## 258. *The Structure of Ozone.*

By M. J. S. Dewar.

A π-complex structure (*J.*, 1946, 406) is proposed for ozone. This electronic interpretation requires the molecule to be an acute-angled triangle in shape. The available evidence is reviewed and shown on balance to support such a structure. Current electronic interpretations of the obtuse-angled structure are criticised.

PHYSICAL evidence has apparently confined the structure of ozone to two possibilities : the obtuse-angled structure (I) based on the electron-diffraction experiments of Shand and Spurr (*J. Amer. Chem. Soc.*, 1943, **65**, 179) and on two interpretations of the infra-red spectrum (Penney and Sutherland, *Proc. Roy. Soc.*, 1936, *A*, **156**, 678; Simpson, *Trans. Faraday Soc.*, 1945, **41**, 209); and the acute-angled structure (II), based on a third interpretation of the infra-red spectrum (Hettner, Pohlman, and Schumacher, *Z. Physik*, 1934, **91**, 372; Mulliken, *Rev. Mod. Physics*, 1942, **14**, 204; Adel and Dennison, *J. Chem. Physics*, 1946, **14**, 379). The dimensions of (I) are those given by Shand and Spurr; of (II) those given by Adel and Dennison.

The most convincing argument for (I), the structure most generally accepted, has been the difficulty of writing conventional electronic formulæ for (II); the only reasonable attempt,

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that (III) of Mulliken (*loc. cit.*), fails, since it would require ozone to be highly polar (the observed moment is small, 0·49 D., Lewis and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 3063).
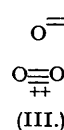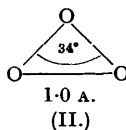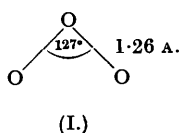

Here we shall show that a novel and satisfactory electronic interpretation can be given for (II), and that nearly all the experimental data on ozone can be explained in terms of it; and we shall also show that, apart from the electron-diffraction results, all the evidence suggests that ozone cannot have the structure (I).

Electronic Interpretation.—In three earlier papers (Dewar, *Nature*, 1945, **176**, 784; *J.*, 1946, 406, 777) it was shown that a number of organic reactions could best be interpreted in terms of a new type of bond, a bond formed by dative sharing of the π electrons of an unsaturated compound with an acceptor molecule containing a vacant atomic or π orbital. This idea is inherently reasonable and it has been further justified by quantum-mechanical calculations (Dewar, *Trans. Faraday Soc.*, in the press). The acute-angled structure (II) for ozone can readily be interpreted in terms of such *molecular* (μ) *bonds*, as follows.

In O_2 ten of the twelve valency electrons occupy in pairs, hybridisation being neglected, two atomic $2s$ orbitals, a σ orbital ($2p_x\sigma$), and two bonding π_u orbitals ($2p_y\pi_u$, $2p_z\pi_u$), the two remaining electrons occupying a degenerate level of the corresponding antibonding π_g orbitals ($2p_y\pi_g$, $2p_z\pi_g$). Removal of the π_g electrons and of one electron from each π_u orbital would leave an ion O_2^{++++} electronically analogous to a ^3P O atom; the former containing two odd electrons in mutually perpendicular π_u orbitals, the latter containing two odd electrons in mutually perpendicular p orbitals. Now the argument of the earlier paper was that π_u orbitals should qualitatively resemble p orbitals in their ability to form bonds with other atoms or groups. Therefore longitudinal overlapping of one odd-electron p orbital of ^3P O with an odd-electron π orbital of O_2^{++++} should give rise to a σ-type molecular bond of the kind considered in the earlier papers, while lateral overlapping of the other odd-electron orbitals should give rise to a π-type molecular bond. The whole process would be analogous to the formation of ethylene from two methylene radicals, and the electron distribution in the resulting O_3^{++++} molecule would be that represented diagrammatically in (IV), σ′ and π′ being the two μ orbitals.

To form neutral O_3, four electrons must be added to (IV). Now each μ orbital in (IV) will be represented in M.O. (molecular orbital) approximation as a linear combination of three atomic $2p$ orbitals; from such combinations one can form (see below) not only a bonding μ orbital but also two antibonding μ orbitals. Thus (IV) contains four antibonding μ orbitals and these are more than sufficient to hold the surplus electrons. It is convenient, when writing this structure in the notation of the earlier papers, to ignore the antibonding electrons and use the symbol (V), implying that the apical oxygen is linked by a double μ-bond to the two pairs of π electrons in O⚌O.
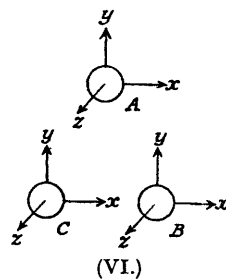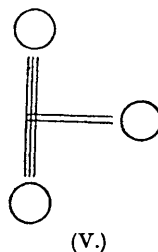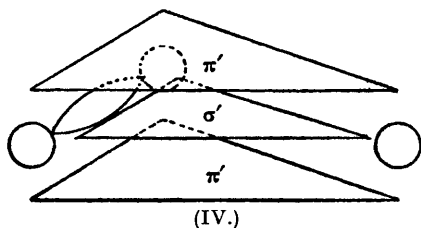
M.O. Treatment.—A more detailed discussion will now be given in terms of molecular orbital theory. The molecular orbitals will be constructed from the $2s$ and $2p$ orbitals of the three oxygen atoms, interactions with other orbitals being neglected. We set up the atomic orbitals with the orientations * indicated in (VI). The $2p_x$ and $2p_y$ orbitals lie parallel and in the plane

* There is no loss of generality in assuming this orientation; the M.O. treatment will lead to the same molecular orbitals whatever orientation is chosen initially. The orientation in (VI) simplifies the calculation, just as the use of " symmetry co-ordinates " simplifies the calculation of normal modes of vibration.

of the nuclei, the $2p_z$ orbitals perpendicular to that plane. Solution of the corresponding 12-row secular equation would give the corresponding energy levels.

This equation can, however, be simplified by using group theory. The structure (VI) belongs to symmetry group C_{2v}. From the $2s$ orbitals (A_s, B_s, C_s) and $2p$ orbitals (A_x, A_y, A_z, etc.) linear combinations are constructed which can serve as bases for irreducible representations of the group and which together are equivalent to the original set of atomic orbitals. The appropriate combinations are :

$$A_1 : \quad A_s \qquad\qquad B_1 : \quad A_x$$
$$A_y \qquad\qquad\qquad B_s - C_s$$
$$B_s + C_s \qquad\qquad B_x + C_x$$
$$B_x - C_x \qquad\qquad B_y - C_y$$
$$B_y + C_y$$
$$B_2 : \quad A_z$$
$$A_2 : \quad B_z - C_z \qquad\qquad B_z + C_z$$

Since exchange and overlap integrals between orbitals belonging to different irreducible representations vanish, the secular equation factorises into four equations, of the fifth (A_1), first (A_2), fourth (B_1), and second (B_2) orders.

Solution of the B_2 equation leads to two molecular orbitals, ($A_z + B_z + C_z$) and ($A_z - B_z - C_z$). The former corresponds to the π-type bonding μ orbital of the previous section (π' in IV) ; the latter is a corresponding antibonding μ orbital. The other antibonding orbital of this type is the single orbital ($B_z - C_z$) of representation A_2.

The A_1 equation can be simplified by neglecting interactions between s orbitals and other orbitals, so that the corresponding resonance integrals can be set equal to zero. Since interaction between the mutually perpendicular $2p_x$ and $2p_y$ orbitals may in any case be neglected, the fifth-order equation factorises into three first-order equations and one second-order equation. The former lead to an atomic A_s orbital, half the B_s and C_s orbitals, and a bonding $2p\sigma_g$ orbital ($B_x - C_x$). The latter gives two orbitals ($A_y + B_y + C_y$) and ($A_y - B_y - C_y$), of which the former corresponds to the σ-type μ orbital (σ' in IV), and the latter to a corresponding antibonding orbital. The other antibonding orbital of this type ($B_y - C_y$) may be obtained by a similar simplification from representation B_1. The other B_1 orbitals in this approximation are the remaining half of the B_s and C_s orbitals, and two μ-type orbitals ($A_x + B_x + C_x$) and ($A_x - B_x - C_x$). Since the overlap of A_x with B_x or C_x will be less than that of the corresponding $2p_y$ or $2p_z$ orbitals, the corresponding resonance integral can probably be neglected ; the two orbitals then reduce to an atomic $2p$ orbital (A_x) and an antibonding $2p\sigma$ orbital ($B_x + C_x$).

It will be seen from this discussion that the earlier qualitative treatment of the μ_z orbitals (π' in IV) was essentially correct, but that the account of the μ_y orbitals tacitly neglected s–p interactions. These interactions will make the μ_y orbitals tend towards bent σ orbitals of the type shown by Coulson and Moffitt (*J. Chem. Physics*, 1947, **15**, 151 ; and private communication) to account best for the properties of *cyclo*propane. However, in the case of ozone the effect is likely to be much smaller, in the same way that the bond orbitals of singly-bound oxygen (*e.g.*, in H_2O) have much less s-character than those in corresponding carbon compounds. The s–p interaction will then perturb, but will not qualitatively alter, the μ_y orbitals and so the earlier description will remain qualitatively satisfactory. In any case the interaction, if large, would make O_3 symmetrical ; therefore any interpretation of the electronic configuration of the acute-angled structure must involve the assumption that such interactions are small. Actual calculation of the interactions would be very difficult
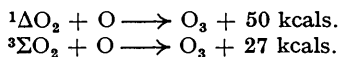
Calculation of Binding Energy.—Here again the s–p interactions will be neglected. The binding energy so calculated will be a lower limit since, according to the variation principle, the interactions cannot decrease the binding energy. The calculations are in any case very approximate since the various resonance integrals, etc., cannot be satisfactorily estimated ; but if the corresponding value for the binding energy is of the right order of magnitude, it will suggest that structure (IV) is at any rate energetically possible for ozone. For the same reason the interaction between A_x and B_x or C_x has been neglected here.

The energies of the μ_z orbitals are then found to be :

$$(\mu_y)_{as}^- \ (A_y + B_y + C_y) : \ \tfrac{1}{2}(- \beta - \sqrt{(\beta + \varepsilon)^2 + 8\alpha^2})$$
$$(\mu_y)_{as}^+ \ (A_y - B_y - C_y) : \ \tfrac{1}{2}(- \beta + \sqrt{(\beta + \varepsilon)^2 + 8\alpha^2})$$
$$(\mu_y)_s \ (B_y - C_y) : \ \beta$$

The energies are referred to the corresponding atomic $2p$ orbitals; β is the resonance integral between B_y and C_y, α that between A_y and B_y or C_y, and ε is the difference in electron affinity between O_A and O_B or O_C. The subscripts s and as refer to symmetry with respect to the twofold axis, and the superscripts $+$ and $-$ describe orbitals where the phases of A_y and $(B_y + C_y)$ are the same $(-)$ or opposite $(+)$ with respect to the plane of the molecule (corresponding to the g–u property of simple π orbitals). Similar expressions hold for the binding energies of the μ_z orbitals.

As a first approximation we may set $\alpha = \beta$, $\varepsilon = 0$. Each set of μ orbitals in O_3 holds four electrons; the total energy of each set is then $- 2\beta$, and the total μ-electron energy in O_3 is $- 4\beta$. The total π-electron energy in O_2 is $- 2\beta$ in this approximation. Since the energies are referred to a $2p$ atomic orbital as ground state, we have for the heat of formation : $O_2 + O \longrightarrow O_3 - 2\beta$. The value of β may be estimated from the π-electron energy of O_2 which is calculated to be $- 2\beta$. This value presumably refers to $^1\Delta O_2$, since the calculation ignores spin-interaction. Taking the known heat of formation of $^1\Delta O_2$ (95 kcals.) and taking the O–O single-bond energy to be 45 kcals.,* we find $\beta = - 25$ kcals. Hence

$$^1\Delta O_2 + O \longrightarrow O_3 + 50 \text{ kcals.}$$
$$^3\Sigma O_2 + O \longrightarrow O_3 + 27 \text{ kcals.}$$

The observed value is $^3\Sigma O_2 + O \longrightarrow O_3 + 25$ kcals. The very close agreement is fortuitous but at any rate shows that the present structure for ozone can lead to a heat of formation of the right order of magnitude.

Since the height of the O_3 triangle is probably somewhat greater than the base length (see below), we may expect α to be somewhat less than β. Also ε must be appreciable since the μ-electrons are introduced into a skeleton composed of O_2^{++++++} and O^{++}, the O_2 oxygens being effectively triply charged. The difference can be estimated very roughly from the energy difference of the reactions $HO^- + H^+ \longrightarrow H_2O$ and $H_2O + H^+ \longrightarrow H_3O^+$, which in M.O. approximation $\simeq \varepsilon$. We find $\varepsilon \simeq 25$ kcals. $= \beta$.

The heat of formation of ozone is not greatly altered by these changes in α and ε; thus α can hardly lie outside the range $0 \cdot 6\beta$—$0 \cdot 9\beta$, and with $\varepsilon = \beta$ the corresponding heats of formation of O_3 from $^3\Sigma O_2 + O$ are 8 and 40 kcals.

Dipole Moment and Chemical Reactivity.—In the μ_s orbital the electrons are concentrated on the base oxygens, in the μ_{as}^+ orbital mainly on the apical oxygen. In the (bonding) μ_{as}^- orbital the electrons are fairly evenly distributed, the apical oxygen having somewhat less than its share. Now with $\varepsilon = \beta$, the orbitals with highest binding energy are μ_{as}^- and μ_{as}^+. Allowing for the different charges on the oxygen atoms in the initial structure, before addition of the μ-electrons, we should expect O_3 to have an appreciable, but not very large, dipole moment directed thus : $\overset{\delta+}{O}\!\!=\!\!\overset{\delta-}{O_2}$. The moment will be further reduced by resonance between the antibonding orbitals, which the simple M.O. treatment neglects. Thus the low dipole moment of ozone can be explained by the present structure.† Moreover, the positive charge on the loosely-bound apical oxygen would account for the cationoid reactivity of ozone—it reacts readily with unsaturated hydrocarbons, which are essentially anionoid reagents, and with compounds such as alcohols and ethers which can act as sources of H^- (*e.g.*, $RO\!\!-\!\!CH_2\!\!-\!\!H$).

Further Comparison with Experiment.—(1) *Infra-red spectrum.* The infra-red evidence may be considered in some detail since it provides an almost conclusive argument for the acute-angled structure (II). The spectrum shows unambiguously that the O_3 molecule is not linear; ozone must then have three infra-red-active fundamental frequencies. The molecule can hardly be completely unsymmetrical, and the infra-red spectrum also eliminates an equilateral structure; hence only isosceles-triangular structures need be considered. Two vibrations (ν_1, ν_2) will then be symmetrical and one (ν_3) antisymmetrical.

Of the six observed bands, at 705, 1043, 1740, 2108, 2800, and 3050 cm.$^{-1}$, the last two have frequencies which are too high for fundamentals. The 1043 cm.$^{-1}$ band must be a fundamental

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* Estimates of the O–O bond-energy vary from 35 kcals. in H_2O_2 (Pauling, " The Nature of the Chemical Bond ", Cornell, 1945) to 55 kcals. in alkyl peroxides and hydroperoxides (Harris and Egerton, *Proc. Roy. Soc.*, 1938, *A*, **168**, 1).

† It is not claimed that the present structure would necessarily imply a low moment; the actual moment could only be derived by detailed calculations in which s–p interactions and also s–s interactions were considered. But the low dipole moment of ozone certainly does not exclude the present structure—as it excludes most other structures that have been suggested.

since it is by far the strongest band in the ozone spectrum, and Wulf (*Proc. Nat. Acad. Sci.*, 1927, **13**, 744) has shown that it must in addition be a symmetrical fundamental. Three selections of fundamental frequencies are then possible. Of these the selection 1043, 1740, 2108 cm.$^{-1}$ given by Simpson (*loc. cit.*) can be definitely eliminated; because the 705 cm.$^{-1}$ band would then be identified as a difference band, (1740—1043), and it is not only much stronger than one component fundamental (1740), which would be unusual, but also much stronger than the corresponding summation band (2800), which is theoretically impossible. (Apart from small second-order corrections, a summation band must be more intense than the corresponding difference band by the Boltzmann factor for the lower combining level. Here the Boltzmann factor $\simeq$ 100.)

The selection 705, 1043, 1740 cm.$^{-1}$ (Penney and Sutherland, *loc. cit.*) is highly improbable for two reasons; first, the band at 2108 cm.$^{-1}$ must be interpreted as an overtone of 1043 cm.$^{-1}$, and its intensity seems much too high for this to be possible. Secondly, the 3050 cm.$^{-1}$ band must be interpreted as a second harmonic of 1043, and the frequencies 1043, 2108, 3050 cannot be fitted to an anharmonic oscillator series (cf. Adel and Dennison, *loc. cit.*). Moreover, since 2108 cm.$^{-1}$ has a Q-branch, and would be symmetrical (being a first overtone), 1043 cm.$^{-1}$, being symmetrical, would have a Q-branch; thus the doublet 705 cm.$^{-1}$ band would be unambiguously assigned to v_3. The only assignment giving real force-constants is then $v_1 = 1750$, $v_2 = 1043$, $v_3 = 705$ cm.$^{-1}$, and this leads to an acute-angled structure. Thus the Penney–Sutherland selection of fundamentals is not only highly unlikely but it is incompatible with structure (I).

The fundamental frequencies are therefore almost certainly 705, 1043, and 2108 cm.$^{-1}$; this conclusion would be anticipated from a cursory examination of the spectrum, since these frequencies correspond to the three strongest bands.

Of these bands, 705 cm.$^{-1}$ is a doublet, while 2108 cm.$^{-1}$ has a Q-branch. Most authors have assumed that 1043 cm.$^{-1}$ is a doublet, but this conclusion is questioned by Adel and Dennison, who have given strong reasons for believing 1043 cm.$^{-1}$ to have a Q-branch. They found that the 705 cm.$^{-1}$ band, unlike 1043 cm.$^{-1}$ or 2108 cm.$^{-1}$, shows a coarse spacing in its structure (average separation 5·7 cm.$^{-1}$), the other bands having a spacing of $\sim$ 1 cm.$^{-1}$. This must imply that in the 705 cm.$^{-1}$ band the electric vector oscillates along the middle axis of inertia, and in the other two bands along the least axis. The apical angle must then be $<60°$, and 705 cm.$^{-1}$ must be the antisymmetric vibration v_3. We are then led to the assignment $v_1 = 2108$, $v_2 = 1043$, $v_3 = 705$ cm.$^{-1}$ which requires 1043 cm.$^{-1}$ to have a Q-branch. A central force treatment gave the constants quoted in Table I, and an apical angle of 39°. Also a very rough calculation of moments of inertia from the observed spacings of the bands gave $I_A = 14 \times 10^{-40}$, $I_B = 50 \times 10^{-40}$, $I_C = 64 \times 10^{-40}$ g.-cm.^{2}, with an estimated accuracy of $\pm$ 20%; the corresponding dimensions are those in (II), the apical angle agreeing with that given by the central force treatment.

A further argument against structure (I) is provided by a consideration of force-constants. The only assignments which are at all compatible with (I), those of Penney and Sutherland and of Simpson, agree in giving $k_1 = 16·0 \times 10^5$ dyne-cm.$^{-1}$, a value considerably greater than that in molecular oxygen ($11·7 \times 10^5$ dyne-cm.$^{-1}$), although the O–O bond length in (I) (1·26 A.) is greater than that in O_2 (1·21 A.). It is difficult to believe that the longer O–O bond in (I) could have the larger force constant. In Table II force constants for an O–O distance of 1·26 A. are calculated from the three best-known empirical relations; the three values agree well with their mean, $9·5 \times 10^5$ dyne cm.$^{-1}$, and this is far less than the value given by Simpson.

The force-constants given by Adel and Dennison may seem anomalous but, after all, the base-stretching constant k_1 would necessarily be very high if the internuclear distance were only 1·0 A. Still more reasonable constants are obtained for the structure (V); the calculation is unusually simple since it can easily be shown that if cross terms are neglected, the three normal vibration frequencies in such a model correspond to pure stretching of the O≡O bond (v_1; k_1), pure stretching of the O_2≡O bond (v_2; k_2), and pure bending of the O_2≡O bond (v_3; k_3). Corresponding values for the constants are given in Table I, h being the altitude of the O_3 triangle (dimensions as in VII below) :

TABLE I.

	Adel and Dennison.	This paper.
k_1	34×10^5	$20·7 \times 10^5$ (O≡O stretching)
k_2	$6·2 \times 10^5$	$6·8 \times 10^5$ (O_2≡O stretching)
k_3/h^2	—	$2·3 \times 10^5$ (O_2≡O bending)

TABLE II.

O–O Bond length (A.).

Relation.	1·00.	1·10.	1·26.	1·33.
Badger [1]	56·8 [2]	25·1	9·6	6·8
Clark [3]	36·5	20·7	9·2	7·0
Gordy [4]	32·1	18·6	9·8	6·9

[1] *J. Chem. Physics*, 1934, **2**, 128.   [2] Force constants in 10^5 dyne-cm.$^{-1}$.   [3] *Phil. Mag.*, 1934 **18**, 459.   [4] *J. Chem. Physics*, 1946, **14**, 305.

In Table II, values for the force-constants are calculated for several O–O distances. There is of course no direct evidence that the usual empirical relations would hold for so unconventional a structure as (V); rough calculation by the molecular orbital method suggests, however, that the variation in μ-bond energy with the resonance integral between the basal oxygens should parallel closely the change in π-bond energy with resonance integral in O_2; although variation in the apex-base resonance integrals may produce a greater change in μ-bond energy. Hence the dimensions (VII) calculated from the empirical relations should give a good value for the O≡O bond-length, but a less certain one for the altitude (*h*) of the O_3 triangle. Moments of inertia calculated for (VII) are also given; they agree well enough with Adel and Dennison's values, particularly since, if (VII) is correct, the molecule departs considerably from a symmetrical top and so their method of calculation would become even less reliable.

$$I_A = 17$$
$$I_B = 33 \left. \right\} \times 10^{-40} \text{ g.-cm.}^2$$
$$I_C = 50$$

(VII.)
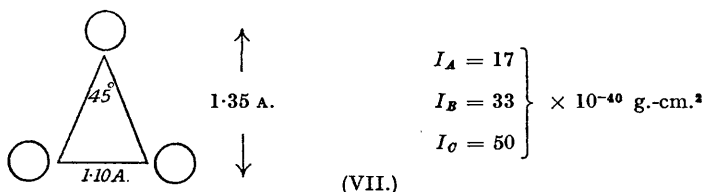
(2) *Bond lengths.* According to the arguments in the first section, the basal oxygens in O_3 are linked by a σ-bond, two strong μ-bonds, and two weak μ-antibonds. We might expect that the effective order of the basal bond would be high (∼ 2). Conversely, the apical oxygen, held by two μ-bonds and two μ-antibonds, should have an order considerably less than 2. The general configuration (VII) thus agrees well with the electronic structure (V). (Pauling gives for the single, double, and triple bond radii of oxygen 0·66, 0·55, and 0·50 A., respectively; " The Nature of the Chemical Bond ", Cornell, 1945.)

(3) *Excited states ; absorption spectrum and specific heat.* The observed specific heat of ozone (10·94 ± 0·30 cals.; Lewis and von Elbe, *J. Chem. Physics*, 1934, **2**, 294) is higher than any value calculated from any possible assignment of fundamental frequencies (cf. Simpson, *loc. cit.*) ; Lewis and von Elbe therefore concluded that ozone must contain a low-lying electronic level. The existence of relatively low-lying excited states is also indicated by the absorption spectrum, which shows weak bands ($\mu_{\text{max.}}$ 0·05) at 5730 and 6020 A. (Wulf, *Proc. Nat. Acad. Sci.*, 1930, **16**, 507). There is a further region of intense absorption ($\mu_{\text{max.}}$ 150) in the ultraviolet, with a maximum at 2540 A.

The visible bands can be assigned to transitions between the μ_{as} and μ_{as}^+ levels. Since the two sets of μ orbitals (σ′ and π′ in IV) are not identical, we should expect the two transitions to differ slightly in energy, giving rise to two absorption bands. The transitions are allowed, but the oscillator strength should be low since the two antibonding μ-orbitals do not overlap efficiently.

Such absorption of light will give rise to singlet excited states; there should also be two corresponding triplet states of lower energy, the odd electrons in the μ_{as} and μ_{as}^+ orbitals having parallel spins. Since the singlet states lie only ∼ 50 kcals. above the ground state, the triplet states may have very low excitation energies. Transition to them will naturally be forbidden and so they will not give rise to appreciable light absorption but they could account well for the specific-heat anomaly.

The strong absorption in the ultraviolet can be ascribed to transition of either an unshared 2*p* electron on the apical oxygen, or of a bonding μ_{as}^- electron, to an antibonding μ_{as}^+ orbital, The transition energies calculated by the simple M.O. method (which should give relative values of the right order of magnitude) are 1·5β and 3β, respectively. The (μ_{as}) — (μ_{as}^+) transition energy, and the π_g — π_n transition energy in O_2, are 0·5β and 2β, respectively. Since O_2 has its

maximum absorption at about 1750 A., we should expect ozone to show absorption bands at about 1200, 2300, and 7000 A. The last two values agree well enough with the observed ultraviolet and visible bands, which we can therefore identify with $(2p) \longrightarrow (\mu_{as}{}^+)$ and $(\mu_{as}) \longrightarrow (\mu_{as}{}^+)$ transitions. We may predict that ozone will also show an absorption in the vacuum ultraviolet at $\sim$ 1200 A., due to a $(\mu_{as}{}^-) \longrightarrow (\mu_{as}{}^+)$ transition. The spectrum of ozone has not been investigated in this region.

(4) *Electron diffraction.* Shand and Spurr claim that their measurements definitely exclude an acute-angled structure for ozone, establishing structure (I) with probable errors of $\pm$ 0·01 A. in the O–O bond lengths and $\pm$ 3° in the apical angle. This structure cannot, however, be reconciled with the infra-red evidence, which seems unambiguously to eliminate any structure for ozone with an apical angle > 60°. The infra-red evidence is much more cogent, since it gives information about the positions of the nuclei while electron-diffraction measurements give information only about the electron-density distribution, from which the nuclear distances are inferred. In a molecule with the unconventional structure (V), where eight electrons occupy μ-orbitals, it is conceivable that standard electron-diffraction methods may fail. Thus the main feature of Shand and Spurr's radial distribution curve, a peak at 1·26 A., may correspond to the altitude of the O_3 triangle (see VII), not much less than our admittedly rough estimate of 1·33 A. Alternatively, a structure such as (VII) with a base-length of 1·00 A. and an apical angle of 47° would be in sufficient agreement with the infra-red evidence and would have an O–O distance of 1·26 A. The other (minor) peak in the radial distribution curve would then be ascribed to spurious reflections by the μ-electron atmospheres.

Further Criticism of the Obtuse-angled Structure (I).—We shall conclude by showing that the current electronic interpretation of (I) is unsatisfactory; (I) is usually represented as a hybrid of the forms (VIII)—(XIV), and it is difficult to see how any other conceivable structure could contribute significantly.

(VIII.)   (IX.)   (X.)   (XI.)   (XII.)   (XIII.)   (XIV.)
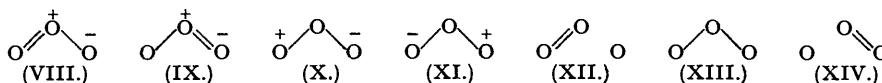
(*a*) The forms (VIII) and (IX) must contribute very little to the hybrid since ozone has so small a dipole moment.

(*b*) The forms (X) and (XI) cannot be important since their energy of formation must be very small. The bond energy of two O–O bonds is less than the heat of formation of O_2, and in these forms there is also an energetically unfavourable charge-separation.

(*c*) The forms (XII)—(XIV) imply in molecular orbital terminology a structure where each odd electron of (XIII) is hyperconjugated with the σ-bond joining the other pair of oxygens. The resonance energy would certainly be less than that of the analogous, but truly conjugated, allyl radical (15 kcals.). If ozone is represented by (XII)—(XIV), taking the highest value for the O–O bond energy (55 kcals.; see above), we obtain as an extreme upper limit to the heat of the reaction $O_2 + O \longrightarrow O_3$, 7 kcals., which is still much too low.

(*d*) It is extremely difficult to see how the forms (VIII) and (IX), analogous electronically to the main forms of the allyl anion, could fail to be important if ozone had the configuration (I); the low polarity of ozone would therefore be difficult to interpret.

(*e*) No low-lying electronic levels would be expected in a hybrid of (X)—(XIV), so the high observed specific heat of ozone could not easily be explained.

Conclusion.—Apart from the electron-diffraction experiments of Shand and Spurr, the evidence very strongly favours the acute-angled configuration (II, VII) for ozone. If this configuration can be conclusively established by further physical measurements (*e.g.*, rotational analysis of the infra-red spectrum), the interpretation of its electronic structure here given seems to follow unambiguously. The problem is therefore one of some importance since its solution may establish very directly the existence of a new type of chemical bond.

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