A correlation diagram is plotted for the orbitals of linear and non-linear triatomic molecules. Simple reasons are given why particular orbitals become more or less tightly bound as the apex angle changes. The diagram is used to interpret and predict the shapes, reactivities, and spectra of non-hydride triatomic molecules. As regards the shapes, the following facts (most of which have been recognised for some time) become understandable : that molecules with not more than 16 valency electrons are linear in their ground states; that molecules with 17, 18, 19, or 20 valency electrons are bent in their ground states, the apex angle decreasing markedly from 16- to 17- and from 17- to 18-electron molecules and less markedly from 18- to 19- and from 19- to 20-electron molecules; and that 22-electron molecules are linear or nearly linear in their ground states. The paper has much in common with an earlier paper by Mulliken.

THE purpose of this paper is to apply to AB_2 and BAC molecules the procedure which in Part I * was applied to AH_2 molecules. We consider first symmetrical, non-hydride, triatomic molecules AB_2.

AB_2 *Molecules.*—The lowest-energy orbitals of a linear AB_2 molecule may, on the assumption that they are built solely from s and p atomic orbitals, be described as follows : (i) Two lone-pair s orbitals, one on each B atom. (ii) Two bond orbitals analogous to the bond orbitals discussed in Part I. For discussion of molecular shape, they may be thought of as built from sp hybrid valencies of A plus $p\sigma$ valencies of the two B atoms and largely localized one to each A–B distance. In discussion of spectroscopic transitions involving them, they would have to be regarded as non-localized combinations of the localized orbitals and be labelled σ_g and σ_u. (For simplicity, hybridization of the s and the p valencies of the B atoms is here neglected. It is unlikely that its inclusion would alter the general form of the correlation diagram plotted in the Figure. A similar comment applies to later papers of this series.) (iii) A π_u orbital built by the in-phase overlap of a $p\pi$ atomic orbital on each of the three atoms. It will be bonding and two-fold degenerate. (iv) A π_g orbital built by the out-of-phase overlap of a $p\pi$ atomic orbital on each of the B atoms. It has zero amplitude at the central atom, being localized entirely on the B atoms. It is two-fold degenerate, weakly B⟵⟶B anti-bonding and A⟵⟶B non-bonding. (v) A $\bar{\pi}_u$ orbital built by the in-phase overlap of a $p\pi$ atomic orbital on each of the B atoms,

these overlapping out-of-phase with a $p\pi$ orbital on the central atom. It is two-fold degenerate, B⟷B bonding and A⟷B anti-bonding. A bar is placed over the symbol to indicate the A⟷B anti-bonding nature.

The π_u orbitals are both built from atomic orbitals on each of the three atoms. Nevertheless they will be partly localized in a way that may be deduced as follows. The sharing of an electron between two atomic orbitals is only likely when those two atomic orbitals have equal, or almost equal, binding energy. If the two atomic orbitals differ widely in binding energy no sharing will take place. It follows that if the $p\pi$ atomic orbitals of A are *much* less tightly bound than those of B the possible π orbitals in the molecule AB_2 are as follows : two orbitals (each two-fold degenerate) practically entirely localized on the B atoms and one higher-energy orbital (also two-fold degenerate) practically entirely localized on the A atom. In most actual AB_2 molecules (*e.g.*, CO_2, SO_2, OF_2, NO_2), B has considerably greater electronegativity (*i.e.*, has considerably more tightly bound valency orbitals) than A. While therefore it would be too extreme to speak of complete localization of any of the π orbitals, it follows that the three two-fold degenerate π-orbitals fall into two groups : (*a*) the two lower-energy ones (π_u and π_g) which should be more localized on the B than on A atoms, and (*b*) ·the higher-energy $\bar{\pi}_u$ orbital which should be more localized on A than on the B atoms. In the case of the π_g orbital, this argument merely reinforces what was already evident from the nature of the orbital [see (iv) above]. In the non-linear molecule the degeneracy of each of the orbitals is split. The π_u orbitals each yield an a_1' and a b_1'' orbital while the π_g orbital yields an a_2'' and a b_2' orbital. The primes are added for clarity to the usual group-theory symbols. A single prime means that the orbital is symmetric with respect to reflection in the plane of the molecule, a double prime that it is anti-symmetric. (vi) A $\bar{\sigma}_g$ orbital which is similar to the $\bar{\sigma}_g$ orbital described in Part I in the discussion of the spectrum of H_2O. It is built by the in-phase overlap of a $p\sigma$ valency on each of the B atoms, these overlapping out-of-phase with an s atomic orbital on the central atom. It is A⟷B anti-bonding, though B⟷B bonding.

In AH_2 molecules, there is general agreement that the π_u lies below the $\bar{\sigma}_g$ orbital. This is likely because the former is non-bonding whereas the latter is A⟷H anti-bonding. In non-hydride, AB_2 molecules, however, the orbital corresponding to π_u of AH_2 is $\bar{\pi}_u$, *i.e.*, an orbital that is A⟷B anti-bonding. A major reason for the orbital's lying lower than $\bar{\sigma}_g$ is therefore removed. We shall see in discussing the spectra of AB_2 molecules, however, that there is no compelling evidence for $\bar{\sigma}_g$ not still lying above $\bar{\pi}_u$.

By arguments similar to those given above, the $\bar{\sigma}_g$ orbital is more localized on the A than on the B atom.

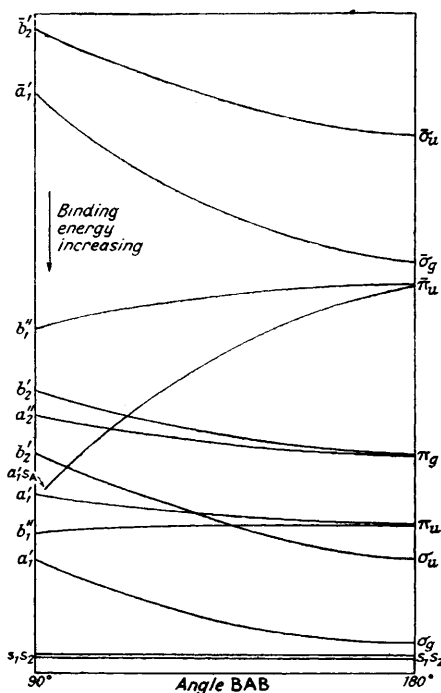The lowest-energy orbitals of a 90° AB_2 molecule may then be described as follows.

(i) Two lone-pair s orbitals, one on each B atom. It is assumed that these play little part in the binding of the B to the A atoms and that, being rather more tightly bound than any of the other valency orbitals of B or than any of the valency orbitals of A, they vary little in energy as the apex angle changes from 90° to 180°. They are therefore represented by horizontal straight lines on the correlation diagram (see Figure).

(ii) Two bond orbitals. Considered as localized orbitals, they are built from pure p valencies of the A atoms overlapping with p valencies of the B atoms. Considered as non-localized orbitals, their symbols are a_1' and b_2'. As described in Part I they both become more tightly bound as the apex angle changes from 90° to 180°.

(iii) An $a_1 s_A$ orbital. This, in first approximation, is a pure s orbital localized on atom A. As the apex angle changes from 90° to 180° this must, as described in Part I, tend to go over into a $p\pi$ orbital localized on atom A. It must therefore tend to correlate with the upper rather than with the lower π_u orbital. The localization on atom A was complete for AH_2 molecules. For AB_2 molecules the orbital will be largely, but not completely, localized on A. The curve representing the orbital rises steeply from left to right on the correlation diagram (Figure). The steep rise may be accentuated because the orbital becomes markedly A⟷B anti-bonding in the linear molecule. The Figure thus incorporates largely unchanged three of the curves of the Figure in Part I.

(iv) Three orbitals anti-symmetrical with respect to reflection in the plane of the

molecule. The first of these (b_1'') is built from a p atomic orbital on each of the three atoms overlapping in-phase. It is A$\leftrightarrow$B and (weakly) B$\leftrightarrow$B bonding, and becomes one of the lower π_u orbitals in the linear molecule. The A atomic orbital concerned in it is pure p in both bent and linear molecules. According to the principles enunciated in Part I any change of binding energy as the apex angle is changed is therefore governed by the fact that it is weakly B$\leftrightarrow$B bonding. This means it will be rather more stable (lead to more evolution of energy) when the two B atoms are as close together as possible (*i.e.*, in the 90° molecule). The curve representing the orbital in the Figure has therefore been drawn to rise slightly from left to right. The second of these orbitals (a_2'') is built from a p atomic orbital on each of the B atoms overlapping out-of-phase. It is A$\leftrightarrow$B non-bonding and B$\leftrightarrow$B anti-bonding, and becomes one of the π_g orbitals in the linear molecule. Because it is B$\leftrightarrow$B anti-bonding it will be more stable when the two B atoms are as far apart as possible (*i.e.*, in the 180° molecule). The curve representing the orbital in the Figure has therefore been drawn to decrease from left to right. The third orbital (b_1'') is built from a p atomic orbital on A overlapping out-of-phase with each of two p orbitals, one on each of the B atoms. In a 60° B_3 molecule this b_1'' orbital would be degenerate with the a_2'' orbital. It is the analogue of the b_1 orbital shown in the Figure of Part I. Because of the presence of low-lying p atomic orbitals on the B atoms it is now, however, A$\leftrightarrow$B anti-bonding and B$\leftrightarrow$B bonding, instead of non-bonding and localized solely on A. Because it is B$\leftrightarrow$B bonding it will be most stable when the two B atoms are as close together as possible. It is represented in the Figure therefore, not by an horizontal line (as in Part I), but by a line that rises from left to right.

(v) Two orbitals symmetrical with respect to reflection in the plane of the molecule and primarily built from two p atomic orbitals lying one on each B atom with axes in the molecular plane and at right angles to the direction of the adjacent B–A line. That which involves in-phase overlap of these two orbitals is of species a_1'. That which involves out-of-phase overlap is of species b_2'. The a_1' orbital becomes one of the lower π_u orbitals in the linear molecule. It is B$\leftrightarrow$B bonding, which supplies a reason why it should decrease in binding energy with increase of apex angle. On the other hand, because the s orbital on A is expected to interact little with the p orbitals on the B atoms from which a_1' is built, in the 90° molecule the a_1' orbital largely loses the A$\leftrightarrow$B bonding character which it has in the linear molecule. This supplies a reason why the a_1' orbital should become more tightly bound as the apex angle increases. The a_1' orbital has therefore been inserted in the Figure as showing comparatively little dependence on angle.* The b_2'–π_g orbital is B$\leftrightarrow$B anti-bonding and is therefore represented in the Figure by a line that falls from left to right.

(vi) An $\bar{a}_1'$ orbital that correlates with the $\bar{\sigma}_g$ orbital of the linear molecule. This

Figure labels: left axis (top to bottom): $\bar{b}_2'$, $\bar{a}_1'$, b_1'', b_2', a_2'', b_2', $a_1's_A$, a_1', b_1'', a_1', s_1s_2; right axis (top to bottom): $\bar{\sigma}_u$, $\bar{\sigma}_g$, π_u, π_g, π_u, σ_u, σ_g, s_1s_2. Left axis annotation: "Binding energy increasing". Bottom axis: 90° — Angle BAB — 180°

* As a net effect the a_1' orbital curve probably falls from left to right in the Figure for the following reason. In a 60° B_3 molecule the a_1' orbital leading to the upper π_u should become degenerate with the b_2' orbital leading to π_g. This might happen if the a_1' orbital leading to the lower π_u curls upwards from right to left. For if orbital curves of the same species cannot cross, the a_1' orbital curve leading to the upper π_u may contain a minimum to the left of which it curves steeply upward to meet the b_2' orbital. It should be emphasized, however, that it is the part of the diagram from 90° to 180° that concerns real molecules.

orbital consists largely of an A atomic orbital. According to the principles given in Part I, it is built from a p_z orbital of A in the 90° molecule but from an s orbital of A in the 180° molecule; and therefore is represented in the Figure by a line that falls steeply from left to right.

If it should happen that the $\bar{\sigma}_g$ orbital lies *below* $\bar{\pi}_u$, then the curve from the $a_1's_A$ orbital will lead, not to the $\bar{\pi}_u$, but to the $\bar{\sigma}_g$ orbital. Orbital curves of the same species cannot cross.* In that case, the steep rise over most of its course of the curve from the $a_1's_A$ orbital could still be regarded as due to the reasons already described, *i.e.*, to its " trying " to reach $\bar{\pi}_u$; but an " avoided crossing " would have to be drawn, with the result that the curve from the $\bar{a}_1'$ orbital which " tended " to proceed to $\bar{\sigma}_g$ would be drawn in fact to proceed to the $\bar{\pi}_u$ orbital. However, we shall see below that the balance of evidence is not unfavourable to $\bar{\sigma}_g$ lying above $\bar{\pi}_u$, *i.e*, no such " avoided crossing " is necessary.

(vii) A total of twelve intra-valency-shell orbitals can be built from one s and three p atomic orbitals on each of the three atoms of AB_2. For completeness therefore a twelfth orbital curve has been added to the Figure. It represents a $\bar{b}_2'$–$\bar{\sigma}_u$ orbital which is built by the out-of-phase overlap of valencies on the B atoms, these themselves overlapping out-of-phase with a p valency of A. It is A←→B and B←→B anti-bonding. Because it involves no change of A valency as the apex angle is changed and is B←→B anti-bonding, it is represented in the Figure by a curve that falls from left to right. It may well lie so high in energy, however, that it is above the lowest extra-valency-shell orbital.

It should be emphasized (1) that the actual forms of the curves in the Figure are uncertain, except that each must be a maximum or minimum on the 180° line, (2) that though the energy order of the orbitals on the 180° ordinate is probably definite (except perhaps for $\bar{\sigma}_g$ and $\bar{\pi}_u$) † that of the orbitals on the 90° ordinate is uncertain, (3) that no stress should be put upon the quantitative energy differences shown even on the 180° ordinate,‡ and (4) that though the above arguments provide plausible support for the rise or fall from left to right of a given orbital they are not always conclusive. In other words, some of the support for much in a correlation diagram such as that illustrated must be empirical. We therefore proceed below to examine how far the Figure can explain known facts.

BAC *Molecules.*—A diagram very similar to the Figure for AB_2 molecules should also hold for BAC molecules. The absence of a centre of symmetry now means that the g and u suffixes for the orbitals in the linear molecule must be abandoned. With the exception of the primes, the symbols for the bent molecule (C_s symmetry) also become inappropriate. The only appropriate symbols are now a' and a''.

Shapes of Non-hydride, Triatomic Molecules.—Of the lowest eight orbital curves on the right-hand side of the Figure, all but one either decrease from left to right or are horizontal. The one exception rises only slightly from left to right. One therefore expects that AB_2 or BAC molecules containing 16 or less valency electrons will be linear in their ground states. So far as is known there are no exceptions to this rule. CO_2, COS, CS_2, N_2O, ClCN, $HgCl_2$, NCO^-, and N_3^- supply well-known examples. Of less well-known molecules, the ions CO_2^+ (see below) and NO_2^+ (see Gillespie and Millen, *Quart. Reviews*, 1948, **2**, 277) are linear, while the radicals C_3 and N_3 would be expected to be linear. The uranium atom has six valency electrons, the configuration in the ground state being $\cdots (5f)^4(7s)^2$, where the (5f)- and the (7s)-orbitals have closely similar binding energies. One would expect, therefore, that the ion UO_2^{++} would be linear in the ground state. This is true (Zachariasen, *Acta Cryst.*, 1948, **1**, 277, 281; Sutton, *Nature*, 1952, **169**, 235). It seems

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* The point is the same as that involved in the familiar diagrams correlating the orbitals of two separated atoms with those of the united atom. " The lowest σ orbital to the right goes into the lowest σ orbital to the left, the second lowest σ orbital to the right goes into the second lowest to the left and so on " (Herzberg, " Molecular Spectra and Molecular Structure," Van Nostrand, New York, 1950, p. 327).

† For CO_2 the ionization energies for electrons in the σ_u, π_u, and π_g orbitals are known to be 18·00, 17·32, and 13·79 ev.; *i.e.*, the σ_u lies only just below the π_u orbital, the π_g orbital lying considerably higher, in accord with the Figure.

‡ In any case these energy differences must vary from molecule to molecule.

that the implications of the Figure are not limited to light atoms but apply throughout the Periodic Table. The ions $AgCl_2^-$ and $AuCl_2^-$ are linear.* One may deduce, either directly by arguments similar to those of this paper or by analogy with the isoelectronic CO_2 that the ground states of keten and allene molecules will have linear CCO or CCC chains respectively.

The ground state of a molecule such as NO_2, however, containing 17 valency electrons, has to have its outermost electron in the $a_1's_A-\overline{\pi}_u$ orbital which rises steeply from left to right in the Figure. The ground state of the NO_2 molecule is therefore bent,† its apex angle showing a considerable drop from 180°. When NO_2^+ reacts, a donation of electrons to it may be considered to occur. These electrons occupy the $a_1's_A-\overline{\pi}_u$ orbital, resulting in the NO_2 group's becoming triangular. NO_2 is the only 17-electron molecule for which an apex angle has been reported. Two rather widely different values for this angle have been given (Table 1). The mean drop from 180° is 37° ± 11°. One would expect the apex

TABLE 1. *Apex angles of ground states of triatomic molecules.*

No. of valency electrons	Molecule	Apex angle	Ref.	Mean value	Method of determn.
16	Numerous	180°		180°	—
17	NO_2	{ 154 ± 4 132 ± 3 *	a b	} 143 ± 11	Electronic spectrum Electron diffraction
18	NOCl	116	c		,, ,,
	NOBr	117	c		,, ,,
	NO_2^- (in crystal) {	114 ± 4 115	d e	117	X-Ray diffraction ,, ,,
	O_3 {	127 ± 3 116·5—117	f g		Electron diffraction Micro-waves
	SO_2	119° 2'	h		,,
19	ClO_2	116·5°	i	116·5	Electron diffraction
20	F_2O	101	j		,, ,,
	Cl_2O	110·8	i		,, ,,
	Cl_2S {	101 ± 4 103 ± 3	k l	103	,, ,, ,, ,,
	Br_2Te	98 ± 3	m		,, ,,
22	$BrIBr^-$		n		X-Ray diffraction
	$ClICl^-$	180° or	o	180	,, ,,
	I_3^-	ca. 180°	p		,, ,,
	$ClIBr^-$		q		,, ,,

* Spurr, using the electron diffraction data of Maxwell and Mosley (*J. Chem. Phys.*, 1940, **8**, 738), found 141° (quoted by Jost and Russell, " Systematic Inorganic Chemistry," Prentice Hall, New York, 1944).
   a Harris and King, *J. Chem. Phys.*, 1940, **8**, 775. *b* Claesson, Donohue, and Schomaker, *ibid.*, 1948, **14**, 207. *c* Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629. *d* Truter, personal communication; Mrs. Truter (*Nature*, 1951, **168**, 344) originally reported the angle as 132° 48', but has since revised her estimate. *e* Carpenter, *Acta Cryst.*, 1952, **5**, 132. *f* Shand and Spurr, *J. Amer. Chem. Soc.*, 1943, **65**, 179. *g* Hughes, *Bull. Amer. Phys. Soc.*, 1951, **26**, 21, No. 6. *h* Crable and Smith, *J. Chem. Phys.*, 1951, **19**, 502. *i* Dunitz and Hedberg, *J. Amer. Chem. Soc.*, 1950, **72**, 3108. *j* Brockway, *Rev. Mod. Phys.*, 1936, **8**, 231. *k* Palmer, *J. Amer. Chem. Soc.*, 1938, **60**, 2360. *l* Stevenson and Beach, *ibid.*, p. 2872. *m* Rogers and Spurr, *ibid.*, 1947, **69**, 2102. *n* Bozorth and Pauling, *ibid.*, 1925, **47**, 1561. *o* Wyckoff, *ibid.*, 1920, **42**, 1100. *p* Mooney, *Z. Krist.*, 1935, **90**, 143. *q* Mooney, *Phys. Review*, 1935, **47**, 807; *Z. Krist.*, 1938, **98**, 324; 1939, **100**, 519.

angle to show a further marked drop if an eighteenth electron were added. The exact value of the apex angle in 18-electron molecules must vary from molecule to molecule because the heights of the various orbitals and the steepness of their change with angle must vary from molecule to molecule. In other words, if it ever becomes possible to plot the Figure in a completely quantitative way, a separate figure really needs to be plotted for each molecule. It is remarkable, however, that the apex angles reported for various

* The hybrid valencies giving linearity may not be *sp* when heavy elements are considered. The general ideas of the present argument should, however, still be valid.
† *Added in Proof.*—It is not obvious that *one* electron in the $a_1's_A-\overline{\pi}_u$ orbital should outweigh the effect of, *e.g.*, the filled $a_1-\sigma_g$ and $b_2-\sigma_u$ orbitals. However, the fall of the $a_1-\sigma_g$ curve from left to right in the Figure is offset by the B ⟷ B bonding nature of the orbital; whereas the rise of the $a_1's_A-\overline{\pi}_u$ curve is accentuated by the B ⟷ B bonding nature of the orbital and by its becoming A ⟷ B anti-bonding in the linear molecule. It is plausible therefore that the latter curve should rise much more steeply than the $a_1-\sigma_g$ curve falls. See also the footnote concerning this point on p. 2263.

18-electron molecules only vary over a range (*ca.* 12° at most and probably only 5°) that is small compared with the total range of the abscissa in the Figure.* These angles are given in Table 1. The mean value implies a drop of *ca.* 26° from the mean value for NO_2. A 19-electron molecule has to place its outermost electron in the $b_1'-\bar{\pi}_u$ orbital. Since the curve of this orbital rises from left to right in the Figure, but not as steeply as that of the $a_1's_A-\bar{\pi}_u$ orbital, one would expect the apex angle of such a molecule to show a further, but smaller, drop from the value characteristic of 18-electron molecules. The only 19-electron molecule for which an apex angle has been reported is ClO_2. The value of the angle reported for this molecule probably has a considerable uncertainty, but is not incompatible with the expected small drop from the mean value for the 18-electron molecules. One would expect a further small drop in the apex angle of a 20-electron molecule. One expects and finds the actual angle reported for such molecules to cover a range of values, but again the range is small (*ca.* 13°: see Table 1). The mean value represents a drop of about 13° from the value for ClO_2.

To sum up, all 17-, 18-, 19-, and 20-electron molecules have ground states that are bent; the apex angle drops considerably from 16- to 17-electron molecules; and also from 17- to 18-electron molecules; the apex angle also drops, but less markedly, from 18- to 19-electron molecules and from 19- to 20-electron molecules; and these facts fit very well with expectations from the Figure. It is remarkable that mere number should determine, for AB_2 and BAC as for AH_2 molecules, the crude magnitude of the apex angle (cf. Cassie, *Nature*, 1933, **131**, 438; Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156**, 654; Sidgwick and Powell, *ibid.*, 1940, *A*, **176**, 153).

The first excited state of the CO_2 molecule has its most weakly bound electron in the $a_1's_A-\bar{\pi}_u$ orbital. It has the same reason as the ground state of NO_2 for being bent, and at the same time has one less electron in the orbitals stabilizing the linear form. One strongly expects therefore the first excited state of CO_2 to be bent. We discuss evidence in favour of this below. The keten and the allene molecule are isoelectronic with CO_2. It follows either directly by arguments similar to those of this paper, or by analogy with CO_2, that the CCO or CCC chains in the equilibrium forms of the lowest-lying excited states of these molecules should be non-linear (cf. Sutcliffe and Walsh, *J.*, 1952, 899). Further examples of molecules which have linear ground states but probably bent upper states are given in a discussion below of the spectra of triatomic molecules. It is probably a very common phenomenon for polyatomic molecules to have different shapes in their excited and in their ground states (cf. the following papers).

The ground state of a 22-electron molecule must have two electrons in the $\bar{a}_1' - \bar{\pi}_u$ orbital. The trend of the apex angle in 16—20-electron molecules should therefore be sharply reversed on proceeding further to 22-electron molecules. Indeed, if the $\bar{a}_1'-\bar{\pi}_u$ curve falls sufficiently steeply, 22-electron molecules should be linear in their ground states. As Table 1 records, the trihalide ions are reported, experimentally, to be linear or nearly so. Pimentel (*J. Chem. Phys.*, 1951, **19**, 446) has earlier discussed the molecular orbitals involved in the ground states of trihalide ions, accepting these states as linear, but he made no attempt to discuss the more difficult problem of why this was so. In essentials Pimentel's conclusions agree with the orbitals that would be predicted from the Figure for the ground state of a 22-electron molecule. In particular agreement with Pimentel, the Figure shows that there is no need to invoke the use of d orbitals to explain (qualitatively) the bonding (and the linearity) of the trihalide ions.

Alternative Statement of the Factors determining the Apex Angle.—It is striking that the apex angles of the ground states of H_2O and F_2O are nearly the same (104° and 101° respectively).† It presumably means that H—H and F—F repulsions are of minor importance in determining the angle. This is readily interpreted in terms of the Figure. The major factors determining the apex angle lie in the $a_1'-\sigma_g$, $b_2'-\sigma_u$, and $a_1s_A-\bar{\pi}_u$, curves, *i.e.*, in the curves largely common to the Figures of the preceding and of the present paper. It can be seen from the Figure that the sum of the $b_1''-\bar{\pi}_u$, $b_2'-\pi_g$, $a_2''-\pi_g$, $a_1'-\pi_u$, and

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* Similarly, it was pointed out in Part I that the known angles for 8-electron AH_2 molecules vary only over a range of 14°.
† I am indebted to Dr. P. Torkington for stressing this to me.

$b_1''-\pi_u$ curves changes comparatively little with the angle. The major changes in binding energy with angle may therefore be regarded as due to the three remaining curves which, for F_2O, must be substantially the same as for H_2O. In other words, the major factor determining the apex angle is a property of the central atom. It is the interaction between the valencies of this atom used for the bonding orbitals and the lone pair a_1' orbital.

So far we have expressed this interaction in terms of hybridization of the valencies of the central atom. One could express the interaction in alternative terms of electrostatic repulsions between the electrons in the bond orbitals and those in the "lone-pair" orbital (cf. Pople, *Proc. Roy. Soc.*, 1950, *A*, **202**, 323). Thus the fundamental reason why 17- and 18-electron molecules have ground states that are bent is because they have 1 and 2 electrons respectively which are in orbitals more localized on the central than on the end atoms and repel the bond electrons. As a consequence of the molecule's bending, the extra electrons come to occupy an orbital whose contribution from the central atom is no longer pure p, but an sp hybrid pointing in the $+z$ direction (axes as in Part I). At the same time the valencies of the central atom used for the bond orbitals become more nearly pure p, *i.e.*, become less electronegative (Walsh, *Discuss. Faraday Soc.*, 1947, No. 2, p. 18). The hybridization changes thus imply that the electrons in the lone-pair orbital move away from the bond orbitals in the z direction (the orbital no longer having its centre of gravity at the nucleus of A as it had in the linear molecule) while the bond electrons move away from atom A towards atoms B. These are just the changes expected to follow from repulsion between lone-pair electrons on A and the bond electrons.

In the ground states of 22-electron molecules, two electrons are placed in a further orbital which is more localized on atom A than on atoms B. This orbital is built from a p_z orbital of A in the 90° molecule and from a pure s orbital of A in the linear molecule. At intervening angles the orbital represents the second sp hybrid that can be formed from the s and p_z orbitals of A. This second sp hybrid points in the $-z$ direction and so restores symmetry to the electron cloud around A. The bond electrons are now subject to repulsions from the electrons in the sp hybrids which tend to cause bending in opposite directions; thus the molecule resumes a linear or nearly linear form.

The key curves causing the major changes of shape are: (a) the bond orbital curves; (b) the $a_1's_A-\bar{\pi}_u(p_z)$ curve; and (c) the $\bar{a}_1'(p_z)-\bar{\sigma}_g(s_A)$ curve.

Reactivity of Triatomic Molecules.—The outermost, unpaired electron of the ground state of the NO_2 molecule lies in the $a_1's_A-\bar{\pi}_u$ orbital. From the arguments above, this electron is more localized on the N atom than on the O atoms. Reaction of NO_2 with a free radical is therefore likely to form a nitro-compound rather than a nitrite. Inhibition of certain free-radical reactions by NO_2 may plausibly be attributed to such reaction: the inhibition occurs under conditions where addition of a nitro-compound has no effect, but addition of a nitrite catalyses the reaction. Similarly, initiation of chains by H-abstraction by NO_2 (see, *e.g.*, McDowell and Thomas, *Trans. Faraday Soc.*, 1950, **46**, 1030) is likely to form $\mathrm{H\cdot N{<}^O_O}$ rather than $HO\cdot NO$. One might expect that, since NO_2 molecules readily associate to form N_2O_4, the latter molecule has the structure $\mathrm{{}^O_O{>}N\cdot N{<}^O_O}$ (cf. Ingold and Ingold, *Nature*, 1947, **159**, 743; Walsh, *J. Chem. Phys.*, 1947, **15**, 688; Claesson, Donohue, and Schomaker, *ibid.*, 1948, **16**, 207; Broadley and Robertson, *Nature*, 1949, **164**, 915). On arguments similar to those given here, the outermost, unpaired electron of the ground state of the NO molecule is more localized on the N than on the O atom. Since NO and NO_2 associate to form N_2O_3, a certain presumption is raised in favour of the structure $\mathrm{O{-}N\cdot N{<}^O_O}$ for N_2O_3 (see also Part V of this series).

The nitrite ion has its two most weakly bound electrons in the $a_1's_A-\bar{\pi}_u$ orbital, *i.e.*, more localized on the N atom than on the O atoms. One might therefore expect reaction with an acceptor entity to take place at the N atom rather than at the O atoms. In agreement, the nitrite ion reacts with a carbonium ion to form a nitro-compound (Austin, Thesis, London, 1950).

The ClCO radical has its outermost, unpaired electron more localized on the C than on

the Cl or O atom. One therefore expects it to react most readily at the C atom. This is in agreement with the reaction that has been postulated for the radical (Rollefson and Montgomery, *J. Amer. Chem. Soc.*, 1933, **55**, 142, 4025), namely, formation of carbonyl chloride : $Cl_2 + ClCO = Cl_2CO + Cl$.

The first excited state of the SO_2 molecule contains one electron in the $a_1's_A$-$\bar{\pi}_u$ orbital and one in the b_1''-$\bar{\pi}_u$ orbital. Both these orbitals are more localized on the S atom than on the O atoms. It is interesting that photochemical reactions of SO_2, presumably involving this excited state, have been shown to form two bonds to the *S* atom (Dainton and Ivin, *Trans. Faraday Soc.*, 1950, **46**, 382). Moffitt (*Proc. Roy. Soc.*, 1950, A, **200**, 414) has previously noted that the most weakly bound electrons of the ground state of the SO_2 molecule lie in an (a_1) orbital (here called $a_1's_A$) which is predominantly localized on the S atom; and that the oxidation (" donor ") reactions of SO_2 to form SO_3 or SO_2Cl_2 can therefore be readily understood.

The discussion in this section is somewhat naive in that reactivity is a complicated matter; but it is sufficiently successful to suggest that the ideas involved are useful in considering not merely the ground state, but also the photochemical, reactions of molecules. Combined with the conclusions of the preceding section concerning the shapes of excited states, they should be of particular use in considering possible photochemical syntheses.

Relation to Other Work.—As mentioned in Part I, Mulliken (*Rev. Mod. Phys.*, 1942, **14**, 204) has earlier plotted a correlation diagram for the orbitals of a linear and a bent triatomic molecule. Mulliken, however, was unable to give any simple reason why particular curves rose or fell with change of apex angle. In many respects, our Figure agrees with that of Mulliken. There are two major differences. The first is that Mulliken supposed $\bar{\sigma}_g$ to lie below $\bar{\pi}_u$ (for his reasons, see *J. Chem. Phys.*, 1935, **3**, 739). As already explained, this results in the curve from $a_1's_A$ leading to $\bar{\sigma}_g$ instead of to $\bar{\pi}_u$ and in the curve from $\bar{a}_1'$ leading to $\bar{\pi}_u$ instead of to $\bar{\sigma}_g$. The second major difference is that Mulliken drew the curve from $\bar{a}_1'$ as rising from left to right, whereas in the present Figure it has the opposite curvature. Mulliken's diagram made the reported linearity of the 22-electron molecules incomprehensible

Mulliken particularly used his diagram to interpret observed spectra of triatomic molecules. In the next section we give a fuller discussion of these observed spectra, indicating our agreement with, or changes from, Mulliken's assignments.

Spectra of Non-hydride, Triatomic Molecules.—(i) CO_2 *and* N_2O. It is striking that, whereas the N_2O and CO_2 molecules are isoelectronic, ultra-violet absorption by the former begins at *ca.* 3000 Å whereas that by CO_2 does not occur until *ca.* 1700 Å.* A simple explanation is as follows. The lowest-energy transition of these molecules, according to the Figure, is of an electron from the π_g to the $\bar{\pi}_u$ orbital. In other words, it is from an orbital largely localized on the end atoms to one largely localized on the central atom. The orbital localized on the end atoms will be less tightly bound in NNO than in OCO since the electronegativity of N is less than that of O.† On the other hand, the orbital largely localized on the central atom will be more tightly bound in NNO than in OCO since the electronegativity of N is greater than that of C. We have therefore the situation represented diagrammatically below and the transition in N_2O should require considerably less energy than that in CO_2.

The first electronic transitions of N_2O *and* CO_2.

} Orbital largely localized on the central atom.

} Orbital localized on the end atoms.

N_2O CO_2
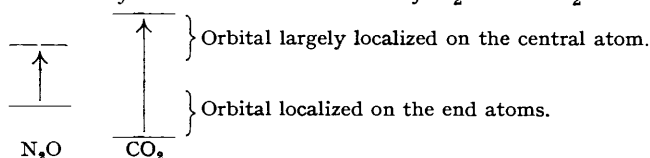
According to our Figure (p. 2268) the upper state of the longest-wave-length-absorption

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* Even in liquid CO_2 no absorption occurs until at least 2150 Å.

† It is easily seen that in N_2O the analogue of the lower π_u orbital is predominantly localized on the O atom, while the analogue of the π_g orbital is predominantly localized on the end N atom.

system of CO_2 should be related to the configuration $(\pi_g)^3(\bar{\pi}_u)$. This gives rise to $^1\Delta_u$ (two-fold degenerate), $^1\Sigma_u^-$, and $^1\Sigma_u^+$ states. By analogy with atoms and diatomic molecules one would expect $^1\Delta_u$ to be the lowest of these states. The transitions

$$\cdots (\pi_g)^3(\bar{\pi}_u), \quad ^1\Delta_u \longleftarrow \cdots (\pi_g)^4. \; ^1\Sigma_g^+ \quad \ldots \ldots \quad (1)$$

and

$$\cdots (\pi_g)^3(\bar{\pi}_u), \quad ^1\Sigma_u^- \longleftarrow \cdots (\pi_g)^4, \; ^1\Sigma_g^+ \quad \ldots \ldots \quad (2)$$

are forbidden; while

$$\cdots (\pi_g)^3(\bar{\pi}_u), \quad ^1\Sigma_u^+ \longleftarrow \cdots (\pi_g)^4, \; ^1\Sigma_g^+ \quad \ldots \ldots \quad (3)$$

is allowed. Now, (3) should be a particularly intense transition since it belongs to the class of so-called " $V \longleftarrow N$ " transitions which, compared with other intra-valency-shell transitions, are expected to have particularly high intensities (Mulliken, *J. Chem. Phys.*, 1939, **7**, 20). The different possible states correspond, in C_{2v} symbols, to the four configurations (see Figure)

$$(a_2'')^2(b_2')(a_1'), \quad ^1B_2$$
$$(a_2'')(b_2')^2(a_1'), \quad ^1A_2$$
$$(a_2'')^2(b_2')(b_1''), \quad ^1A_2$$
$$(a_2'')(b_2')^2(b_1''), \quad ^1B_2$$

The first two of these configurations represent states that are expected to be strongly bent, and the second two states that are expected to be slightly bent or linear. $^1\Delta_u$ correlates with $^1A_2$ and $^1B_2$; $^1\Sigma_u^+$ and $^1\Sigma_u^-$ correlate with $^1B_2$ and $^1A_2$ respectively. For bent upper states, the degeneracy of $^1\Delta_u$ is split, so that (1) has to be replaced by the two transitions

$$^1A_2 \longleftarrow \cdots (\pi_g)^4, \; ^1\Sigma_g^+ \quad \ldots \ldots \ldots \quad (1A)$$

and

$$^1B_2 \longleftarrow \cdots (\pi_g)^4, \; ^1\Sigma_g^+ \quad \ldots \ldots \ldots \quad (1B)$$

Both transitions would be weak, partly because forbidden by the Franck–Condon principle and partly because both are related to the forbidden transition (1). In addition, (1A) is forbidden by the symmetry-selection rules and has therefore an extra reason to be weak compared with (1B). Similarly, for bent upper states, (2) and (3) have to be replaced respectively by

$$^1A_2 \longleftarrow \cdots (\pi_g)^4, \; ^1\Sigma_g^+ \quad \ldots \ldots \ldots \quad (2A)$$

and

$$^1B_2 \longleftarrow \cdots (\pi_g)^4, \; ^1\Sigma_g^+ \quad \ldots \ldots \ldots \quad (3A)$$

(2A) should be very weak because it is forbidden by the symmetry-selection rules and is related to the forbidden transition (2). Provided, however, that the upper state is not *strongly* bent, (3A) should be strong since it is allowed by the selection rules and is related to the intense transition (3).

The lowest-energy absorption of CO_2 falls into two regions, 1700—1400 and 1390—1240 Å. The latter region has $\lambda_{max.}$ at *ca.* 1335 Å (Price and Simpson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 501) and is much stronger than the 1700—1400-Å region, though not as strong as the Rydberg bands at shorter wave-lengths. There is no doubt that it represents an allowed intra-valency-shell transition. Indeed its intensity makes it only plausibly identified as transition (3) or (3A). In the latter case the upper state cannot be *strongly* bent. The appearance pressure of the 1390—1240-Å absorption, relative to the Rydberg bands, appears to be of the order found in other molecules for $V \longleftarrow N$, relative to Rydberg, transitions (*e.g.*, acetylene; see Part III). The 1700—1400-Å absorption contains a peak of $\varepsilon_{max.}$ ~110 * (*ca.* 1495 Å; Wilkinson and Johnston, *J. Chem. Phys.*, 1950, **18**, 190). This is too strong for the transition to be plausibly interpreted as a triplet $\longleftarrow$ singlet transition (which would be expected to have an extinction coefficient < 1; Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 72). It is also too strong to be plausibly interpreted as (2) or (2A). Further, it is not plausibly interpreted simply as (1), partly because of its intensity and partly because of the strong expectations that the first absorption of CO_2 should lead to a bent upper state. The only plausible interpretation is as transition (1B). In view of the expectation (see Figure) that the lowest-energy

* See footnote, p. 2264

absorption should lead to a *strongly* bent upper state, the 1495-Å peak may be interpreted, in more detail, as

$$\cdots (a_2{''})^2(b_2{'})(a_1{'}), \; {}^1B_2 \; (\text{correlating with } {}^1\Delta_u) \longleftarrow \cdots (\pi_g)^4, \; {}^1\Sigma_g{}^+ \quad . \quad (1B')$$
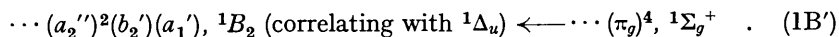
This leaves the interpretation of the 1390—1240-Å region to be given in more detail as

$$\cdots (a_2{''})(b_2{'})^2(b_1{''}), \; {}^1B_2 \; (\text{correlating with } {}^1\Sigma_u{}^+) \longleftarrow \cdots (\pi_g)^4, \; {}^1\Sigma_u{}^+ \quad . \quad (3A')$$
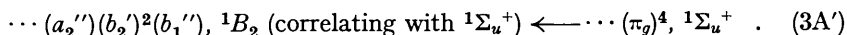
raising the expectation that the upper state may be *slightly* bent. That the expectation is correct is strongly supported by the fact that in the analogous region of CS_2 (see below) there is evidence that the upper state is bent through a few degrees. In view of the remarkable dependence of apex angle upon number of occupied orbitals (irrespective of the particular nuclei concerned) we would expect the apex angle in the upper state of the ~1495-Å absorption to be less than the ground state angle of NO_2 ($143° \pm 11°$) by a small amount which represents the effect of losing an electron from the linear-stabilizing π_g orbital. A reasonable expectation for the apex angle would be $135° \pm 10°$.

It is interesting that Wilkinson and Johnston find, besides the peak at *ca.* 1495 Å, three still weaker bands at 1690, 1673, and 1662 Å, which appear to represent a separate system. These bands, which are very diffuse, are also mentioned by Price and Simpson (*loc. cit.*). It is possible that they represent transition (1A).

The 3000—1760-Å absorption of N_2O is also known to subdivide into at least two regions ($\lambda_{max.}$ *ca.* 2900 and *ca.* 1900 Å), requiring different appearance pressures (see summary given by Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75).

As stated above, Mulliken (*loc. cit.*; *J. Chem. Phys.*, 1935, **3**, 720) supposes the $\bar{\sigma}_g$ to lie below the $\bar{\pi}_u$ orbital. Since if that were true we should need to draw our Figure with an "avoided crossing" and the $a_1{'}s_A$ curve leading to $\bar{\sigma}_g$ instead of to $\bar{\pi}_u$, Mulliken's interpretation of the longest-wave-length absorption is identical with the present interpretation, provided that the upper state is formulated in the C_{2v} symbols given above. The difference is that Mulliken's interpretation implies that the ${}^1B_2$ upper state correlates with the $(\pi_g)^3(\bar{\sigma}_g)$, ${}^1\Pi_g$ linear state instead of with the $(\pi_g)^3(\bar{\pi}_u)$, ${}^1\Delta_u$ linear state. [In a bent molecule, the degeneracy of the ${}^1\Pi_g$ state would be split, leading to transitions (1A) and (1B) above.] Now, if the upper state of the first absorption correlates with ${}^1\Pi_g$, one might expect the analogous absorption in N_2O to be much stronger, since it should be related to the *allowed* transition

$$\cdots (\pi)^3(\bar{\sigma}), \; {}^1\Pi \longleftarrow \cdots (\pi)^4, \; {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad (4)$$
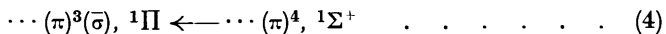
The first absorption of N_2O, however, remains weak. It seems better, therefore, to regard the first absorption as related to the transition

$$\cdots (\pi)^3(\bar{\pi}), \; {}^1\Delta \longleftarrow \cdots (\pi)^4, \; {}^1\Sigma^+ \quad . \quad . \quad . \quad . \quad . \quad (5)$$
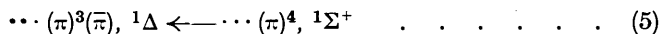
which is forbidden in N_2O, as is (1) in CO_2, *i.e.*, at least with N_2O, to regard $\bar{\sigma}$ as lying above $\bar{\pi}$. [Doubtless altogether the 3000—1760-Å absorption of N_2O involves absorption to the three bent upper states which correspond to ${}^1B_2$, ${}^1A_2$ (correlating with ${}^1\Delta_u$) and ${}^1A_2$ (correlating with ${}^1\Sigma_u{}^-$) of CO_2.] It is true that with COS the first absorption becomes stronger than in CO_2, but (as we explain below) this is not compelling evidence in favour of $\bar{\sigma}_g$ lying below $\bar{\pi}_u$. Further, in other molecules [*e.g.*, diatomic molecules, C_2H_2 (see Part III) and HCHO] the details of the spectra are only plausibly interpreted by supposing that the orbital analogous to $\bar{\sigma}_g$ lies above that analogous to $\bar{\pi}_u$. With no molecule does there appear to be any compelling evidence that $\bar{\sigma}_g$ (or its analogue) lies below $\bar{\pi}_u$. At least pending further evidence, therefore, we shall proceed on the assumption that $\bar{\sigma}_g$ lies above $\bar{\pi}_u$, since this implies a simpler form for our Figure. If later work should show that after all $\bar{\sigma}_g$ lies below $\bar{\pi}_u$, it would not be difficult to make the necessary changes in the present assignments.

The continuous nature of the absorption in CO_2 and N_2O does not seem surprising in view of the fact that the energy absorbed is sufficient to cause dissociation into the ground states of CO and O or N_2 and O respectively. It is clear, however, that the equilibrium form of the upper state may possess much less energy than the form reached in absorption

at $\lambda_{max.}$ from the ground state. The upper state may therefore be stable in the equilibrium form and a discrete emission spectrum may be possible. If the absorption spectrum of CO_2 at high temperatures were studied, so that transitions from high vibrational levels of the ground state were possible at sufficiently long wave-lengths, the absorption spectrum would presumably become banded.

Returning now to the 1390—1240-Å region of CO_2, we should expect from the interpretation given above that both the ν_2 bending frequency and (more strongly) the ν_1 stretching frequency of the upper state would appear in the absorption. The latter expectation follows from the fact that the π_u orbital is $C\leftarrow\rightarrow O$ anti-bonding. For an allowed transition, only frequencies that represent vibrations which are totally symmetrical should appear strongly; if the upper state remained linear, ν_2, being then non-totally symmetrical, would not appear strongly. The bands in the region are diffuse and shaded to the red. Their separation is ~500—600 cm.$^{-1}$, but is too irregular for the structure to be interpreted in terms of a single frequency of this magnitude. Price and Simpson suggest that two progressions are present, one starting at 1380 Å and the other at 1368 Å, each with frequency intervals of *ca.* 1225 cm.$^{-1}$ and each rising to a maximum intensity at the same wave-length. However, the measured intervals of these supposed progressions vary from 1080 to 1350 cm.$^{-1}$. No doubt the difficulty of measuring the diffuse bands can partly explain this irregularity, but the variation is so great that it seems more probable that two different frequencies are involved. In this connection it should be noted that, for a reason that will be made clear in Part III, it would be possible for the bending frequency to be slightly *increased* in the upper state relative to the value of 667 cm.$^{-1}$ in the ground state (cf. N_2O below).* The stretching frequency, on the other hand, is expected to be decreased in the upper state from its value of *ca.* 1340 cm.$^{-1}$ in the ground state.

The analogue of the CO_2 1390—1240-Å system in N_2O appears to be the absorption occurring between 1520 and 1425 Å (Duncan, *J. Chem. Phys.*, 1936, **4**, 638), although the appearance pressure of this absorption is only about a tenth of that for the CO_2 system. The absorption consists of nine diffuse bands. Duncan represents their spacing by a frequency of 621 cm.$^{-1}$ in the upper state. This might represent the totally symmetrical ν_1 vibration of 1285 cm.$^{-1}$ in the ground state, though if so the drop is very great. Alternatively, 621 cm.$^{-1}$ might represent the bending vibration which has a frequency of 589 cm.$^{-1}$ in the ground state; the small increase is not implausible (see Part III). If the latter interpretation is correct, then it implies that the upper state is (slightly) bent. Sponer and Teller (*loc. cit.*, p. 109) suggest the further interpretation that two separate progressions, each with a spacing of *ca.* 1240 cm.$^{-1}$ (representing the 1285-cm.$^{-1}$ ground-state frequency), are present; but if so the drop in frequency seems surprisingly small. However, the spacing between the bands is irregular and, though this is doubtless partly due to the difficulty of measurement, it is not improbable that *two* frequencies are involved, one representing ν_2' and the other ν_1'. It is unfortunate that the diffuseness of the bands precludes resolution of the rotational fine structure to decide whether the bands are parallel or perpendicular. Whatever the correct interpretation, if ν_2' is involved the progression in it is fairly short (maximum intensity occurs at the fifth band), so that the upper state is slightly, rather than strongly, bent.

An extensive emission band system believed to be due to the CO_2 molecule is known. It appears in the carbon monoxide flame spectrum (see Gaydon and Wolfhard, *Nature*, 1949, **164**, 22). The bands lie between 5500 and 3000 Å, with maximum intensity around 4200 Å. Smyth (*Phys. Review*, 1931, **38**, 2000) was unable to find emission bands that could be ascribed to CO_2 over the range 2700—1400 Å. In other words, there appeared to be no bands corresponding to those found in absorption around 1500 Å. However, as Gaydon (*Proc. Roy. Soc.*, 1940, *A*, **176**, 505; " Spectroscopy and Combustion Theory," Chapman and Hall, London, 2nd Edn., 1948) pointed out, if the upper state is considerably bent one would expect the emission system to lie at wave-lengths much longer than those of the corresponding absorption bands. This follows from the Franck–Condon principle. The extensive range covered by the emission spectrum confirms that the molecular

* In the first absorption of CS_2, however, $\nu_2' < \nu_2''$.

dimensions change considerably in the transition. Excited CO_2 molecules in the carbon monoxide flame almost certainly arise by the reaction

$$O(^3P) + CO(^1\Sigma^+) \longrightarrow CO_2^* \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It follows that the excited molecules are in a triplet state (Laidler, *J. Chem. Phys.*, 1949, **17**, 221) and that this triplet state is not more than *ca.* 130 kcal./mole above the ground state. If the excited state arises from the first excited configuration, then the system is due to the transition

$$\cdots (b_2')(a_1'), {}^3B_2 \longrightarrow \cdots (\pi_g)^4, {}^1\Sigma_g^+ \quad . \quad . \quad . \quad . \quad . \quad (7)$$
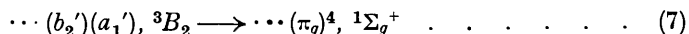
i.e., involves a change of multiplicity. Gaydon assumes that the transition is to the ground state but does not point out that this must mean the transition is forbidden because of the change of multiplicity. If the ground state is not involved, the lower state must be strongly bent and (probably) triplet. Only so will it be possible for the height of the lower state above the ground state to be sufficiently low for an emission stretching to *ca.* 3000 Å to arise from an upper state produced by (6). The lower state should not be more than 30—40 kcal. above the ground state. If the ground state is not involved, then, for obvious reasons apart from one of the states' being strongly bent, the emission system does not correspond to any known absorption system; and the vibrational frequencies present are not, as Gaydon supposes, those of the ground state.

In fact, the evidence that the lower state is the ground state is unconvincing. Thus Gaydon interprets frequency differences of 2065 and 565 cm.$^{-1}$ as the 2349 cm.$^{-1}$ (v_3) and 667 cm.$^{-1}$ (v_2) frequencies of the ground state. The discrepancies are very large if they are due to anharmonic factors concerned in transitions to high vibrational levels of the ground state. The anharmonic factors for the lower ground-state levels are known to be very small [*e.g.*, $(x_e w_e)_2 = -1\cdot3$ cm.$^{-1}$]. The observed progressions are so long that the bands can hardly *all* be to very high levels of the ground state. In the ground state Fermi resonance occurs between the v_2 and v_1 levels, the resonance splitting being $\sim$102 to 144 cm.$^{-1}$. This separation does not appear in the emission spectrum. Further, the upper state is expected to involve an excited orbital that, in comparison with the ground state, is strongly C$\longleftrightarrow$O anti-bonding. In other words, if the ground state is concerned, the transition should show progressions in v_1 of the ground state. These progressions should be represented by pairs of bands separated by the Fermi resonance splitting and with $\sim v_1$ of the ground state between the pairs. The v_1 frequency in the ground state is known to have the approximate value of 1340 cm.$^{-1}$. The anharmonicity $(x_e w_e)$ is known to be very small ($-0\cdot3$ cm.$^{-1}$), but, if the other two frequencies are markedly reduced by anharmonic factors, the v_1'' progressions should be represented by pairs of bands separated by markedly less than 1340 cm.$^{-1}$. Now the most commonly occurring intervals in the flame spectrum (Gaydon, *loc. cit.*) are 565, 1130, and 1500 cm.$^{-1}$. Intervals that occur less frequently are 345, 925, 1355, 1700, 2065, and 2260 cm.$^{-1}$; intervals that occur still less frequently are 160, 230, 515, 780, 1865, and 1915 cm.$^{-1}$. In addition Gaydon refers to the bands' tending to occur in pairs with a separation of *ca.* 60 cm.$^{-1}$ between the members of a pair. None of these frequency differences is plausibly identified as v_1 of the ground state. The only two that are close to the expected magnitude are 1130 and 1355 cm.$^{-1}$; but the first of these is rather low and is much more plausibly interpreted as 2×565 cm.$^{-1}$, while the second is too high. Gaydon makes no attempt to identify any of the observed frequency differences as v_1. If the lower state is the ground state, non-appearance of progressions in v_1 of the ground state is difficult to understand.

Let us see what interpretation of the observed frequency differences can be given if the ground state is not involved. Gaydon assumes long progressions in v_3. However, there is no precedent in the known spectra of triatomic molecules for long progressions in the unsymmetrical stretching frequency v_3. Further, such progressions would imply that one of the low-lying states of CO_2 has the C atom nearer to one O atom than to the other; and there is no theoretical expectation of such a lack of symmetry. In fact, if the emission involves a single upper state and a single lower state, we may confidently expect the system to be capable of interpretation in terms of four fundamental frequencies alone,

viz., v_1', v_2', v_1'', and v_2''. v_1' and v_1'' should both be less than 1340 cm.$^{-1}$. v_2' and v_2'' are likely to be less than or close to 667 cm.$^{-1}$ (the value of v_2 in the ground state). *All* the frequency differences greater than 1340 cm.$^{-1}$ must be interpreted as overtones or combination bands of the fundamentals. 60, 160, 230, and probably 345 cm.$^{-1}$ are too small to be plausibly interpreted as fundamentals. The very commonly occurring 565-cm.$^{-1}$ frequency is an obvious choice for one of the fundamentals. It immediately enables 1130, 1700, and 2260 cm.$^{-1}$ to be interpreted as 2×565, 3×565 and 4×565 cm.$^{-1}$ respectively. Moreover, the magnitude 565 cm.$^{-1}$ makes it practically certain that this frequency is a bending one; it is too low to be plausibly chosen as a v_1 frequency. $v_2'' = 565$ cm.$^{-1}$ is the obvious choice, since in an emission transition v_2'' is likely to be more prominent than v_2'. The existence of long progressions in v_2'' then implies that the two states concerned differ markedly in apex angle. Since we have argued that the lower state must be strongly bent, the upper must therefore be linear or only slightly bent. This is in contrast to Gaydon's interpretation that the transition is from a strongly bent upper to a linear lower (ground) state. Since the emission takes place from a hot source ($\sim 600°$ c in the " glow " of oxidizing carbon monoxide and a much higher temperature in the ordinary flame of carbon monoxide), we expect v_2' also to appear in the system, but probably less prominently than v_2''. $v_2' = 515$ cm.$^{-1}$ is the obvious choice to try. Such a choice may at once explain the tendency of bands to occur in pairs with *ca.* 60 cm.$^{-1}$ between the members of a pair since 565—515 is close to 60. On account of Boltzman factors, we should not expect the frequency 2×515 cm.$^{-1}$ to be prominent; and, in agreement, no frequency of *ca.* 1030 cm.$^{-1}$ appears. The only likely choices for the v_1 frequencies (since they must be less than *ca.* 1340 and since 1130 cm.$^{-1}$ has already been identified) are 925 and 780 cm.$^{-1}$. Of these, it is 925 cm.$^{-1}$ which, being the commoner of the two, is likely to represent v_1''. Such a choice probably accounts also for (*a*) *ca.* 1865 cm.$^{-1}$, since $2 \times 925 = 1850$, (*b*) *ca.* 345 cm.$^{-1}$, since $925 - 565 = 360$, (*c*) *ca.* 1500 cm.$^{-1}$, since $925 + 565 = 1490$, and (*d*) *ca.* 2065 cm.$^{-1}$, since $925 + (2 \times 565) = 2055$. The commonness of occurence of, *e.g.*, 1500 cm.$^{-1}$ is understandable, since it is composed from a very commonly and a fairly commonly occurring interval. This leaves $v_1' = 780$ cm.$^{-1}$. Just as 2×515 cm.$^{-1}$ did not occur, so we should not expect 2×780 cm.$^{-1}$ to appear; nor is it found. The choice, however, plausibly identifies (*a*) *ca.* 1355 cm.$^{-1}$, since $780 + 565 = 1345$, (*b*) *ca.* 1915 cm.$^{-1}$, since $780 + (2 \times 565) = 1910$, (*c*) *ca.* 160 cm.$^{-1}$, since $925 - 780 = 145$, and (*d*) *ca.* 230 cm.$^{-1}$, since $780 - 565 = 215$. This accounts for all the observed frequency intervals and moreover the whole forms an entirely reasonable, consistent, interpretation. The magnitudes of $2v_2''$ and $2v_2'$ are such that no Fermi resonance is expected with the v_1 frequencies; and in agreement no further spearation remains to be accounted for by such resonance. Moreover, it is very reasonable that v_2'' should be less than v_2', and v_1'' less than v_1'; for the lower, strongly bent state (*a*) is likely, for a reason that will be referred to again in Part III, to have more resistance to bending than the upper linear or nearly linear state and (*b*) almost certainly involves the $a_1's_A-\bar{\pi}_u$ orbital which tends to lose its C$\longleftrightarrow$O anti-bonding character as the molecule bends.

Summarizing, $v_2'' = 565$, $v_1'' = 925$, $v_2' = 515$, $v_1' = 780$ cm.$^{-1}$ and it is clear that the ground state is not involved and that the system consists of a single electronic transition. All the vibrations concerned are totally symmetrical with respect to the bent molecule and therefore there is no symmetry restriction on the number of quanta of each that may occur. The O(^{3}P) atom in (6) is expected to approach the C atom of the CO molecule along the C–O line, in such a way that an unpaired $p\sigma$ electron of the O atom interacts with a σ lone pair on the C atom. It appears probable therefore that the resulting state of CO_2 is $^3\Pi$. Having regard to what are the low-lying states (see the Figure), this must be $^3\Pi_g$. Our analysis of the flame bands requires this state to be linear or nearly linear; it is satisfactory that our Figure (though not Mulliken's correlation diagram) predicts linearity for the $^3\Pi_g$ state. The lowest excited state of CO_2, according to the Figure, should be the strongly bent $^3B_2$ (or less probably $^3A_2$) state. The flame bands are therefore most probably to be identified as due to the allowed transition

$$^3\Pi_g \longrightarrow {}^3B_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Further, there is a very low probability that a triplet, strongly bent (apex angle $135° \pm 10°$), excited state of CO_2 would emit radiation and pass to the ground state. It would behave almost like a separate chemical species, a fact that may have something to do with the " latent energy " that has been reported for carbon monoxide flames (David, Leah, and Pugh, *Phil. Mag.*, 1941, **31**, 156).

(ii) CO_2^+. Discharges through CO_2 give rise to a pair of strong bands at 2882 and 2896 Å. It is known (Bueso-Sanllehí, *Phys. Review*, 1941, **60**, 556) that these are due to the CO_2^+ molecule; that they represent the transition $\cdots (\sigma_u)(\pi_u)^4(\pi_g)^4$, $^2\Sigma_u^+ \longrightarrow$ $\cdots (\sigma_u)^2(\pi_u)^4(\pi_g)^3$, $^2\Pi_g$; that (as would be expected from the present considerations) the molecule is linear in both upper and lower states; and that the transition causes little change of the molecular dimensions.

The negative glow of discharges through streaming CO_2 or excitation of CO_2 by electron impact gives rise to an extensive system of weaker bands lying between 5000 and 2900 Å. The bands were first observed by Fox, Duffendack, and Barker and have been studied by Smyth, by Schmid, and especially by Mrozowski (*Phys. Review*, 1941, **60**, 730; 1942, **62**, 270; *Rev. Mod. Phys.*, 1942, **14**, 216). According to Pearse and Gaydon (" The Identification of Molecular Spectra," Chapman and Hall, London, 2nd Edn., 1950) these bands are believed to be due to the neutral CO_2 molecule, but this neglects the work of Mrozowski which appears to show conclusively that the bands are due to CO_2^+ and that they represent the transition $\cdots (\pi_u)^3(\pi_g)^4$, $^2\Pi_u \longrightarrow \cdots (\pi_u)^4(\pi_g)^3$, $^2\Pi_g$. As would be expected from the present arguments, rotational analysis shows that the molecule is linear in both upper and lower states. In accord with this, only v_1 vibrations appear strongly. The degradation of the bands to the red and the extensive range covered by the spectrum are understandable in view of the properties of the π_u and π_g orbitals.

(iii) CS_2. From our Figure we should expect the first absorption of the CS_2 molecule to be due to transition to a configuration correlated to $(\pi_g)^3(\overline{\pi}_u)$. The first absorption consists of a large number of bands between 3980 and 2767 Å ($\lambda_{max.} \sim 3200$ Å) (Wilson, *Astrophys. J.*, 1929, **69**, 34). It is weak, requiring several cm. pressure with a 1-m. absorption path, and is, like the first absorption peak of CO_2, plausibly interpreted as (1B′). That the CS_2 spectrum, unlike that of CO_2, consists of discrete bands is understandable since the excitation energy for CS_2 lies below that required for dissociation. One would expect the upper state to be considerably bent and to possess a considerably increased C–S distance over the ground state. Mulliken (*J. Chem. Phys.*, 1935, **3**, 720) early concluded that the upper state of the system was bent in its equilibrium form. Liebermann (*Phys. Review*, 1941, **60**, 496), from a partial vibrational analysis, showed that long progressions in v_2' occur and also that the intensity of bands originating from $v_2'' = 2$, relative to bands originating from $v_2'' = 0$ but proceeding to the same upper level, is considerably greater than would be expected from the Boltzmann factor alone. Both these facts strongly suggest a considerably bent upper state. In addition, one-quantum jumps of v_2' occur, which would be expected for a bent upper state but not for a linear one. Rotational analysis of six of the bands (at 3673, 3637, 3601, 3535, 3501, and 3468 Å) by Liebermann (*ibid.*, 1940, **58**, 183; 1941, **59**, 106A; 1941, **60**, 496) has shown them to be of the parallel type with simple P and R branches, closely resembling $^1\Sigma_u^+ \longleftarrow \ ^1\Sigma_g^+$ bands of a molecule in which both states were linear. If, however, the upper state *were* linear, alternate bands of the v_2' progression should be of a $\Pi \longleftarrow \Sigma$ type, which they are not. In fact, Liebermann has shown that the observed simple rotational structure is equally compatible with any apex angle between 125° and 180°. (As estimated above for the first excited state of CO_2, $135° \pm 10°$ would be a reasonable value for the apex angle in the excited state.) If the upper state is bent, the parallel nature of the bands identifies them as $^1B_2 \longleftarrow \ ^1\Sigma_g^+$, in agreement with the expected interpretation (1B′). Mulliken (*ibid.*, 1941, **60**, 506) has earlier shown how the observed characteristics are compatible with interpretation (1B′). The only difference between his and the present interpretation is that he supposed the upper state correlated with $^1\Pi_g$ rather than with $^1\Delta_u$. The rotational structure, on the assumption of a markedly bent molecule, indicates a considerable increase of C–S length on excitation. This is as expected for transition (1B′) and implies that progressions in v_1' should be present. These have not yet been identified. It may be

noted that v_1', when found, is expected to be somewhat greater than its value (410 cm.$^{-1}$) in the $^1\Sigma_u^+$ state (see below) since the $a_1's_A$–π_u orbital is expected to lose some of its anti-bonding character as the molecule bends; on the other hand, v_1' should be less than v_1'' which is 657 cm.$^{-1}$. The magnitude of the angular restoring forces is considerably reduced by the excitation, the frequency v_2 being 275 cm.$^{-1}$ in the upper state as against 401 cm.$^{-1}$ in the ground state. Transition (1A) has not yet been identified, but may be present in the 3980—2767-Å system.

The second absorption system of CS_2 consists of a much more intense set of bands with $\lambda_{max.}$ *ca.* 1970 Å. Almost certainly this system corresponds to the CO_2 system of $\lambda_{max.}$ *ca.* 1335 Å (Price and Simpson, 1939, *loc. cit.*) and may be interpreted as (3A'). Mulliken has previously briefly suggested that the absorption represents (3). According to the present considerations, the upper state would be expected to be slightly bent, while the C–S length would be expected to be considerably increased relatively to the ground state. That the transition covers an extensive range of the spectrum (2300—1800 Å) is not therefore surprising. Price and Simpson have already concluded that the upper state is bent through a few degrees. As a result the molecule acquires one low moment of inertia and this explains the many heads, separated by about 40 cm.$^{-1}$, observed in each band under high dispersion. The bands as a whole are shaded to the red, as expected. Only one upper-state vibration appears as a long progression. This has a frequency of *ca.* 410 cm.$^{-1}$ (390—430 cm.$^{-1}$), and undoubtedly represents the symmetrical valency-stretching frequency v_1 which is 657 cm.$^{-1}$ in the ground state.

(iv) COS. The first absorption of COS (2550—1600 Å) is much stronger than that of CO_2 or CS_2. This might be taken as evidence that the first absorption of CO_2 or CS_2 is to an upper state that correlates with $^1\Pi_g$ rather than with $^1\Delta_u$, *i.e.*, that $\bar{\sigma}_g$ lies below $\bar{\pi}_u$. The corresponding absorption of COS might then be expected to be much stronger because of the absence of a centre of symmetry in linear COS; the transition $^1\pi \longleftarrow \,^1\Sigma^+$ is allowed, whereas $^1\Pi_g \longleftarrow \,^1\Sigma_g^+$ is forbidden. An alternative explanation is equally valid, however, *viz.*, that, though the transitions $^1A_2 \longleftarrow \,^1\Sigma_g^+$ are symmetry-forbidden for CO_2 and CS_2, the analogous transitions $^1A'' \longleftarrow \,^1\Sigma^+$ are allowed for COS (apart from the Franck–Condon restriction on intensity). There should be two of these $^1A'' \longleftarrow \,^1\Sigma^+$ transitions, corresponding to the $^1A_2$ upper states of CO_2 or CS_2 correlating with $^1\Delta$ and $^1\Sigma_u^-$. In addition there should be a third transition, to a bent upper state, corresponding to the $^1B_2$ state of CO_2 or CS_2 correlating with $^1\Delta_u$. It is significant that at very low pressures ($\sim$0·01 mm. in a 1-m. path length) the absorption sub-divides into several wide diffuse bands (2380—2150, 2120—2080, and 2050—1860 Å) apparently involving three separate electronic transitions (Price and Simpson, 1939, *loc. cit.*). [That the first absorption of N_2O remains weak, while that of COS becomes comparatively strong, may be because the electronegativities of N and O are closer than those of S and O (Walsh, *Proc. Roy. Soc.*, 1951, *A*, **207**, 13), so that a bent state of NNO is not so far removed from C_{2v} symmetry as a bent state of COS.]

The second absorption region consists of some seven diffuse bands extending from *ca.* 1550 to *ca.* 1410 Å with $\lambda_{max.}$ at 1510 Å (Price and Simpson, 1939, *loc. cit.*). It undoubtedly corresponds to the CO_2 absorption of $\lambda_{max.}$ 1335 Å and the CS_2 absorption of $\lambda_{max.}$ 1970 Å. A progression probably involving v_1' is present with a difference of *ca.* 760 cm.$^{-1}$. The corresponding frequency in the ground state is 859 cm.$^{-1}$. Price and Simpson refer to the 1510-Å system as a possible first member of a Rydberg series, but this would not accord with the present interpretation as an intra-valency-shell transition and as corresponding to the CO_2 and the CS_2 system discussed above.

(v) $HgCl_2$, $HgBr_2$, HgI_2. According to analyses by Wehrli (*Helv. Phys. Acta*, 1938, 339; 1940, **13**, 153) and Sponer and Teller (*J. Chem. Phys.*, 1939, **7**, 382; *Rev. Mod. Phys.*, 1941, **13**, p. 106), the upper states of the 1731—1670, 1862—1813, and 2108—2066 Å absorption regions of $HgCl_2$, $HgBr_2$, and HgI_2 respectively are probably $^1\Sigma_u^+$. The absorption regions are therefore to be interpreted as (3). As expected, the bands are degraded to the red; and the stretching frequencies in the upper states are considerably reduced relative to the ground state. The excited states do not depart appreciably from linearity. This of course is quite possible according to the present arguments. Although the b_1''–$\bar{\pi}_u$ curve falls from right to left in the Figure its curvature is not necessarily

sufficient to cause the $^1\Sigma_u{}^+$ states to be bent. Indeed, since the $b_1{}''{-}\pi_u$ curve falls from right to left because the orbital is bonding between the end atoms, it is not unlikely that the curvature would be less when the central atom is very large (as Hg) and the end atoms are therefore far apart, whatever the molecular shape. It is significant that $\nu_2{}'$ does occur in the spectra though, in accord with the selection rules for a strictly linear upper state, always as two quanta; its occurrence indicates that the forces controlling bending have changed as a result of the transition. $\nu_3{}'$ does not occur in the spectra. $\nu_2{}'$ is less than $\nu_2{}''$ by a few cm.$^{-1}$ for each molecule (65, 36, and 30 cm.$^{-1}$, compared with 70, 41, and 33 cm.$^{-1}$ for $HgCl_2$, $HgBr_2$, HgI_2 respectively). In accord with the above absorption representing transitions to $^1\Sigma_u{}^+$ upper states a longer-wave-length absorption continuum has been observed for each molecule (Wieland, *Z. Physik*, 1932, **76**, 801; **77**, 157). The maxima of these continua are at *ca.* 1810 Å ($HgCl_2$), *ca.* 1950 Å ($HgBr_2$), and *ca.* 2660 Å (HgI_2). The continua should represent transitions to strongly bent $^1B_2$ upper states, correlating with $^1\Delta_u$.

(vi) NO_2. That a Rydberg series exists in the spectrum of NO_2 (Price and Simpson, *Trans. Faraday Soc.*, 1941, **37**, 106), the members of which are accompanied by very little vibrational structure, implies that a state of $NO_2{}^+$ exists which is non-linear and has an angle not very different from that in the ground state of NO_2. As Price and Simpson have already remarked, the Rydberg series can hardly proceed to the ground state of $NO_2{}^+$ since there is strong evidence that the latter is linear and the Franck–Condon principle would forbid photo-ionization to such a state without a large amount of accompanying vibration. The magnitude of the ionization limit obtained from the Rydberg series (12·3 v) makes it very probable that the series leads to the *first* excited state of $NO_2{}^+$ (certainly to a very low-lying excited state). We have, therefore, evidence that the first (or at least a very low-lying) excited state of $NO_2{}^+$ is considerably bent, as the present arguments would lead one to expect.

(vii) NO_2. From our Figure, for a ground-state angle of $143° \pm 11°$, the allowed transitions of longest wave-length for NO_2 should be

$$\cdots (a_2'')^2(b_2')^2(b_1''),\ ^2B_1 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad . \quad (10)$$

$$\cdots (a_2'')^2(b_2')^2(\bar{a}_1'),\ ^2A_1 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad . \quad (11)$$

$$\cdots (a_2'')^2(b_2')(a_1')^2,\ ^2B_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad . \quad (12)$$

Transitions of the types

$$\cdots (a_2'')(b_2')^2(a_1')^2,\ ^2A_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad . \quad (13)$$

$$\cdots (a_2'')^2(b_2')(a_1')(b_1''),\ ^2A_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad . \quad (14)$$

would be forbidden. By Mulliken's reasoning (*Rev. Mod. Phys.*, 1942, **14**, 204), the observed absorption bands of NO_2 between 9000 and 3200 Å (strongest between 5750 and 3520 Å) may be attributed to one or more of the transitions (10), (11), and (12). Pearse and Gaydon (*loc. cit.*) comment that more than one electronic system may be involved in the bands. Expressions (10), (11), and (12) supply examples of transitions that might be polarized in any of the three possible axes, might lead to an increase or a decrease of apex angle, and might markedly increase or hardly change the N–O distance. Transitions that cause a marked change of angle or N–O distance would be expected to occupy an extensive region of the spectrum.

Towards shorter wave-lengths should come the transitions

$$\cdots (a_2'')^2(b_2')(a_1')(\bar{a}_1'),\ ^2B_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad (15)$$

and $$\cdots (a_2'')(b_2')^2(a_1')(b_1''),\ ^2B_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \qquad . \quad . \quad (16)$$

followed at still shorter wave-lengths by

$$\cdots (b_2')(a_2'')^2(b_2')^2(a_1')^2,\ ^2B_2 \longleftarrow \cdots (b_2')^2(a_2'')^2(b_2')^2(a_1'),\ ^2A_1 \quad . \quad (17)$$

Both these are allowed and they are of the same symmetry type.

NO_2 has a second absorption system between 2600 and 2270 Å. Certain of the observed bands of this system are known to be of the parallel type with red-degraded

K-structure (Mulliken, 1942, *loc. cit.*), *i.e.*, polarized parallel to the axis of least moment of inertia and so to the O $\cdots$ O line, NO_2 being an approximately symmetric top molecule. This implies that the bands are part of a $B_2 \longleftarrow A_1$ system, the transition being assumed to be electronically allowed. Mulliken chooses either (15) or (16) to represent the system. (17) might be considered as another possibility, but, whereas (15) should lead to a small *increase* of apex angle and (16) to only a small decrease, (17) should cause a very marked decrease. Rotational analysis of the 2491-Å band has yielded angles in the ground and the excited state ($154° \pm 4°$ and $154° \pm 6°$ respectively) which differ little (Harris and King, *J. Chem. Phys.*, 1940, **8**, 775). This favours assignment to (15) or (16) rather than to (17). However, some doubt must attach to the conclusions from the rotational analysis since (*a*) the ground state angle obtained is very different from the angle reported from electron-diffraction studies (132°), and (*b*) it is not based on a complete resolution of the J-structure. That the angle has in fact changed from the ground state to the upper state is indicated by the appearance in the spectrum of vibrational bands probably representing the upper-state bending frequency v_2 (Harris, King, Benedict, and Pearse, *ibid.*, p. 765). The frequency is 523 cm.$^{-1}$, compared with 648 cm.$^{-1}$ in the ground state. Expressions (15) and (16) should lead to a considerable increase of N–O distance. In agreement, from the rotational analysis of the band at 2491 Å, it has been concluded that this distance is 1.41 ± 0.06 Å in the upper state, compared with 1.28 ± 0.03 Å in the ground state. One would expect the totally symmetrical stretching vibration (probably 1320 or 1373 cm.$^{-1}$ in the ground state) to appear in the upper state. A frequency of 714 cm.$^{-1}$ possibly represents this. However, the vibrational analysis of the system is as yet far from satisfactory, one difficulty being that the separations to long wave-lengths of the apparent origin of the system do not obviously correspond to the frequencies found in the infra-red spectrum. (In order to avoid absorption by N_2O_4, the spectrum has been studied at temperatures above 100° c, so that a number of bands due to transitions from vibrational levels of the ground state appear.) The difficulty is enhanced by the fact that the Raman spectrum of NO_2 has not yet been observed (owing to the molecules absorbing throughout the visible and the near ultra-violet regions) with the result that the v_1'' frequency is not definitely known. It should also be noted that predissociation of the bands of shorter wave-length shows that a second electronic upper state is concerned in the absorption.

A further absorption system of NO_2 occurs between 1600 and 1350 Å with $\lambda_{max.}$ at 1467 Å (Price and Simpson, *Trans. Faraday Soc.*, 1941, **37**, 106). This contains a very long vibrational progression, covering at least some fifty bands. The frequency difference is 200 cm.$^{-1}$ and almost certainly represents the v_2a_1 deformation vibration. It follows that the equilibrium form of the upper state has an apex angle very different from that of the ground state, and also has considerably reduced angular restoring forces. This suggests that the upper orbital concerned is $a_1'–\pi_u$, whose curve rises so steeply in the Figure, and perhaps that the lower orbital is one of the bonding orbitals. In other words, it is very plausible to assign transition (17) to the system. The bands of the system should be of the parallel type, but a decision awaits study under higher dispersion.

According to the Figure, the following transition should lie very close to (17) :

$$\cdots (a_1')(b_2')^2(a_2'')^2(b_2')^2(a_1')^2, \; {}^2A_1 \longleftarrow \cdots (a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1'), \; {}^2A_1 \quad (18)$$

It too should lead to a considerable decrease of apex angle, though not quite as much as (17). It should also lead to an increase of N–O distance. It is an allowed transition that should be z-polarized. Price and Simpson (*loc. cit.*) find a second absorption system to be present in the 1600—1350-Å region. It too shows a long vibrational progression, the frequency difference being roughly the same as for the system identified as (17). It seems very plausible that this represents transition (18). When the 1600—1350-Å system is examined under high dispersion, it should be possible to test whether the bands ascribed to (18) are in fact of the expected perpendicular type.

A further transition,

$$\cdots (b_1'')(a_1')^2(b_2')^2(a_2'')^2(b_2')(a_1')^2, \; {}^2B_1 \longleftarrow \cdots (b_1'')^2(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1'), \; {}^2A_1 \quad (19)$$

should lie at slightly shorter wave-lengths than (17) and (18). Transition (19) is allowed, and x-polarized, and should lead to an increase of N—O distance and a small decrease of apex angle. According to Price and Simpson's photograph (*loc. cit.*), there are faint narrow bands in the 1350—1300-Å region (which may be a continuation of the 1600—1350-Å system) followed by a strong progression beginning at 1280 Å and undoubtedly representing one of the Rydberg transitions of the molecule. Just on the long-wave-length side of the latter occur weaker, diffuse bands which Price and Simpson ascribe to transitions from vibrating ground states. This seems unlikely in view of the Boltzmann factors involved. More plausibly, the bands either represent (19) or form part of the Rydberg transition, all being due to excitation from the vibrationless ground state and the (O, O) band not being the strongest member of the system.

The absorption in the 1600—1350-Å region is strong, requiring an appearance pressure hardly greater than that required to bring out the Rydberg bands at shorter wave-lengths. In part this can be attributed to the presence of two (and perhaps three) transitions all occurring in the same region. Further, a transition such as (17) can be regarded as belonging to the $V \longleftarrow N$ class. It is related to a $\sigma_g \longleftarrow \sigma_u$ transition, wherein there is no change of angle and the wave function of the upper orbital is of the same type as that of the lower except for the possession of an extra node along the chain of atoms. Both (17) and (18) have the characteristic of $V \longleftarrow N$ transitions in that an electron is partially transferred from the end atoms to the central atom. However, a fuller discussion of why transitions (17) and (18) should have high intensity (as well as an examination of the bands under high dispersion) is required before the assignments can be considered really satisfactory. Until this is done, the assignments must be regarded as tentative, though plausible.

Price and Simpson attribute the absorption to excitation of a " π " electron in the NO bonds. According to the present assignments, however, the absorption primarily involves only orbitals which are symmetrical with respect to reflection in the molecular plane.

(viii) SO_2. In the ground state of SO_2 the only low-lying vacant orbital (see the Figure) should be the uppermost b_1''. Next in order but considerably above b_1'' comes $\bar{a}_1'$. Remembering that the apex angle in the ground state is 119°, we see that the transitions of longest wave-length should fall into two groups. The first should sub-divide as follows :

$$\cdots (a_2'')^2(b_2')^2(a_1')(b_1''), \ {}^1B_1 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2, \ {}^1A_1 \quad . \quad . \quad (20)$$

This is an allowed transition that should give rise to perpendicular bands (the molecule being assumed to be an approximately symmetric top in both lower and upper states). Further, it should lead to a small increase of apex angle and probably to a small increase of S—O length :

$$\cdots (a_2'')(b_2')^2(a_1')^2(b_1''), \ {}^1B_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2, \ {}^1A_1 \quad . \quad . \quad (21)$$

This is an allowed transition that should give rise to parallel bands and lead to a moderate decrease of apex angle and increase of S—O length.

$$\cdots (a_2'')^2(b_2')(a_1')^2(b_1''), \ {}^1A_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2, \ {}^1A_1 \quad . \quad . \quad (22)$$

This is a forbidden transition.

Experimentally, SO_2 is known to have absorption bands stretching from *ca.* 3900 to 2600 Å. Metropolis and Beutler (*Phys. Review*, 1940, **58**, 1078) showed that the regions from *ca.* 3900 to 3400 Å ($\lambda_{max.}$ *ca.* 3740 Å) and from *ca.* 3400 to 2600 Å ($\lambda_{max.}$ 2940 Å) belonged to separate transitions. The origin of the former is at 25,775 cm.$^{-1}$ (3880 Å). The latter region is the stronger, having a maximum molecular extinction coefficient of ~400 (Garrett, *J.*, 1915, 1324). The characteristics of the bands in the 3900—3400-Å region are as follows. They possess a *J*-structure degraded towards the red and a *K*-structure degraded towards the violet, the latter diverging more slowly than the former. Metropolis (*ibid.*, 1941, **60**, 283) has shown that this implies a small increase both of apex angle and of S—O length in the excited state. The conclusion is confirmed by the

vibrational structure of the transition, especially by the absence of long progressions involving the deformation frequency. That the changes are small is also confirmed by the fact that the strongest band is that representing a combination of only one quantum of each of the totally symmetrical vibrations. The arrangement of the K sub-bands shows that the transition is probably of the perpendicular type. The 3900—3400-Å system thus agrees very well with the expected characteristics of transition (20). Mulliken has previously assigned (20) to the region.

From a vibrational analysis of the 3400—2600-Å region, Metropolis (*ibid.*, p. 295) showed that (1) the origin lay at 29,622 cm.$^{-1}$ (3376 Å), the transition thus covering a very extensive region, (2) both apex angle and bond distance change markedly in the transition, (3) the frequencies in the upper state are 794 (symmetrical stretching), 345 (symmetrical deformation), and 833 cm.$^{-1}$ (anti-symmetrical stretching), compared with 1152, 525, and 1361 cm.$^{-1}$ respectively in the ground state, (4) from the vibronic selection rules, because both a_1 and b_2 vibrations appear in the upper state, the electronic part of the latter is either $^1A_1$ or $^1B_2$, and (5) the values for the excited-state frequencies when substituted in theoretical formulæ for a valence force model yield an apex angle of probably *ca.* 100° compared with 120° in the ground state, *i.e.*, they show that the apex angle decreases in the transition. Metropolis also noted that the rotational structure showed none of the regularity present in, *e.g.*, the 3900—3400-Å bands. This implies that the dimensions of the molecule have so changed that the upper state is not, even approximately, a symmetric top. This in turn makes rotational analysis difficult, but at least makes it practically certain that the angle must have decreased and the length increased during the excitation. The characteristics of the 3400—2600-Å bands thus agree very well with identification of the transition as (21). Mulliken has previously assigned (21) to the system.

The second group of transitions expected from the Figure is as follows :

$$\cdots (b_2')(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^1A_2 \longleftarrow \cdots (b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad (23)$$

This is a forbidden transition.

$$\cdots (a_1')(b_2')^2(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^1B_1 \longleftarrow \cdots (a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad (24)$$

This is an allowed transition which should lead to a moderate decrease of apex angle and a moderate increase of S—O distance. It should give rise to perpendicular bands.

$$\cdots (b_1'')(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1')^2(b_1''),\ ^1A_1 \longleftarrow$$
$$\cdots (b_1'')^2(a_1')^2(b_2')^2(a_2'')^2(b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad (25)$$

This is also an allowed transition which should give rise to bands of the perpendicular type. It should cause a greater increase of S—O distance than transition (24) [because the (a_1') orbital is less S$\leftarrow$$\rightarrow$O bonding than the (b_1'')], but comparatively little change in apex angle.

The following two allowed transitions may lie fairly close to the second group above :

$$\cdots (b_2')^2(a_1')(a_1'),\ ^1A_1 \longleftarrow \cdots (b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (26)$$
$$\cdots (b_2')(a_1')^2(\bar{a}_1'),\ ^1B_2 \longleftarrow \cdots (b_2')^2(a_1')^2,\ ^1A_1 \quad . \quad . \quad . \quad . \quad (27)$$

Transition (26) would be perpendicular, and (27) parallel. The former should cause a very marked, and the latter a small increase of apex angle.

Experimentally, SO$_2$ shows a region of absorption from *ca.* 2400 to 1800 Å ($\lambda_{max.}$ *ca.* 2000 Å). Its maximum molecule extinction coefficient is several times that of the 3400—2600-Å system. Duchesne and Rosen (*J. Chem. Phys.*, 1947, **15**, 631) have shown, by vibrational analysis, that at least two and probably three electronic transitions are involved in the region.* The first of these has its origin at 42,170 cm.$^{-1}$ (2371 Å), the vibrational frequencies appearing in the upper state being 963 (symmetrical stretching)

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* The possible third transition is to an upper state having vibrational frequencies of 845 (symmetrical stretching) and 360 cm.$^{-1}$ (symmetrical bending). Rosen (*J. Phys. Radium*, 1948, **9**, 155) gives its origin as 45,499 cm.$^{-1}$ (2198 Å) and mentions the existence of a fourth transition whose origin is at 47,510 cm.$^{-1}$ (2105 Å) with upper-state frequencies of ∼800 (ν_1) and 350 cm.$^{-1}$ (ν_3).

and 379 cm.$^{-1}$ (symmetrical bending). The high intensity and the absence of anti-symmetrical vibrations show that the transition is an allowed one. The partially resolved rotational structure of the bands of this system shows that they are of the perpendicular type, the K-structure being degraded towards the red. The J-structure remains almost completely unresolved, but seems also to be degraded towards the red. Duchesne and Rosen conclude that the transition causes a fairly marked decrease in apex angle and a small increase in bond length. These conclusions are the more reasonable when the upper-state frequencies are compared with those obtained by Metropolis for the 3400—2600-Å system. In agreement with the small increase in bond length, transitions with many quanta of the symmetrical stretching frequency are not strong. These conclusions are not as definite as one could wish, but are in fair agreement with the characteristics expected for transition (24). Mulliken has assigned (26) and (27) to the *ca.* 2000-Å region, but both these should cause a considerable increase of apex angle; in addition, (27) would be of the parallel type.

The second electronic transition involved in the 2400—1800-Å system has its origin at 44,236 cm.$^{-1}$ (2260 Å) and is stronger than the first. The vibrational frequencies appearing in the upper state are 775 (v_1) and 375 cm.$^{-1}$ (v_2). The intensity and the absence of anti-symmetrical vibrations make it virtually certain that the transition is electronically allowed. No rotational analysis has yet been made, except to show that the structure is not identical with that of the first transition in the region. However, the magnitude of the symmetrical stretching frequency suggests that the bond length has increased more in the second electronic transition than in the first. This conclusion is supported by the appearance of strong bands representing many quanta of the symmetrical stretching frequency. The rather scanty known characteristics of the transition are therefore not incompatible with its assignment to (25).

If the possible third and fourth transitions in the 2400—1800-Å region should be confirmed, the expectation is that they will be found to represent (26) and (27).

(ix) SeO_2. Selenium dioxide possesses the following absorption regions :

(*a*) 5000—3400 Å ($\lambda_{max.} \sim 4080$ Å) (Duchesne and Rosen, 1947, *loc. cit.*). The origin appears to be at $\sim$4570 Å. Prominent progressions involving the symmetrical bending frequency of the upper state ($\sim$200 cm.$^{-1}$) are present. Progressions involving the symmetrical stretching frequency are not prominent. It follows that whereas the apex angle changes appreciably in the transition, the Se–O bond length changes little. The absorption is fairly strong. This and the complete absence of anti-symmetrical vibrations show the transition to be allowed.

Duchesne and Rosen (*Nature*, 1946, **157**, 692) at first suggested that the absorption region might be analogous to that of SO_2 between 3900 and 3400 Å. Later, because this SO_2 absorption causes a more marked change of length than of angle, while the SeO_2 absorption causes a change of angle more marked than that of bond length, they abandoned this suggestion in favour of one whereby the SeO_2 transition was analogous to the SO_2 transition of origin at 2371 Å. The latter suggestion seems the more probable also because the former entails that the next absorption system of SeO_2 (3300—2300 Å) would be analogous to the SO_2 3400—2600-Å system and therefore show little or none of the expected long-wave-length shift. This implies that two electronic absorption systems of SeO_2 should be found in the infra-red region, and that the 5000—3400-Å region may be tentatively interpreted as (24).

(*b*) 3300—2300 Å ($\lambda_{max.} \sim 2700$ Å) (Duchesne and Rosen, *Physica*, 1941, **8**, 540). The origin is at 3000 Å. The most prominent feature or this absorption is the presence of progressions involving the symmetrical stretching vibration (*ca.* 665 cm.$^{-1}$ in the upper state compared with 900 or 910 cm.$^{-1}$ in the ground state). It therefore appears that the transition causes a marked change of bond length but little change of apex angle. It is probably analogous to the SO_2 system of origin at 2260 Å, and may be tentatively identified as (25).

(x) TeO_2. Tellurium dioxide possesses an absorption region from 4500 and 3000 Å with $\lambda_{max.}$ near 3550 Å (Duchesne and Rosen, 1947, *loc. cit.*). The only upper-state frequency that appears strongly is one of 650 cm.$^{-1}$, representing the symmetrical

stretching frequency (815 cm.$^{-1}$ in the ground state). This indicates that whereas the length has increased considerably during the excitation, the apex angle has changed comparatively little. There is little doubt that the system corresponds to that at 3300—2300-Å for SeO_2. It may be interpreted as (25). There should be several systems of longer wave-length to be found.

(xi) O_3. Ozone is an 18-electron molecule and has a ground-state apex angle not greatly different from that of SO_2. Its spectroscopic transitions should therefore correspond to those of SO_2. It has a weak absorption system in the visible region (7585—4380 Å; $\varepsilon_{max.} = 1\cdot12$), centred particularly on two strong, diffuse bands in the orange at about 5730 and 6020 Å (Colange, *J. Phys. Radium*, 1927, **8**, 254; Wulf, *Proc. Nat. Acad. Sci.*, 1930, **16**, 507). There are also very weak absorption bands in the infra-red (Wulf, *loc. cit.*). We suggest that one of these weak absorption regions represents transition (20), and that they therefore correspond to the SO_2 absorption of $\lambda_{max.}$ *ca.* 3740 Å. Ozone has a fairly strong absorption system in the region 2900—2300 Å ($\lambda_{max.}$ 2550 Å; $\varepsilon_{max.} \sim 2800$), which has about the same maximum extinction coefficient as the 2400—1800-Å system ($\lambda_{max.}$ *ca.* 2000 Å) of SO_2 (Wulf and Melvin, *Phys. Review*, 1931, **38**, 330). We suggest, therefore, that the 2900—2300-Å system is to be interpreted as involving some of the transitions (24) to (27). Transition (21) may give rise to known weaker absorption bands of O_3 between 3525 Å and the long-wave-length end of the 2900—2300-Å system (Fowler and Strutt, *Proc. Roy. Soc.*, 1917, *A*, **93**, 577; Wulf and Melvin, *loc. cit.*; Jakowlewa and Kondratjew, *Physikal. Z. Sowjetunion*, 1932, **1**, 471). If so, these absorption bands correspond to the 3300—2600-Å system for SO_2 ($\lambda_{max.}$ 2940 Å). The bands are diffuse and tend to degrade to the red, as expected for bands belonging to transition (21), but with no rotational structure resolved. Upper-state vibrational frequencies of ~300 and ~600 cm.$^{-1}$ appear. The former is probably ν_2 (705 cm.$^{-1}$ in the ground state), and the latter probably ν_1 (1110 cm.$^{-1}$ in the ground state). If these tentative interpretations are accepted, each transition in O_3 is shifted to long wave-lengths of its analogue in SO_2. This appears resonable, at least for those transitions [(21), (24), (25) and (27)] that involve transfer of an electron from the end atoms to the central atom.

Ozone emission bands have been observed between 4465 and 3090 Å in a mild condensed discharge through oxygen (Johnson, *Proc. Roy. Soc.*, 1924, *A*, **105**, 683). It is probable that these represent the reverse of one of the transitions involved in the 2900—2300-Å system. Transitions involving a considerable decrease in apex angle in the equilibrium form of the upper state could appear in emission (see the Figure) well to the long-wave-length side of the corresponding absorption bands.

(xii) NOCl. Nitrosyl chloride is a further 18-electron molecule, whose transitions should therefore correspond to those of SO_2 and O_3. It possesses two systems of weak absorption in the visible region (Goodeve and Katz, *Proc. Roy. Soc.*, 1939, *A*, **172**, 432). The shorter-wave-length system (maximum at 4750 Å) shows little structure. The longer-wave-length system (maximum at 6017 Å) is associated with seven more or less discrete, red-degraded bands, showing frequency differences of 1580 and 380 cm.$^{-1}$. The ground-state frequencies of nitrosyl chloride are given by Burns and Bernstein (*J. Chem. Phys.*, 1950, **18**, 1669) as 1799 cm.$^{-1}$ (a stretching vibration mainly localized in the O–N bond), 592 cm.$^{-1}$ (a stretching vibration mainly localized in the N–Cl bond), and 332 cm.$^{-1}$ (bending). The 1580-cm.$^{-1}$ upper-state frequency can only well correspond to the 1799-cm.$^{-1}$ ground-state frequency. The 380-cm.$^{-1}$ upper-state frequency may represent either the 592- or 332-cm.$^{-1}$ ground-state frequency. Both the banded absorption ($\varepsilon_{max.} \sim 1$) and the shorter-wave-length visible absorption ($\varepsilon_{max.} \sim 5$) have very low intensity. While it is possible, therefore, that one of the systems corresponds to the 3900—3400-Å region for SO_2, assignment is quite uncertain. The 3900—3400-Å region for SO_2 has been interpreted as (20). These transitions may readily be re-formulated in terms of the symbols appropriate to the C_s symmetry of NOCl.

A much stronger region of continuous absorption has a maximum at about 1900 Å (Price and Simpson, 1941, *loc. cit.*). With increasing pressure, this absorption spreads somewhat to short wave-lengths and much more to long wave-lengths. Price and Simpson suggest it is the analogue of the 1600—1350-Å system for NO_2 and the 2400—1800-Å system

for SO_2. In terms of the present assignments the former analogy cannot be very close, since the analogue of the $(a_1'-\bar{\pi}_u)$ orbital is completely filled in the ground state of NOCl. Closer analogies are likely to be found with other 18-electron rather than with 17-electron molecules. We agree with Price and Simpson that the 1900-Å region of NOCl is probably analogous to the 2400—1800-Å system of SO_2. Its interpretation is therefore probably analogous to some of the transitions (24) to (27). Like the SO_2 system, the absorption is quite strong, $\varepsilon_{max.}$ being >2000 (Goodeve and Katz, *loc. cit.*).

Between the absorption in the visible region and that of the 1900-Å system, a broad maximum of absorption occurs (see Goodeve and Katz, *loc. cit.*), some of which may represent transition (21).

(xiii) CF_2. An uncondensed discharge through the vapour of a fluorocarbon gives rise to an extensive emission spectrum of many-headed bands lying between 2340 and *ca.* 5000 Å. A vibrational analysis of the shorter-wave-length end of this system has been made by Venkateswarlu (*Phys. Review*, 1950, **77**, 676) and the transition was assigned to the molecule CF_2. The analysis, and also the presence of both J- and K-rotational structure, of the bands shows, as expected from the present considerations, that the molecule is not linear. The frequencies of the sub-heads (*i.e.*, the K-structure) fit the relation expected for parallel bands.

Laird, Andrew, and Barrow (*Trans. Faraday Soc.*, 1950, **46**, 803) have observed some of the same bands in absorption between 2350 and 2650 Å. This establishes that the lower state is the ground state, so that the polarization of the transition identifies it as $^1B_2 \longleftarrow {}^1A_1$. The vibrations to appear in the emission transition are the two that are totally symmetrical (v_1 and v_2). It follows that $^1B_2$ is the symmetry of the electronic part of the upper-state wave function. The vibrational structure then agrees with the transition being an electronically allowed one. In absorption, the bands form a single progression with successive excitation of the bending vibration in the upper electronic state (495·5 cm.$^{-1}$ compared with 666·5 cm.$^{-1}$ in the ground state). This makes it clear that the apex angle changes considerably during the transition. Venkateswarlu found the K-structure of the bands to be shaded towards the violet, while the J-structure is shaded towards the red. This implies that the apex angle is larger in the upper than in the ground state; the question whether the bond length has increased or decreased must be left open. The existence, in the emission spectrum, of a long progression involving the symmetrical stretching frequency (1162 cm.$^{-1}$ in the ground state, 750 cm.$^{-1}$ in the upper state) but with the first and second bands the strongest indicates that the change of bond length is appreciable but not large.

Considering only the transitions so far formulated for an 18-electron molecule, we find only one—*viz.*, (27)—that is a parallel transition and leads to an increase of apex angle. It may therefore be that the transition just described is to be interpreted as (27). On the other hand, one would not expect (27) to lead to a very marked increase of apex angle. There is another possibility not so far formulated; it is (see the Figure)

$$\cdots (a_1')(\bar{b}_2'),\ {}^1B_2 \longleftarrow \cdots (a_1')^2,\ {}^1A_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where $(\bar{b}_2')$ represents the $(\bar{b}_2' - \bar{\sigma}_u)$ orbital. This should lead to a marked increase of both apex angle and bond length. Mulliken (quoted by Venkateswarlu) has earlier suggested this assignment. If correct, it means that there should be several longer-wave-length systems of CF_2. Weak bands on the long-wave-length side (3700—3300 Å) of the main part of the above emission system may represent one of these additional systems.

(xiv) ClO_2. Chlorine dioxide is a 19-electron molecule. According to the Figure its ground state should be $^2B_1$.

In absorption, the molecule possesses an extensive system of red-degraded absorption bands lying between 5225 and 2600 Å (Coon, *Phys. Review*, 1940, **58**, 926L; *J. Chem. Phys.*, 1946, **14**, 665). The (000) $\longleftarrow$ (000) band is at 21,016 cm.$^{-1}$ and $\lambda_{max.}$ is at *ca.* 3300 Å. The transition is a strong one ($\varepsilon_{max.}$ at least 2000; Goodeve and Stein, *Trans. Faraday Soc.*, 1929, **25**, 738) and is therefore to be regarded as electronically allowed. Rotational analysis of the bands (Coon, 1946, *loc. cit.*) shows them to be of parallel type. Of the

longest-wave-length group of expected allowed transitions there are only two of parallel type. These may be formulated

$$\cdots (a_2'')(b_2')^2(a_1')^2(b_1'')^2, \,^2A_2 \longleftarrow \cdots (a_2'')^2(b_2')^2(a_1')^2(b_1''), \,^2B_1 \quad . \quad . \quad (29)$$

$$\cdots (b_2')(a_1')^2(b_1'')(\bar{a}_1'), \,^2A_2 \longleftarrow \cdots (b_2')^2(a_1')^2(b_1''), \,^2B_1 \quad . \quad . \quad (30)$$

Transition (29) should cause a small decrease, and (30) a small increase, of apex angle. Both should cause a considerable increase of Cl–O distance and should occupy a fairly extensive region of the spectrum. Coon (1940, *loc. cit.*) points out that twenty or more bands due to the symmetrical stretching vibration appear in the transition, but not more than two of the symmetrical bending vibration; this indicates a much more profound change of Cl–O length than of OClO angle. The magnitude of both the breathing and the bending frequency is reduced from the ground state to the upper state (945 to 708, and 447 to 290 cm.$^{-1}$, respectively). Further, the rotational analysis reveals that both K- and J-structure degrade to the red at approximately the same rate. This confirms that the change of length is more important than that of angle. Coon showed in fact that, while the Cl–O distance increased markedly, there was a small decrease in apex angle. (The figures given for the angle were 109° $\pm$ 3° in the ground state and 92° $\pm$ 6° in the upper state; but these were based upon an old electron-diffraction value for the Cl–O bond length and are subject to correction.) The observed characteristics of the system thus fit with assignment to (29). Mulliken earlier came to the same conclusion. Assignment to (29) makes the electron jump analogous to that supposed responsible for the SO_2 3400—2600-Å bands. It should be noted, however, that the latter bands are considerably weaker.