471. *The Electronic Orbitals, Shapes, and Spectra of Polyatomic Molecules. Part VI.** H_2AB *Molecules.*

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The correlation diagram between the orbitals possible for planar and non-planar H_2AB molecules is obtained as a special case of the diagram given in Part V for AB_3 molecules. The diagram is used to interpret the shapes of H_2AB molecules and especially to discuss the near ultra-violet spectrum of formaldehyde. It is shown that the first excited state of formaldehyde should be non-planar, though possibly only slightly so. Confirmatory evidence is found in the fluorescence spectrum. Various interpretations of the near ultra-violet spectrum are discussed, without it being possible to reach a final decision. There are, however, strong arguments for the occurrence of ν_5 in the spectrum; occurrence of this may be regarded as due to the O atom in the upper state lying very slightly out of the mirror plane which bisects the HCH angle.

PLANAR C_2AB molecules belong to the symmetry class C_{2v}. The symbols appropriate to their orbitals have been defined in Part I of this series of papers. The only symmetry element present in non-planar C_2AB molecules is the reflection plane that contains the A–B bond and bisects the CAC angle. Such molecules belong to the C_s symmetry class. For them the only orbital symbols to be used are a' and a'' according as an orbital is symmetrical or anti-symmetrical, respectively, with respect to reflection in the only plane of symmetry. The present paper deals with H_2AB molecules, leaving the non-hydride C_2AB molecules for a following paper.

Orbitals of H_2AB *Molecules.*—For H_2AB molecules the Figure shown in Part V reduces to that below. There is now only one low-lying *s* lone-pair orbital on the peripheral atoms,

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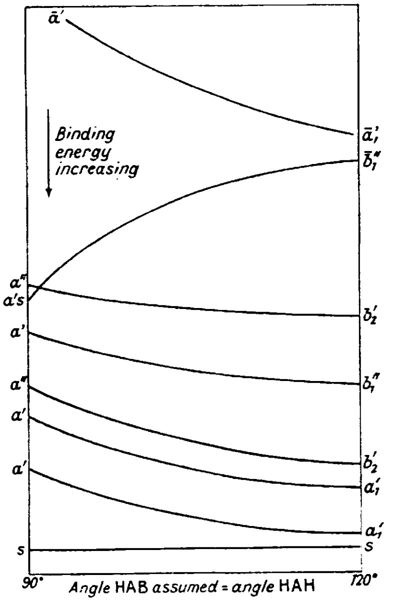
* Part V, preceding paper.

namely, that on atom B. As before we assume this to take no part in the bonding, whatever the angle HAH or HAB. For simplicity we shall assume angle HAH to be equal to angle HAB. This is unlikely always to be true (cf. $SOCl_2$ in the Table of Part V), but the assumption enables us to plot the binding energy as a function of one instead of two quantities and will not invalidate any of the conclusions reached in this paper. The lowered symmetry of H_2AB relative to AB_3 means that the degeneracy present in several pairs of orbitals of AB_3 is removed in H_2AB. Thus the three main bonding orbitals are now all separate. One of them will be localized largely in the A–B bond. In formaldehyde, CH_2O, judged from the electronegativities of the O(2*p*) and H(1*s*) orbitals (see, *e.g.*, Walsh, *Proc. Roy. Soc.*, 1951, *A*, **207**, 13) this orbital will be the most tightly bound of the three. The appropriate label for this orbital will be a_1 for C_{2v} symmetry (or a_1' if we symbolize its symmetrical nature with respect to reflection in the molecular plane) and a' for C_s symmetry. The other two main bonding orbitals are largely localized in the H_2A group. One of them corresponds to the in-phase and the other to the out-of-phase overlap of the two AH bond orbitals with each other. The C_{2v} symbols are respectively a_1 and b_2; and the C_s symbols a' and a''. The three bonding orbitals increase in binding energy from left to right in the Figure because they are built from A *p* orbitals on the left but A sp^2 orbitals on the right. The a_2'', e'', e'' group of AB_3 orbitals is now represented by a single orbital localized in the A–B bond. Generally speaking, it is more localized on B than on A. In the planar molecule this orbital is "π" with respect to the local symmetry, and b_1 with respect to the C_{2v} symmetry. In the non-planar molecule it is labelled a'. In the planar molecule the orbital is built from a *p* orbital on atom A overlapping in-phase with a *p* orbital on atom B. When angle HAH = angle HAB = 90°, however, the three *p* orbitals of the A atom are taken up in forming the three main bonding orbitals. The b_1 orbital therefore becomes more and more A$\longleftrightarrow$B bonding as the angles increase. The curve representing the orbital has consequently been drawn to drop from left to right. The corresponding orbital for AB_3 was B$\longleftrightarrow$B bonding, which offset to some extent this tendency to become more tightly bound in the planar molecule. No such offsetting factor is present for the H_2AB molecule. The e', e', a_2' group of AB_3 orbitals is now represented by a single lone-pair orbital largely localized on the B atom. In the planar molecule the axis of this orbital lies of course in the molecular plane. The C_{2v} symbol is b_2. The C_s symbol is a''. The orbital is largely non-bonding and must therefore be represented by a curve that is not far from horizontal. To some extent, however, the orbital must interact with the a''–b_2 AH_2 group orbital. This interaction increases the binding energy of the latter orbital and decreases that of the former. The interaction will obviously be the greater the nearer the AH_2 group is to the C atom. It follows that the upper a''–b_2' orbital will descend to some extent from left to right. In other words, the reason is that the upper a''–b_2' orbital is somewhat $AH_2$$\longleftrightarrow$C anti-bonding. Considering the non-bonding or anti-bonding nature of the a''–b_2' orbital compared with the bonding nature of the a'–b_1'' orbital, we see that the former is likely to be the more weakly bound. The steep a_1s–$\bar{a}_2''$ curve of the AB_3 correlation diagram has an analogue labelled $a's$–$\bar{b}_1''$ in the H_2AB diagram. It is more localized on the A than on the B atom. In the non-planar H_2AB molecule it is largely an A *s* orbital. In the planar molecule it becomes built from a *p* orbital on atom A overlapping out-of-phase with a B *p* orbital. Both these *p* orbitals have their axes at 90° to the molecular plane. In the planar molecule the molecular orbital is thus A$\longleftrightarrow$B anti-bonding. The orbital decreases greatly in binding energy



from left to right in the Figure, partly because it becomes built from A *p* rather than from A *s*, and partly because it becomes $A \leftrightarrow B$ anti-bonding instead of non-bonding.

The $\bar{a}_1$–$\bar{a}_1'$ curve of the AB_3 diagram also has its analogue, now labelled $\bar{a}'$–$\bar{a}_1'$, in the H_2AB diagram. Three anti-bonding orbitals, symmetric with respect to reflection in the molecular plane, are possible. These will be labelled $\bar{a}_1'$, $\bar{a}_1'$, and $\bar{b}_2'$ corresponding to the three bonding orbitals a_1', a_1', and b_2' of the planar molecule. Two of these orbitals ($\bar{a}_1'$ and $\bar{b}_2'$) will be more localized in the AH_2 than in the AB group; $\bar{a}_1'$ will be $H \leftrightarrow H$ bonding and $A \leftrightarrow H$ anti-bonding, $\bar{b}_2'$ will be $H \leftrightarrow H$ and $A \leftrightarrow H$ anti-bonding. The other (lowest) $\bar{a}_1'$ orbital will be largely localized in the AB group, being $A \leftrightarrow B$ anti-bonding.

The Figure has been drawn on the assumption that $\bar{b}_1''$ lies lower than the lowest $\bar{a}_1'$-orbital.

Shapes of H_2AB *Molecules.*—It is clear from the Figure that the ground state of the formaldehyde molecule, possessing 12 valency electrons, should be planar, in agreement with the known fact. On the other hand, the ground state of the H_2NF molecule, containing 14 valency electrons, will have two electrons in the $a's$–$\bar{b}_1''$ orbital; the molecule should therefore be non-planar. The ground state of the molecule H_2BF should be planar. The hypothetical radicals H_2NO and H_2CF should be non-planar in their ground states. The first excited state of formaldehyde is also expected to be non-planar, since it has lost an electron from an orbital stabilizing the planar form and has gained an electron in the $a's$–$\bar{b}_1''$ orbital.

Reactivity of H_2AB *Molecules.*—The Figure may be used in discussion of the reactivities of molecules in either their ground or their excited states. As a single example, the most weakly bound electron in the first excited state of CH_2O should be mostly localized on the C atom. If, therefore, the excited CH_2O molecule reacts with, *e.g.*, a H atom one would expect it to form the methoxyl radical.

Spectrum of Formaldehyde.—According to our Figure the lowest electronic states of the formaldehyde molecule should be

$$\cdots (b_2')^2,\ {}^1A_1 \text{ (the ground state)} \qquad (1)$$

$$\cdots (b_2')(\bar{b}_1''),\ {}^3A_2 \text{ or } {}^1A_2 \qquad (2)$$

$$\cdots (\bar{b}_1'')^2,\ {}^1A_1 \qquad (3)$$

A two-electron jump would be necessary to reach state (3) by absorption from the ground state. These four states correspond to the known low-lying states of the O_2 molecule. The latter states, in order of increasing energy, are ${}^3\Sigma_g^-$ (the ground state), ${}^1\Delta_g$ (two-fold degenerate), and ${}^1\Sigma_g^+$. If protons are pulled out of one of the O nuclei to form CH_2O, ${}^3\Sigma_g^-$ becomes ${}^3A_2$; ${}^1\Delta_g$ becomes ${}^1A_1$ and ${}^1A_2$; and ${}^1\Sigma_g^+$ becomes ${}^1A_1$. A correlation diagram between the states of O_2 and of CH_2O therefore makes it clear (since curves of the same species cannot cross) that the ground state of CH_2O correlates with one of the components of the ${}^1\Delta_g$ state of O_2, while state (3) above correlates with the ${}^1\Sigma_g^+$ state of O_2.

Also according to the Figure, the lowest-energy absorption electronic transition of formaldehyde should be

$$\cdots (b_2')(\bar{b}_1''),\ {}^3A_2 \text{ or } {}^1A_2 \longleftarrow \cdots (b_2')^2,\ {}^1A_1 \qquad (4)$$

Mulliken (*J. Chem. Phys.*, 1935, **3**, 564) and McMurry and Mulliken (*Proc. Nat. Acad. Sci.*, 1940, **26**, 312) have previously arrived at the conclusion that ${}^1A_2 \longleftarrow {}^1A_1$ represents the lowest-energy singlet←singlet transition. They believe the near ultra-violet absorption of formaldehyde represents this singlet←singlet transition. Burawoy (*Discuss. Faraday Soc.*, 1950, **9**, 70) believes the absorption to represent a triplet←singlet transition.*

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* Burawoy objects to the orbitals formulated in (4) being regarded as concerned in the transition. His evidence is not conclusive. For example, he takes as evidence against (4) the fact that a short-wave-length shift of the absorption takes place when the polarity of the double bond is increased. This, however, could easily be qualitatively explained in terms of (4). Consider the change from formaldehyde to acetone. Substitution of methyl groups will affect primarily the C atom of the CO group, and will reduce the binding energy of orbitals on that atom. Since therefore the upper orbital of (4) is largely on the C atom, a reason exists for a short-wave-length shift of the spectrum in acetone.

The transitions (4) are largely localized in the CO group, being from an orbital largely non-bonding and on the O atom to one that is rather more on the C than on the O and is C$\longleftrightarrow$O anti-bonding. It is understandable therefore that, if one of the transitions (4) represents the near-ultra-violet absorption, this absorption in many carbonyl compounds should be very similar.

What has not been previously pointed out is that the upper states of the transitions (4) should be non-planar. One might, therefore, more properly write (4) as

$$\cdots (a'')(a's),\ {}^3A'' \text{ or } {}^1A'' \longleftarrow \cdots (b_2')^2,\ {}^1A_1 \qquad . \ . \ . \ . \quad (5)$$

the upper states in their equilibrium forms having C_s rather than C_{2v} symmetry. However, the departure from planarity may be sufficiently small for the formulation (4) to be meaningful. This is especially likely when one remembers that even in NH_2F the inter-bond angle is probably ~107° (as in NH_3) and therefore that the inter-bond angle in the first excited state of formaldehyde (containing only one electron instead of two in the $a's$–$\bar{b}_1''$ orbital) is unlikely to be less than about 113°, *i.e.*, the upper state is likely to be bent by only a few degrees from planarity. None the less, a slight departure from planarity in the upper state leads to the expectation that, in either absorption or fluorescence, progressions in the out-of-plane bending vibration ($\nu_6 b_1$ *) should appear in the system. Transitions (4) should also cause a marked lengthening of the CO bond. In addition to ν_6 one therefore expects the CO valency vibration ($\nu_2 a_1$) to appear both in absorption and in fluorescence.

In contrast to the upper states (2), the upper state (3) should be *strongly* bent. The bending tends to make (3) lie lower than would otherwise be the case.

In the light of these expectations let us now consider the formaldehyde spectrum.

Fluorescence Spectrum of Formaldehyde.—The fluorescence spectrum of formaldehyde has been studied by Brand (*J. Chem. Phys.*, 1951, **19**, 377), who succeeded in assigning quantum numbers to the vibrational bands such that the frequencies of those bands could be expressed by the formula

$$\nu = (28312{\cdot}7 - 113{\cdot}2p) + [(1191{\cdot}8 - 11{\cdot}4p)n_2' - 9{\cdot}4n_2'^2] - (1165{\cdot}9n_6'' - 2{\cdot}3n_6''^2) \\ - (1755{\cdot}0n_2'' - 10{\cdot}3n_2''^2) + 6{\cdot}5n_2''n_6''.$$

A similar formula held for heavy formaldehyde (CD_2O) :

$$\nu = (28378 - 67p) + [(1173{\cdot}5 + 4{\cdot}1p)n_2' - 8n_2'^2] - (937{\cdot}8n_6'' - 3{\cdot}1n_6''^2) \\ - (1713{\cdot}1n_2'' - 9{\cdot}0n_2''^2) + 7{\cdot}0n_2''n_6''$$

The agreement between the calculated and the observed frequencies is sufficiently impressive to make it certain that Brand's analysis is largely correct. One notes that the analysis introduces only the frequencies ν_2 and ν_6. It may be taken as strong evidence that in the upper state the C–O length has changed relatively to the ground state and that also the upper state is non-planar. ν_6'' changes by as many as 8 quanta for CH_2O and 11 quanta for CD_2O. The greater number for CD_2O is understandable since the amplitude of ν_6 (mainly involving movement of the H or D atoms) will be less for CD_2O than for CH_2O, the departure from planarity in the equilibrium upper states of the two molecules being the same. Table 1 shows how in various progressions for CD_2O the intensity increases up to *ca.* 5 quanta of ν_6''. This would be expected, by the Franck–Condon principle, for a non-planar upper state.

TABLE 1. *Intensities and assignments of bands in fluorescence spectrum of* CD_2O, *according to Brand.*

n_2''	n_6''	Intensity	n_2''	n_6''	Intensity	n_2''	n_6''	Intensity	n_2''	n_6''	Intensity
0	1	5	0	2	6	1	1	5	1	2	6
0	3	7	0	4	9	1	3	9	1	4	9
0	5	10	0	6	10	1	5	6	1	6	5
0	7	6	0	8	4	1	7	2			
0	9	1									
0	11	0									

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* Many authors call this b_2 (see footnote in Part I). In the present paper the definitions of b_1 and b_2 given in Part I have been adhered to

Brand's analysis is not, however, complete. His formulæ contain the factor Xp in which p has to be given the value 1 if n_6'' is odd and 0 if n_6'' is even. Since ν_6 is not a totally symmetrical frequency, the total symmetry of the lower level differs according to whether n_6'' is even or odd. It therefore appeared that there were two principal fluorescing levels, one of which was able to combine with the ground state only when n_6'' was even and the other only when n_6'' was odd. The relation of these levels to each other was left unexplained.

Before we suggest more detailed interpretations of the fluorescence spectrum, however, let us first survey what is known of the absorption spectrum.

Absorption Spectrum of Formaldehyde.—The near ultra-violet absorption of formaldehyde stretches from *ca.* 3700 to *ca.* 2310 Å (Henri and Schou, *J. Chim. phys.*, 1928, **25**, 665; 1929, **26**, 1; Everett and Minkoff, *Trans. Faraday Soc.*, 1948, **44**, 816). The maximum intensity occurs at *ca.* 3400 Å. Henri and Schou classified the bands into series $A, B, C, D \cdots$; $B', C', D', E' \cdots$; $C''', D''', E''' \cdots$*; $C'', D'', E'' \cdots$. The main bands $A, B, C, D \cdots$ in the longer-wave-length region (A lies at 3533 Å) form a progression with a separation of *ca.* 1180 cm.$^{-1}$. In dideuteroformaldehyde the separation is almost identical (Ebers, quoted by Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 112). This implies that the vibration is almost completely localized in the CO group, in accordance with its representing the totally symmetrical ν_2 C=O valency vibration which has a frequency 1744 cm.$^{-1}$ in the ground state of CH_2O and 1700 cm.$^{-1}$ in the ground state of CD_2O. The drop in frequency implies a big lengthening of the C=O bond in the upper state, which fits with the fact that the progression does not reach maximum intensity until the sixth member and that the whole transition occupies an extensive range of the spectrum. $A, B, C \cdots$ thus form a ν_2' progression. $B', C', D' \cdots$, $C''', D''', E''' \cdots$, and $C'', D'' \cdots$ probably represent further ν_2' progressions. The $B', C', D' \cdots$ separations, however, are a little greater than those of the $A, B, C \cdots$ series; or, put in another way, the separations A–B', B–C', C–$D' \cdots$ increase towards shorter wave-lengths. The interpretations of the first members of these progressions (*viz.*, A, B', C''', C'') remain to be determined.

Towards shorter wave-lengths, the regularity and nature of the spectrum change. It is discrete to *ca.* 2750 Å, but diffuse thenceforward. The disturbance may be exemplified by the behaviour of the $A, B, C \cdots$ progression. At band G the fine structure begins to become more complex and more diffuse, the bands becoming completely diffuse after band H (*ca.* 2750 Å). Even at band F some perturbation of the progression occurs, as is evident from the separations given in Table 2. The separation E–F is greater than expected. Similar statements apply to bands G''' and G' in the spectrum. A continuous background is present from *ca.* 2670 Å onwards. Hydrogen atoms are produced by absorption of wave-lengths at least as great as 3130 Å (Calvert and Steacie, *J. Chem. Phys.*, 1951, **19**, 176). It appears obvious that at least one further electronic transition is concerned in the spectrum towards shorter wave-lengths.

TABLE 2. *Separations* (*cm.*$^{-1}$) *of the main bands in the absorption spectrum of formaldehyde. Measurements from Schou* (J. Chim. phys., 1929, **26**, 24).

A		*B*		*C*		*D*		*E*		*F*
28,278		29,464		30,630		31,771		32,900		34,032
	1186		1166		1141		1129		1132	

To the long-wave-length side of A occurs a weaker band (called α), at 3703 Å. Earlier authors have pointed out that this almost certainly represents a $0 \leftarrow 1$ band of the electronic transition, involving one of the possible ground state frequencies. The observed temperature dependence of the intensity of α (Reid and Dyne, personal communications, which revise a statement to the contrary by Schüler and Reinebeck, *Z. Naturforsch.*, 1950, **5a**, 604) supports this identification, as does the fact that the band is comparatively strong in the fluorescence spectrum.

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* Henri and Schou found an earlier band B''' of this progression. Dr. Brand has informed the author, however, that his own plates do not support the existence of such a band; though they show a progression in addition to those listed by Henri and Schou, starting at 28,744 cm.$^{-1}$ (3479 Å).

The only principal band common to the fluorescence and absorption spectra is the α one, though in addition (Brand, personal communication) (i) a band at 26,569 cm.$^{-1}$ appears weakly in both spectra and (ii) bands called β and γ (see Table 3 below) appear in the fluorescence spectrum excited by a discharge at low pressures and also in the absorption spectrum of CD_2O (they probably appear also in the absorption spectrum of CH_2O, but are overlain by bands A and B).

Dieke and Kistiakowsky (*Phys. Review*, 1934, **45**, 4), from a study of the rotational fine structures, showed that the bands *A*, *B*, *C*, *B′*, *C′*, and *C‴* were perpendicular, being polarized in the plane of the molecule and parallel to the H · · · H line (CH_2O is an approximately symmetric top molecule with the axis of least moment of inertia along the C=O line). Presumably therefore each band in the *A*, *B* · · ·, *B′*, *C′* · · ·, and *C‴*, *D‴* · · · progressions is polarized in this way. No definite evidence exists for the *C″*, *D″* · · · bands, but Dieke and Kistiakowsky state that certain bands in the spectrum appear to be of the parallel type, a statement that probably refers to the *C″*, *D″* · · · bands. The extra progression observed by Brand and beginning at 28,744 cm.$^{-1}$ also appears to consist of parallel-type bands (Brand, personal communication). The bands analysed by Dieke and Kistiakowsky show an intensity alternation of the sub-bands; this implies that the upper states of the *A*, *B* · · ·, *B′*, *C′*, · · · and *C‴*, *D‴* · · · progressions are planar or nearly so. The rotational constants found by Dieke and Kistiakowsky do not differ much from band to band. It is consistent with their analysis therefore (though not absolutely certain) that the analysed bands have the same electronic lower level (probably the vibrationless ground state) and also the same electronic upper state (though with different superimposed vibrations).

The rotational fine structure of the α band in absorption has also been partly analysed (Dyne, *J. Chem. Phys.*, 1952, **20**, 811). The structure of the part analysed is qualitatively the same as that found by Dieke and Kistiakowsky for the bands of shorter wave-length. The sub-bands again show an intensity alternation, implying that the upper state is not far from planar. The rotational constants are consistent with the band's having the same lower electronic state and also the same upper electronic state as the bands studied by Dieke and Kistiakowsky. The temperature dependence, however, shows that the lower level of α is not vibrationless. Determination of the K'' numbering shows that the lower level has total symmetry B_1 or B_2; which makes it practically certain that the lower level is the ground state with one quantum of the $\nu_5 b_2$ or one quantum of the $\nu_6 b_1$ vibration. The spacing of the sub-bands in α and in the fluorescence progression to which it belongs is not quite the same as in the absorption bands studied by Dieke and Kistiakowsky. Brand (*Trans. Faraday Soc.*, 1950, **46**, 805), assuming the rotational constants of the *A* band to apply to the fluorescence bands, has shown that this can be accounted for by a Coriolis interaction between the ν_5 and ν_6 fundamentals. According to Dyne, the α band appears to be double, the short-wave-length part having the lower level $n_6'' = 1$ and the long-wave-length part $n_5'' = 1$.

Interpretations of the Spectrum.—At the outset we have to decide whether the bands *A*, *B* · · · belong to (1) a different, or (2) the same, electronic transition as all the fluorescence bands including α. The rotational analyses are certainly consistent with (2), but it is difficult to be certain. The main fact in support of (1) is the failure of *A*, *B* · · · to appear in fluorescence. Because of this, Schüler and Reinebeck (*loc. cit.*) have adopted hypothesis (1). They suppose the fluorescence system to involve a triplet upper state and the long-wave-length part of the absorption system (bands *A*, *B* · · ·) a singlet upper state. Their particular analysis supposes α to arise from the vibrationless level of the ground state, which now appears to be definitely wrong in view of the revised data on the temperature dependence of α in absorption. Moreover, if the *A*, *B* · · · bands involve an upper state different from that of the fluorescence bands, it is remarkable that both upper states should have practically the same value of ν_2' (cf. Table 2 and Brand's formula for the fluorescence bands), and that *A*, *B* · · · should in fact occur in just the positions predicted by Brand's formula. Further, assuming α to arise from the $n_5'' = 1$ or $n_6'' = 1$ level of the ground state and allowing for the resulting Boltzmann factor, we find that the intensity of α in absorption is much too great, relatively to that of A, for α to belong to a triplet←singlet transition and A to a singlet←singlet transition (Dyne, *loc. cit.*). It appears that the balance of the evidence favours the same upper state for A, $B \cdots$ and the fluorescence bands, though one cannot rule out hypothesis (1) with certainty.

If we accept the supposition that A and α belong to the same electronic transition, we have then to interpret the observed separation of A and α, and to try to explain why A does not appear in fluorescence. The separation of A and α is *ca.* 1277 cm.$^{-1}$. Two interpretations of this separation may be given.

(i) Brand's analysis of the fluorescence bands suggests there are two fluorescing levels separated by 113 cm.$^{-1}$. The upper of these levels only combines with the ground state when n_6'' is even, the lower only when it is odd. An obvious possibility is to interpret the figure 113 cm.$^{-1}$ as the frequency $\nu_6'b_1$ in the upper state. If then the upper state were ${}^{e1}A_2$, its total symmetry would be ${}^1A_2$ or ${}^1B_2$ according as n_6' was 0 or 1. A ${}^1A_2$ level would combine with a ${}^1B_1$ lower level (n_6'' odd) but would not combine with a ${}^1A_1$ lower level (n_6'' even), whereas a ${}^1B_2$ level would combine with a ${}^1A_1$ lower level but not with a ${}^1B_1$. This interpretation has been adopted by Dyne (*loc. cit.*). It implies that α is a transition from the level $n_6'' = 1$ to the vibrationless level of the upper state and A is a transition from the vibrationless ground state to the level $n_6' = 1$ of the upper state. The interpretation of the 1277 cm.$^{-1}$ between A and α is therefore 1166 + 113 cm.$^{-1}$. α is a (0,1) band, A is a (1,0) band, and the two form part of a symmetry-forbidden electronic transition. The interpretation of the upper state as ${}^{e1}A_2$ is certainly in accord with expectations from our Figure. However, if we assume, with all previous workers, that the upper state is planar, the interpretation of 113 cm.$^{-1}$ as ν_6' is quite unconvincing. There is no precedent in the known spectra of molecules for production by a low-lying single-electron jump of such an enormous reduction of a vibrational frequency as 1166 to 113 cm.$^{-1}$. Because of this difficulty in interpreting the A–α separation as the sum of a ground-state and an upper-state frequency, the lowest ground-state frequency reported being 1166 cm.$^{-1}$, earlier authors (see Sponer and Teller, *loc. cit.*; Herzberg, " Infra-red and Raman Spectra," van Nostrand, New York, 1945) were led to question the correctness of the ground-state frequencies. Brand's analysis of the fluorescence spectrum, however, leaves no doubt of the correctness of the 1166 cm.$^{-1}$ ground-state frequency.

Another objection to interpreting the upper state as planar and $\nu_6' = 113$ cm.$^{-1}$ is that we should then expect fluorescence to occur from levels with $n_6' > 1$ and we might expect absorption bands to a level with $n_6' = 3$ (*i.e.*, *ca.* 226 cm.$^{-1}$ from A) to appear; neither of these expectations is realized. (A further, minor objection to interpretation of 113 cm.$^{-1}$ as ν_6' is that in writing a formula to express the observed frequencies as accurately as possible one then has to include a cross term between n_2' and n_6' which is of opposite sign to Brand's cross term between n_2'' and n_6''. However, the measurements of the fluorescence bands given by Brand are from low-dispersion spectrograms; and, as Dyne has pointed out, the band origins may differ appreciably from Brand's measurements, so that the data for a thoroughly satisfactory analysis do not exist and the present objection to $\nu_6' = 113$ cm.$^{-1}$ may not be significant.)

If, as the present series of papers and Brand's vibrational analysis strongly suggest, the upper state is non-planar, then a possible loophole exists in our main objection to $\nu_6' = 113$ cm.$^{-1}$. At first sight, if the upper state is non-planar, it is even more difficult to accept $\nu_6' = 113$ cm.$^{-1}$; for we should expect the bending to oppose any considerable decrease of ν_6 or even to increase it [cf. the bending frequency in the first excited state of acetylene (Part III)]. However, both the present theory and the rotational analysis suggest that the departure from planarity is not great. One has therefore to take into account the possibility of inversion in the upper state.* The appropriate symbols for the vibrations and orbitals of a C_{2v} molecule may be defined as follows :

$$\begin{array}{llcc@{\qquad}llcc@{\qquad}llcc@{\qquad}llcc} & & \sigma_v & \sigma_h & & & \sigma_v & \sigma_h & & & \sigma_v & \sigma_h & & & \sigma_v & \sigma_h \\ a_1 & \cdots\cdots & + & + & b_1 & \cdots\cdots & + & - & a_2 & \cdots\cdots & - & - & b_2 & \cdots\cdots & - & + \end{array}$$

where σ_h stands for a reflection in the plane of the molecule. These definitions come to the same thing as those based on $C_2(z)$ and σ_v given and explained in Part I. If the CH_2O

* I am indebted to one of the referees for stressing this to me, though not in the present context.

molecule becomes far from planar, the appropriate symbols become a' and a'' according to whether a + or a − is placed in the σ_v column—the σ_h column is no longer appropriate. If the molecule is far from planar the bending-vibrational levels may simply all be described as a'. If, however, the departure from planarity is only slight, these levels occur in pairs. The spacing is then alternately short and long. The lower level of each pair is symmetrical with respect to reflection in the (lost) molecular plane of symmetry and may still be described as a_1. The upper level of each pair is anti-symmetrical with respect to reflection in the (lost) plane of symmetry and may still be described as b_1. If the molecule is far from planar, *i.e.*, has a high barrier to inversion, the levels in each pair become degenerate. If, however, the molecule is only slightly non-planar, *i.e.*, has a low barrier to inversion, the splitting of the levels may become appreciable. A diagram and discussion given by Herzberg (*op. cit.*, p. 222) make the situation clear. The splitting also decreases as the reduced mass of the molecule increases, *i.e.*, it should be less for CD_2O than for CH_2O. Further, the splitting should be most marked for the levels of the vibration which most affects the departure from planarity, *i.e.*, of the $\nu_6 b_1$ vibration in this case.

It might be possible therefore for 113 cm.$^{-1}$ to represent the splitting of the first vibrational level of the expected slightly non-planar upper state of CH_2O. The corresponding figure for CD_2O is less (67 cm.$^{-1}$), as expected. The lowest vibrational level would be appropriately described as having symmetry a_1, the next (113 cm.$^{-1}$ higher) b_1, the next (higher by an amount considerably greater than 113 cm.$^{-1}$) a_1, and so on. Only by assuming a non-planar upper state and taking account of the possibility of inversion does it seem reasonable to interpret 113 cm.$^{-1}$ as a vibrational spacing. (The known inversion splitting of the lowest levels of NH_3 is much less than 113 cm.$^{-1}$., *viz.*, 0·8 cm.$^{-1}$ for the vibrationless level, 36 cm.$^{-1}$ for $n_2 = 1$, but the departure from planarity may be much less in the excited state of CH_2O than in the ground state of NH_3 and so may more than offset the greater reduced mass of CH_2O. It is known that the splitting increases very rapidly as the vibrational quantum number increases or as the height of the potential barrier to inversion decreases.)

Neither Dyne nor Brand analysed the absorption spectrum beyond band *A*. We know from the rotational analyses that, if bands B' and C''' are assumed to arise from the vibrationless ground state, they behave like ${}^1B_2 \longleftarrow {}^1A_1$ transitions. B' and C''' are 825 and 1353 cm.$^{-1}$, respectively, from *A*. Just as *A* is interpreted as the transition to the $n_6' = 1$ level, either B' or C''' might be interpreted as the transition to the $n_6' = 3$ level of the upper state. " Normally " the A–B' and probably the A–C''' separations would be regarded as too small for this to be likely, but, because of the possible alternate short and long spacing of the ν_6' vibrational levels, the interpretation is not unreasonable. The $n_6' = 3$ level would have the same total symmetry as the upper level of *A*, *viz.*, ${}^1A_2 \times b_1 = {}^1B_2$, and the polarization of the transition would be as observed. If *A* belongs to the same electronic transition as the fluorescence bands, one certainly expects *A* to have associated with it changes in n_6'. Moreover, the band apparently analogous to *A* in the spectrum of acetaldehyde (Part VII) has associated with it a progression in a frequency other than that of the C=O stretching vibration, so that one expects *A* to have associated with it bands other than *A*, *B*, *C* · · ·. The difficulty is that if only ν_2 and ν_6 are supposed to be involved in the fluorescence, one would expect only ν_2 and ν_6 to be involved in the corresponding absorption. While one of the bands B' and C''' might be interpreted as a transition to the $n_6' = 3$ level, the interpretation of the other is difficult to see. The need to interpret also C'' and the band at 28,744 cm.$^{-1}$ adds to the difficulty. Parallel bands can arise in a ‘${}^1A_2 \longleftarrow {}^1A_1$ transition, but only if we invoke a b_2 in addition to a b_1 frequency. It looks as though the absorption spectrum involves *two* electronic transitions, and/or more frequencies than ν_6 and ν_2 must be invoked.

A possible explanation of the failure of band *A* to appear in fluorescence might be given as follows. According to Sponer and Teller (*loc. cit.*) the temperature dependence of the intensity of α and the intensity of α in relation to *A* suggest a Boltzmann factor corresponding to only 600 or 700 cm.$^{-1}$. According to the present analysis, the Boltzmann factor should correspond to 1166 cm.$^{-1}$. It appears therefore that α may be appreciably stronger than is expected on the basis of a Boltzmann factor alone. The explanation is presumably that the intensity is increased because of the Franck–Condon principle, in accord with the expected non-planarity in the upper state. In emission, A will be weak relatively to α, partly because of a Boltzmann factor corresponding to 113 cm.$^{-1}$ and partly because of the effect of the Franck–Condon principle.

A main difficulty with this interpretation (as indeed with any other) of the fluorescence and absorption spectra is to achieve certainty. The explanations, as far as they go, appear possible but unproved. We turn now to the second interpretation of the A–α interval.

(ii) It may be significant that the separation of $\nu_5''b_2$ and $\nu_6''b_1$ (1280—1166 cm.$^{-1}$) is just about 113 cm.$^{-1}$. Further, the corresponding separation for CD_2O (990—938 cm.$^{-1}$), within the accuracy with which the data are known, is equal to 67 cm.$^{-1}$ which corresponds to 113 cm.$^{-1}$ for CH_2O. In other words, the separation of A and α is just equal to the ν_5'' frequency for both CH_2O and CD_2O. The separations are $28{,}313 - 27{,}036 = 1277$ cm.$^{-1}$ and $28{,}380 - 27{,}376 = 1004$ cm.$^{-1}$, respectively. It seem unlikely that these agreements are coincidental.

The supposition that ν_5 is involved receives support from Noyes' statement (*Trans. Faraday Soc.*, 1937, **33**, 1495) that the $\nu_5''b_2$ frequency is involved in the near-ultra-violet absorption spectrum of acetone. We may also note that in-plane deformation is known to occur in the 2600-Å absorption of benzene and may have fundamentally the same cause as is involved with formaldehyde. It is possible to suggest an explanation of the occurrence of ν_5 in the spectrum. If X is the mid-point of the H · · · H line, ν_5 is a vibration that causes bending of the XCO line in the plane of the molecule. From the arguments given in Parts I and II we should expect this bending to tend to occur when an orbital is occupied that is largely built from a p orbital on the C atom which has its axis in the molecular plane. There are two b_2 orbitals occupied in the ground state of CH_2O. One is largely in the CH_2 group and the other largely on the O atom. The former is probably built more from the appropriate H_2 group orbital than from the C p orbital. When an electron is excited from the O b_2 orbital [as in (4)], however, the coefficients of the components of the CH_2 b_2 orbital will change, *i.e.*, there will be a change in the restoring forces controlling in-plane bending. Hence we may expect the $\nu_5 b_2$ vibration to be aroused. If so, in the excited state the XCO line may be regarded as slightly bent in the molecular plane, much as in a certain excited state of CH_3I the I atom lies slightly off the 3-fold axis of the CH_3 group (see Part VIII). One expects the bending to be very slight, however, so that ν_5 is unlikely to be involved to an extent of more than one quantum.

Suppose we accept the fact that ν_5'' is involved in the fluorescence spectrum along with ν_2'' and ν_6''. A is then a vibrationless electronic transition. The small *short*-wave-length shift that this band undergoes in CD_2O is in accord with the usual behaviour of a vibrationless band on substitution of deuterium for hydrogen. α is the $n_5'' = 1$ band. It becomes possible to alter Brand's formula for CH_2O to the following which now contains no mysterious factor 113·2 cm.$^{-1}$:

$$\nu = 28312{\cdot}7 + (1190n_2' - 12n_2'^2) - (1165{\cdot}9n_6'' - 2{\cdot}3n_6''^2) - (1755{\cdot}0n_2'' - \\ 10{\cdot}3n_2''^2) + 6{\cdot}5n_2''n_6'' - (1280n_5'' - 3n_5''^2) + 4n_5''n_6'' + 7n_2''n_5''$$

The corresponding formula for CD_2O is

$$\nu = 28378 + (1183n_2' - 8n_2'^2) - (937{\cdot}8n_6'' - 3{\cdot}1n_6''^2) - (1713{\cdot}1n_2'' - 9{\cdot}0n_2''^2) + \\ 7{\cdot}0n_2''n_6'' - (1000n_5'') + 5{\cdot}5n_5''n_6'' + 5n_2''n_5''$$

Table 3 shows the new assignments for the bands and the observed and calculated values of the frequencies. The agreement is about as good as that given by Brand with the old assignments.

It will be observed that only lower-state levels of total symmetry $^1A_1$ or $^1B_2$ occur. Bands to lower $^1A_2$ (*e.g.*, $^{e1}A_1 \times b_1 \times b_2$) or $^1B_1$ (*e.g.*, $^{e1}A_1 \times b_1$) levels do not occur. n_5'' is never more than one. n_6'' is always even. The lower levels of the A and α bands are respectively $^1A_1$ and $^1B_2$. According to the analysis, these bands have a common upper level. Yet it is known that both bands are perpendicular. This is impossible if the upper level is singlet. One is thus driven to the conclusion that the upper level is triplet.

It is necessary to enquire what the total symmetry of the upper level will be when the effect of the triplet spin operator on the space wave function is taken into account. The product representations of spin and orbital function for C_{2v} symmetry have been given by McClure (*J. Chem. Phys.*, 1949, **17**, 665) and by Weissman (*ibid.*, 1950, **18**, 232, 1258). It is readily seen from these that the transition $^3A_2 \longrightarrow {}^1A_1$ may proceed by mixing with (*i.e.*, "stealing" intensity from) any of the three allowed transitions $^1A_1 \longrightarrow {}^1A_1$ (z-polarized), $^1B_1 \longrightarrow {}^1A_1$ (x-polarized), or $^1B_2 \longrightarrow {}^1A_1$ (y-polarized),* provided that the energies of these are sufficiently similar. In the same way, the transition $^3A_2 \longrightarrow {}^1B_2$ may proceed by mixing with either of the two allowed transitions $^1A_1 \longrightarrow {}^1B_2$ (y-polarized) or $^1B_2 \longrightarrow {}^1B_2$ (z-polarized). On the other hand, the transition $^3A_2 \longrightarrow {}^1A_2$ can only occur by mixing with either of the two allowed transitions $^1B_1 \longrightarrow {}^1A_2$ (y-polarized) or $^1B_2 \longrightarrow {}^1A_2$ (x-polarized), while the transition $^3A_2 \longrightarrow {}^1B_1$ can only occur by mixing with one of the two allowed transitions $^1A_1 \longrightarrow {}^1B_1$ (x-polarized) or $^1B_1 \longrightarrow {}^1B_1$ (z-polarized).

TABLE 3. *New assignments and calculated frequencies. Observed frequencies of band centres according to Brand.*

	n_2'	n_2''	n_5''	n_6''	Total ground-state symmetry	CH_2O		CD_2O	
						$\nu_{obs.}$, cm.$^{-1}$	$\nu_{calc.}$, cm.$^{-1}$	$\nu_{obs.}$, cm.$^{-1}$	$\nu_{calc.}$, cm.$^{-1}$
Band "*B*"	1	0	0	0	$^1A_1$	29,495	29,491	29,553	29,553 (Observed in absorption only)
Band γ ...	2	0	1	0	$^1B_2$	29,359	29,369(5)	29,715	29,714
Band "*A*"	0	0	0	0	$^1A_1$	28,313	28,313	28,380	28,378 (Observed in absorption only)
Band β ...	1	0	1	0	$^1B_2$	28,207	28,214	28,550	28,553
	1	0	0	2	$^1A_1$	27,173 *	27,168	27,690	27,690
Band "α"	0	0	1	0	$^1B_2$	27,036	27,036	27,376	27,378
	0	1	0	0	$^1A_1$	26,569 *	26,568	—	—
	1	1	1	0	$^1B_2$	26,470	26,476	—	—
	1	0	1	2	$^1B_2$	—	—	26,704	26,701
	0	0	0	2	$^1A_1$	25,990	25,990	26,515	26,515
	1	0	0	4	$^1A_1$	—	—	25,848	25,851
	0	1	1	0	$^1B_2$	25,297	25,298	25,679	25,679
	0	0	1	2	$^1B_2$	24,721	24,721	25,524	25,526
	0	1	0	2	$^1A_1$	24,258	24,258	24,824	24,825
	0	0	0	4	$^1A_1$	23,687 *	23,686	24,675	24,676
	0	2	1	0	$^1B_2$	23,579	23,581	24,003 *	23,998
	0	1	1	2	$^1B_2$	22,997	22,996	23,840	23,840
	0	0	1	4	$^1B_2$	—	—	23,698	23,698
	0	2	0	2	$^1A_1$	22,547	22,547	23,154	23,153
	0	1	0	4	$^1A_1$	21,970 *	21,967	22,999	23,000
	0	3	1	0	$^1B_2$	21,881 *	21,883	22,344 *	22,335
	0	0	0	6	$^1A_1$	21,393	21,400	22,863	22,863
	0	2	1	2	$^1B_2$	21,294	21,292	22,174 *	22,174
	0	1	1	4	$^1B_2$	—	—	22,029	22,027
	0	0	1	6	$^1B_2$	—	—	21,899	21,896
	0	3	0	2	$^1A_1$	—	—	21,499	21,499
	0	2	0	4	$^1A_1$	—	—	21,340	21,342
	0	4	1	0	$^1B_2$	20,207 *	20,211(5)	—	—
	0	1	0	6	$^1A_1$	—	—	21,201	21,201
	0	0	0	8	$^1A_1$	19,125 *	19,133	21,075	21,074
	0	3	1	2	$^1B_2$	19,613	19,607	20,528	20,525
	0	2	1	4	$^1B_2$	—	—	20,375	20,374
	0	1	1	6	$^1B_2$	—	—	20,243	20,239
	0	0	1	8	$^1B_2$	—	—	20,122	20,118
	0	2	0	6	$^1A_1$	—	—	19,552	19,557
	0	3	1	4	$^1B_2$	—	—	18,750	18,739
	0	2	1	6	$^1B_2$	—	—	18,609	18,600
	0	1	1	8	$^1B_2$	—	—	18,479	18,475
	0	0	1	10	$^1B_2$	—	—	18,366	18,365
	0	1	0	10	$^1A_1$	—	—	17,672	17,676

* These bands are overlapped each by another transition.

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* As used here, the z-axis is in the plane of the molecule and bisects the HCH angle; the y axis is in the molecular plane and parallel to the H···H line; the x axis is perpendicular to the molecular plane. McClure and Weissman interchange the x and the y axis.

Presumably the intensity of a forbidden transition in the near-ultra-violet region is "stolen" from the first really strong transition of the formaldehyde molecule which occurs at *ca.* 1745 Å. The absorption at 1745 Å is to be interpreted either as the first member of a "*s*" Rydberg series, *viz.*,

$$\cdots (b_2)(3sa_1),\ {}^1B_2 \longleftarrow \cdots (b_2)^2,\ {}^1A_1$$

where $3sa_1$ stands for a 3*s* orbital on the O atom (Walsh, unpublished work); or as

$$\cdots (b_2)(\bar{a}_1),\ {}^1B_2 \longleftarrow \cdots (b_2)^2,\ {}^1A_1$$

where $\bar{a}_1$ is the highest orbital shown in our Figure (McMurry and Mulliken, *loc. cit.*). In either case, the absorption represents a ${}^1B_2 \longleftarrow {}^1A_1$ transition. The upper state of the fluorescence bands lies almost midway between the ground state and the upper state of the 1745-Å system. One may suggest therefore that only those triplet$\longleftrightarrow$singlet transitions will occur in the near-ultra-violet region that are able to mix with the strong ${}^1B_2 \longleftrightarrow {}^1A_1$ transition. This implies that all the triplet$\longleftrightarrow$singlet bands must be *y*-polarized. Presumably the triplet upper state may be perturbed by either end of the ${}^1B_2 \longleftrightarrow {}^1A_1$ transition, provided the resulting bands are *y*-polarized. It follows that, if the upper state of the fluorescence bands is ${}^3A_2$, transitions will only be observed to ground-state levels that have total symmetry ${}^1A_1$ or ${}^1B_2$. Further, it is readily seen that no other triplet upper state can be substituted for ${}^3A_2$ in order to explain the observed facts. It is satisfactory that the conclusion that the upper state must be ${}^3A_2$ accords with the expectation from our Figure that ${}^3A_2$ is the only triplet state likely to be involved.

To recapitulate, (1) acceptance of the vibrational analysis given above forces the conclusion that the upper state is triplet and that the upper state is in fact ${}^3A_2$; (2) the ${}^3A_2$ upper level gives rise to fluorescence bands that proceed only to ${}^1A_1$ or ${}^1B_2$ lower levels and are always *y*-polarized; (3) the ${}^3A_2$ upper level behaves as ${}^1B_2$ when it combines with ${}^1A_1$ lower levels, and as ${}^1A_1$ when it combines with ${}^1B_2$ lower levels, in agreement with the vibrational analysis and the polarization data.

Interpretation of the long-wave-length end of the absorption spectrum as a triplet$\leftarrow$singlet transition is not ruled out on intensity grounds. The extinction coefficients for triplet$\leftarrow$singlet transitions in light molecules are less than unity (Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 72). Unfortunately, the extinction coefficients for the formaldehyde near-ultra-violet absorption are not known. In aqueous solution formaldehyde is hydrated and polymerized. In hexane at $-70°$ the rate of polymerization is sufficiently slow for the spectrum of the monomer to be obtained (Schou, *J. Chim. phys.*, 1929, **26**, 72), but sufficiently fast to preclude measurement of the extinction coefficients because of the difficulty of knowing the concentration of monomer. A further difficulty is that the whole near-ultra-violet absorption, as we have seen, undoubtedly involves more than one electronic transition. It should be stressed that the tentative conclusion that the upper state is triplet applies only to the fluorescence bands and to certain of the longest-wave-length bands of the absorption spectrum. It probably applies in fact only to that part of the absorption spectrum which corresponds to the long-wave-length tail of the absorption spectrum of acetaldehyde (see Part VII). For acetaldehyde the extinction coefficients are known; the long-wave-length tail stretches from *ca.* 3300 to 3400 Å and has $\varepsilon_{\text{max.}} \sim 0{\cdot}1$—$0{\cdot}2$. It is probable therefore that the extinction coefficient of the corresponding part of the formaldehyde absorption agrees with Kasha's rule.

It is of particular interest, as Burawoy has pointed out, that the origin of the first electronic absorption system in formaldehyde is moved towards shorter wave-lengths as a result of methyl substitution (see Part VII). This is the opposite of the usual effect of methyl substitution and may have an important bearing on the nature of the transition involved.

The failure of band *A* to appear in fluorescence might be explained essentially as suggested above in our discussion of the first alternative interpretation of the *A*–α interval. According to Dyne, α in absorption is about 1/20 as intense as *A*. According to Sponer and Teller, it is about 1/15 as intense. If α represents the $n_5'' = 1$ band, then in absorption at room temperature the Boltzmann factor leads to the expectation that the intensity ratio of $\alpha : A$ should be *ca.* 1/450. α is thus much stronger than it is expected to be on the basis of the Boltzmann factor alone. Presumably an intensity factor due to the Franck–Condon principle is important. It follows that, in emission, A (having, according to the present interpretation, the same upper level as α) should be weaker than α by a factor of 23—30 and may therefore not be observed.

It is readily shown from the symmetries of the spin operator given above that, in absorption from the vibrationless ground state to an ${}^{e3}A_2$ upper state, only those bands will appear for which the upper state has vibrational symmetry a_1, b_2 or a_2. A transition to ${}^3A_2$ with vibrational symmetry b_1 could not mix with the allowed ${}^1B_2 \longleftarrow {}^1A_1$ transition. This means that the absorption bands which arise from the vibrationless ground level and belong to the triplet$\leftarrow$singlet transition have vibrational interpretations limited to an odd number of quanta of b_2-vibrations, a quantum of any totally symmetrical vibration, an even number of quanta of either a b_2- or the b_1-vibration, or an odd number of quanta of b_2-vibrations in combination with an odd number of quanta of the b_1-vibration. The analysis of the fluorescence spectrum makes it probable that the only b_2-vibration which need be considered is ν_5 and that only one quantum of this will be present. B' and C''' could be interpreted in terms of these expectations. (The fact that the separations in the B', $C' \cdots$ progression are rather larger than in the A, $B \cdots$ progression may well be due to a positive interaction term between a bending and a stretching frequency such as is known to occur in the ground state vibrational formula for CO_2. The increasing separation A–B', B–C' . . . of course follows from the greater spacings in the B', $C' \cdots$ than in the A, $B \cdots$ progression.)*

On the triplet$\leftarrow$singlet explanation, however, it seems certain that, if the z-polarization of C'' and the band at 28,744 cm.$^{-1}$ is confirmed, these bands belong to a separate absorption transition, perhaps to the upper state (3).

It should be emphasized that the analysis depends on the assumption that the separation of A and α is not *accidentally* equal to ν_5''. As long as this is granted, it follows inevitably that the upper electronic state cannot be singlet. In essence, the argument is that one of the lower levels of the two bands must then belong to species A and the other to species B, and that both bands must have a common upper level. In that case, the fact that both bands are perpendicular means that the common upper level, whatever its species, cannot be singlet. On the other hand the conclusion that the upper state is triplet is not without serious difficulties. One of these is that one might have expected from the ready polymerization of formaldehyde that the lowest triplet state (expected to be ${}^3A_2$) would lie considerably lower than 80 kcal./mole above the ground state. Another difficulty lies in the fine structure of the α band. According to Brand and Dyne this fine structure implies that the short-wave-length portion of α has the lower level $n_6'' = 1$, not $n_5'' = 1$. Further, the long-wave-length component of α remains unexplained. On the present interpretation, the transition from $n_6'' = 1$ to the vibrationless upper state would lie to the *violet* side of the $n_5'' = 1$ band, but, having a ${}^1B_1$ lower level, would not be expected to occur. Finally, if the triplet$\leftarrow$singlet interpretation is correct, the ${}^1A_2 \longleftarrow {}^1A_1$ transition (and possibly other transitions) remain to be identified in the shorter-wave-length portions of the near-ultra-violet absorption.

The final interpretation of the near-ultra-violet spectrum of formaldehyde must thus await further work. However, there is no doubt that the correlation diagram (p. 2307) and the deductions that can be made from it about the shapes expected for the low-lying excited states are likely to prove useful in achieving a final satisfactory interpretation.

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* Herzberg (*Trans. Faraday Soc.*, 1931, **27**, 378) suggests that the A–B' separation represents the in-plane, totally symmetrical, CH bending frequency which is 1503 cm.$^{-1}$ in the ground state. The appearance of ν_3 would not be surprising since it is improbable that the angle HCH remains exactly equal to the angle HCO when the molecule is excited. More probably angle HCH changes relatively to angle HCO, and ν_3 may occur in consequence. However, ν_3 is not involved in the fluorescence spectrum and also the drop from 1503 to *ca.* 830 cm.$^{-1}$ seems rather large. Possibly 830 cm.$^{-1}$ represents ν_5'.