184.   *The Electronic Spectrum of Formaldehyde.*

By J. C. D. BRAND.

The banded ultraviolet spectrum of formaldehyde (2500—5500 Å) is characterised as an electronic transition to a singlet $^eA''$ excited state. The stereochemical configuration of the upper state is non-planar, but the plane bisecting the H–C–H bond angle is a symmetry plane of the nuclei (point-group C_s) and the excited electronic wave-function is antisymmetric to this plane. The transition is allowed by the selection rules if the dipole moment change is parallel to the b-axis of inertia; and the low intensity is attributed partly to the change of nuclear configuration (Franck–Condon principle) and partly to the intrinsically small overlap of the electronic wave functions.

The rotational constants $A_{[v]}$ and $D_{[v]} = (B_{[v]} + C_{[v]})/2$ of the vibrationless level of the A'' state are evaluated from the resolved rotational structure of the fluorescence bands. The values are consistent with the following set of geometrical parameters: C–H $= 1.09_1$ Å (assumed), C–O $= 1.32_2$ Å, $\widehat{HCH} = 120°$, and $\widehat{HCO} = 116\frac{1}{2}°$. The hybridisation at the central carbon atom (between sp^2 and sp^3) is not well defined, and possible reasons for this are discussed.

THE electronic band spectrum of formaldehyde has been discussed in many papers. The absorption bands, extending from 2300 to about 3530 Å,[1,2] were first recorded by Henri and Schou, and a brilliant analysis of the rotational structure was later completed by Dieke and Kistiakowsky.[3] The vibrational analysis has been developed more slowly, but absorption intervals of 1180 and 824 cm.$^{-1}$ were noted in the early work and the assignment of the former to the C–O stretching frequency of the excited state[4] has been confirmed by measurements with isotopic formaldehyde.[5] The fluorescence spectrum,

[1] (a) Henri and Schou, *Z. Physik*, 1928, **49**, 774; (b) Schou, *J. Chim. phys.*, 1928, **25**, 665; 1929, **26**, 1.
[2] Everett and Minkoff, *Trans. Faraday Soc.*, 1948, **44**, 816.
[3] Dieke and Kistiakowsky, *Phys. Rev.*, 1934, **45**, 4.
[4] Herzberg, *Trans. Faraday Soc.*, 1931, **27**, 378.
[5] Sponer and Téller, *Rev. Mod. Physics*, 1941, **13**, 75.

first observed as a chemiluminescence,[6] is readily excited either optically [7] or in a discharge,[8] progressions in the ground state carbonyl frequency being strongly marked. As there is outwardly very little resemblance in the structure of the fluorescence and the absorption spectra, it has frequently been argued that different electronic levels (or levels of different multiplicity) are involved,[8b] and attempts to interpret the spectrum in terms of a single electronic transition and a *planar* excited state have always run into serious difficulty.[9] The assumption of a *pyramidal* excited state, however, offers a promising solution of several outstanding problems in the analysis :[10] this hypothesis is adopted in the present paper, and all the important transitions and resolved rotational structure are interpreted, new experimental results for [$^2H_1$]- and [$^2H_2$]-formaldehyde being used. A brief account of these experiments has already been published.[11]

EXPERIMENTAL

[$^2H_2$]Formaldehyde was prepared by photosensitised combination of deuterium and carbon monoxide.[12] [$^2H_1$]Formaldehyde (mixed with the [$^1H_2$]- and the [$^2H_2$]-isomer) was obtained similarly, a mixture of hydrogen and deuterium being used.

Spectra.—Spectra were recorded in absorption with a Hilger E 2 quartz spectrograph, and in emission with a medium glass spectrograph (9 Å/mm. at 3700 Å). The absorption path was 0·005—1 m. atm. (to 0·1 m. atm. only with [$^2H_2$]formaldehyde) and the effect of temperature was observed qualitatively in tubes heated to 250°. The emission spectrum was excited by a h.f. electrodeless discharge through flowing formaldehyde vapour at a pressure of a few mm. and was recorded in exposures of up to 5 min. with a 0·02-mm. slit. Partial decomposition occurred in the discharge, the spectra of CO (Ångström and Herzberg systems), CH, and atomic hydrogen being excited in addition to the formaldehyde fluorescence; a number of weak fluorescence bands may have been lost in the background. Wavelengths, referred to iron arc standards, were determined with a Pye comparator, and the rotational structure of the bands was measured with a Hilger non-recording microphotometer.

INTERPRETATION OF THE SPECTRUM.

(1) *The Absorption Spectrum.*—The representation of the fundamentals of a C_s (pyramidal) excited state is $4a' + 2a''$, the breakdown into stretching (ν), deformational (δ), and rocking (γ) modes being

a'		a''
ν (CH)	ν (CO)	ν' (CH)
δ (CH$_2$)	γ (CH$_2$)	γ' (CH$_2$)
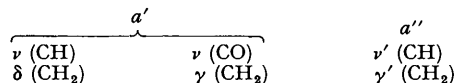
Perpendicular and parallel bands both occur in absorption. The latter are relatively weak and have not been recorded previously; under medium dispersion they have a sharp head on the violet side and traces of closely-spaced rotational sub-maxima (probably R sub-heads) degrading to the red region. Progressions with the interval ν(CO) are strongly marked in absorption,[1a] the arrangement of the first members (or " origins ") being shown in Fig. 1. The A($\perp$) and a($\parallel$) progressions involve only the excited state fundamental ν(CO).* With H·CHO, strong origins occur 824 (B$_0$), 1322 (C$_0$), and 2872 (E$_0$) cm.$^{-1}$ higher in frequency than A$_0$, the first interval being repeated between the bands F$_0$ and E$_0$.

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* In the present notation $\perp$ and $\parallel$ bands are distinguished by upper and lower case letters, respectively. The subscript gives the number of quanta of ν(CO) excited in the upper state; all " origins " therefore have subscript zero. The assigned progressions are labelled A (or a) to F in order of increasing magnitude of the fundamentals, *excluding* ν(CO), excited in the upper state. Schou's original notation, which is difficult to adapt to changes of assignment, is noted in Table 2.

[6] Emeléus, *J.*, 1926, 2948.
[7] Herzberg and Franz, *Z. Physik*, 1932, **76**, 720; Gradstein, *Z. phys. Chem.*, 1933, *B*, **22**, 384.
[8] (*a*) Schuler, *Physikal. Z.*, 1944, **45**, 61; (*b*) Schuler and Reinebeck, *Z. Naturforsch.*, 1950, **5a**, 604; (*c*) Dyne, *J. Chem. Phys.*, 1952, **20**, 811.
[9] See Dyne, ref. 8(*c*), and earlier references.
[10] Walsh, *J.*, 1953, 2306.
[11] Brand, *Chem. and Ind.*, 1955, 167.
[12] *Idem, Trans. Faraday Soc.*, 1954, **50**, 431.

TABLE 1. A' *Fundamental frequencies of excited formaldehyde.*

Funda-mental	Spectral interval (cm.⁻¹)			Fundamental	Spectral interval (cm.⁻¹)		
	H·CHO	D·CHO	D·CDO		H·CHO	D·CHO	D·CDO
ν(CH) ... $E_0 - A_0$	2872	—	2078	δ(CH₂) .... $C_0 - A_0$	1322	—	missing
				$d_0 - b_0$	1318	1071	989
ν(CO) ... $A_1 - A_0$	1182	1188	1176	γ(CH₂) { $1^- - 0^-$ $B_0 - A_0$	824	701	604
$B_1 - B_0$	1204	1182	1178	$F_0 - E_0$	817	—	598
$a_1 - a_0$	1172	—	1178				
$b_1 - b_0$	1187	1195	1174	$1^+ - 0^+$ $b_0 - a_0$	540	458	386

Rotational constants of excited formaldehyde.[3]

Band	A_0	B_0	A_1	C_0	B_1	A_2
ν_0	28,312·7	29,136·6	29,495·1	29,634·5	30,340·1	30,658·7
$A'_{[v]}$	8·749	8·613	8·701	8·893	8·24	8·653
$D'_{[v]}$	1·067	1·067	1·056	1·066	1·055	1·046

The 1180 [$= \nu$(CO)] cm.⁻¹ and 1320 cm.⁻¹ frequencies are present in the parallel system of bands, together with a new interval (540 cm.⁻¹) which appears in place of 824 cm.⁻¹. The assignments suggested for all these frequencies are in Table 1, although a closer examination of the 824 and 540 cm.⁻¹ intervals, at present grouped together under γ(CH₂), is deferred to
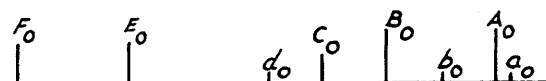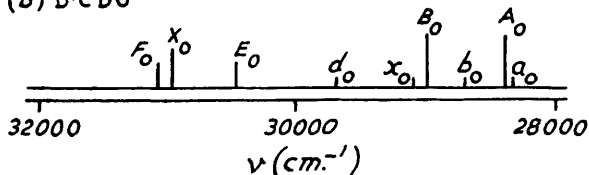

FIG. 1. *Active origins in the absorption spectrum of formaldehyde.*

a later section (cf. Fig. 3). The information obtained from the parallel system is rather limited, owing to the low intensity of the bands; thus the e progression of parallel bands was not observed, probably because it is hidden by the broad and much stronger bands of the E progression, and the a bands are partly covered in absorption by the A progression.

The assignment of the A, B, and C progressions is supported by the upper-state rotational constants [3] of the A_0, B_0, A_1, C_0, B_1, and A_2 bands of [¹H₂]formaldehyde. The appropriate constants are summarised at the foot of Table 1. In first approximation the constant $D = (B + C)/2$ is determined by the C–O bond length, and therefore is sensitive to the quantum level of ν(CO) but not to the principally hydrogen vibrations; accordingly, we find $D'_{[v]} = 1·067 \pm 0·001$ cm.⁻¹ for the origins A_0, B_0, and C_0, the decrement being $\sim$0·01 cm.⁻¹ per quantum in higher members of the progressions. The constants $A'_{[v]}$ are somewhat less regular (particularly in the B progression, which is subject to a rotational perturbation) but it is noteworthy that the highest value is for the band C_0. This is consistent with the assignment of $C_0 - A_0$ to the fundamental δ(CH₂) which is the only vibration expected to lead on excitation to an increment in $A'_{[v]}$.

Band frequencies in absorption are listed in Table 2, the recorded frequency being for the strongest " line " of the partially resolved envelope of a perpendicular band, or for the sharp R head of a parallel band. The present assignments are limited to the region between 28,000 and 34,000 cm.⁻¹; at higher frequencies the bands are predissociated and finally become diffuse. The transitions in Table 2 are non-temperature sensitive, emanating from the vibrationless ground state. The temperature-sensitive absorption bands are more conveniently classed with the fluorescence system (Table 3).

The weak C progression is apparently missing from the spectrum of [²H₂]formaldehyde, but the interval $d_0 - b_0 = 989$ cm.⁻¹ has approximately the correct isotopic shift and is

TABLE 2. *Band centres in the absorption spectrum of formaldehyde.*

Notation		Frequency (cm.⁻¹)		Notation		Frequency (cm.⁻¹)	
This paper	Schou	H·CHO	D·CDO	This paper	Schou	H·CHO	D·CDO
a_0	—	28,196 ᵃ (ww)	28,309 ᵃ (ww)	B_2	D'	31,533 (ms)	31,319 (s)
A_0	A	28,315 (m)	28,377 (m)	x_2	—	—	31,390 (www)
b_0	—	28,736 (ww)	28,695 (ww)	A_3	D	31,804 (ms)	31,853 (s)
B_0	B'	29,137 (m)	28,981 (m)	b_2	—	—	31,025 (ww)
x_0	—	—	29,081 (www)	F_0	E'''	32,004 (mw)	31,053 (w)
a_1	—	29,368 ᵃ (ww)	—	E_1	E''	32,363 (m)	31,616 (mw)
A_1	B	29,496 (ms)	29,553 (ms)	X_1	—	—	32,122 (m)
C_0	C'''	29,694 ᵇ (w)	—	B_3	E'	32,701 (s)	32,455 (s)
b_1	C''{	29,923 (ww)	29,869 (ww)	A_4	E	32,930 (s)	32,970 (ss)
d_0		30,054 (ww)	29,684 (ww)	F_1	F'''	33,168 (m)	32,229 (mw)
B_1	C'	30,343 (m)	30,159 (ms)	E_2	F''	33,536 (s)	32,754 (m)
x_1	—	—	30,244 (www)	X_2	—	—	33,284 (ms)
a_2	—	30,524 ᵃ (ww)	—	B_4	F'	33,868 (s)	33,583 (s)
A_2	C	30,659 (ms)	30,710 (s)	F_2	—	—	33,380 (mw)
C_1	D'''	30,875 ᵇ (w)	—	E_3	—	—	33,876 (m)
E_0	D''	31,187 (mw)	30,455 (w)	A_5	F	34,035 (ss)	34,082 (s)
X_0	—	—	30,945 (mw)				

s = strong, m = medium, w = weak, etc.

ᵃ Band partly covered by the red branches of the neighbouring *A*-band. ᵇ *R*-head of the $K'' = 3$ sub-band. The band centre is covered by the violet branches of the adjacent *A*-band.

assigned provisionally to $\delta(CD_2)$. The X progression of [²H₂]formaldehyde ($X_0 - A_0 = 2568$ cm.⁻¹) has no obvious counterpart in the spectrum of the light molecule and is difficult to assign. Ostensibly, a 2568 cm.⁻¹ interval might (with allowance for anharmonicity) be identified with $2\delta(CD_2) + 600 = 2578$ cm.⁻¹, but if this is correct it is difficult to see why $2\delta(CD_2)$ is not itself an active interval in the spectrum. The weak x progression (|||) falls close to the B progression and is almost certainly covered by this progression in the spectrum of [¹H₂]formaldehyde. (The rotational perturbation known to affect the B_0 and B_1 bands of [¹H₂]formaldehyde may be due to coupling with the upper state of a neighbouring x band.) It is consistent with the selection rules to assign $x_0 - A_0 = 704$ cm.⁻¹ to the a'' fundamental $\gamma'(CD_2)$.

A few, very weak bands are visible between 28,000 and 25,300 cm.⁻¹; they are not intensified by temperature and look different from the bands of the 28,000 cm.⁻¹ system. These bands must belong to a separate electronic transition, presumably [13] to the T ◄— S transition corresponding to the stronger S ◄— S system at 28,000 cm.⁻¹.

(2) *The Fluorescence Spectrum* : *Vibrational Structure.*—An interesting aspect of the fluorescence spectrum is the extreme weakness of transitions to the vibrationless level of the ground state; band A_0, for example, has not been detected in emission with H·CHO and is very feeble with D·CDO. The strongest fluorescence bands combine with ground-state levels in which several quanta of the vibration $\nu_6''(b_2)$ are excited; and this is an immediate argument in favour of a nonplanar excited state, as was first perceived by Walsh.[10]

The fluorescence bands are all perpendicular. The carbonyl vibration, $\nu_2''(a_1)$, is active in forming progressions which, when well developed, run positively for several members and negatively for one or two members, the origins being arranged in a regular manner (Fig. 2) that has no obvious resemblance to the corresponding diagram for the absorption spectrum. Two principal (α and β) and two subsidiary (γ and δ) systems of bands can be distinguished, all the bands of a given system (apart from the members of the negatively-running progressions) emanating from the same upper-state level.* The absorption band A_0, in spite of its weakness in emission, is the hinge of the whole spectrum; the origins of the β system are spaced out at intervals of $2\nu_6''$, commencing with A_0, and terminate on the *even-numbered* levels ($n_6'' = 0, 2, 4 \ldots$) of a stack of ν_6'' quanta built up from the vibrationless level of the ground state. These transitions are designated

$$\beta_{0,0} \ (= A_0), \ \beta_{2,0}, \ \beta_{4,0} \ldots$$

* The fluorescence spectrum of [¹H₂]formaldehyde is less well-developed than that of [²H₂]formaldehyde and shows the principal α and β systems only.

[13] Cf., however, Reid, *J. Chem. Phys.*, 1953, **21**, 1906.

the first and second subscripts denoting, respectively, the quantum levels of v_6'' and v_2''. All the bands of the β system therefore terminate on ground state A_1 vibrational levels. The α system develops from the band $\alpha_{1,0}$ (band " α " in Schou's original notation) and consists of transitions to the *odd-numbered* (B_2) quantum levels of v_6''. The evidence for these assignments is, at present, that the interval between consecutive members in a band system, allowing for a regular decrement due to anharmonicity, is always $2v_6''$; but in the following section a characteristic difference in the rotational structure of the α and β bands

FIG. 2.   *Vibrational structure of the fluorescence spectrum.*
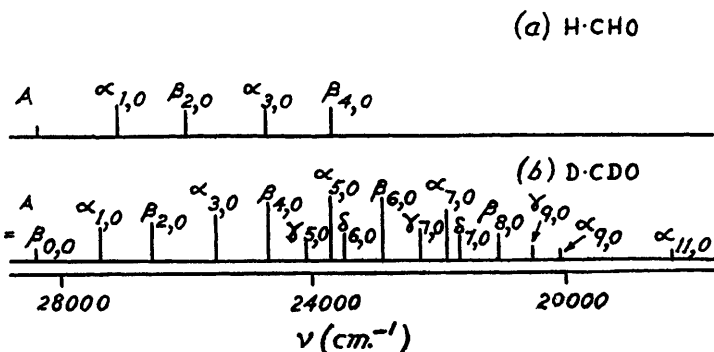
The transitions shown are origins of progressions in the carbonyl-stretching frequency, v_2''. The α- and γ-bands terminate on odd-numbered, and the β- and δ-bands on even-numbered, levels of the planar deformation vibration, v_6, of the ground state.
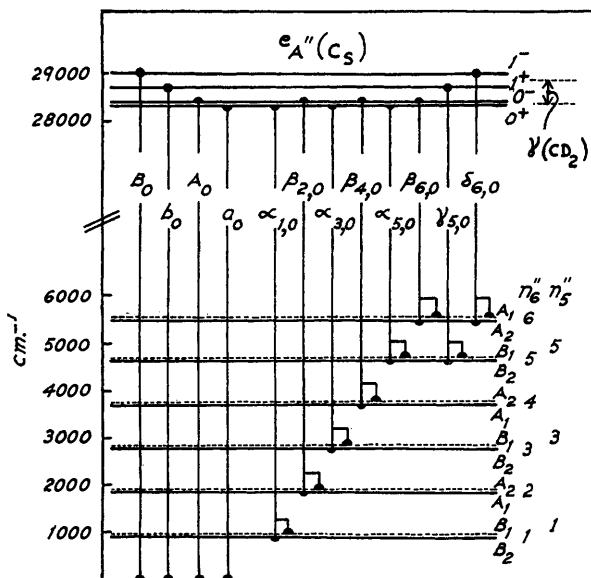
FIG. 3.   *Vibronic states and transitions of [²H₂]formaldehyde.*

is shown to confirm this conclusion beyond doubt. The height of the upper level of the α bands can be evaluated from $v(\alpha_{1,0}) + v_6''$, $v(\alpha_{3,0}) + 3v_6''$, etc., and comparison with the absorption frequencies shows that the parallel transition a_0 is almost certainly a transition to the same upper state. The δ bands of [²H₂]formaldehyde lie 600 cm.$^{-1}$ to the violet of the β bands and this interval is identical with $B_0 - A_0$ in absorption (Table 1); the δ bands, therefore, have the same upper state as B_0. Similarly, the γ system of [²H₂]form-aldehyde is found 385 cm.$^{-1}$ above the α system (cf. $b_0 - a_0 = 386$ cm.$^{-1}$; Table 1)

and the upper state of the γ bands is common with that of b_0. These relations are summarised in Fig. 3. The γ and δ bands are weakened in emission by their Boltzmann factors and appear only in the strong, central region of the spectrum.

The frequencies of the band centres in the fluorescence spectrum are listed in Table 3. Only two ground-state vibrations, ν_2'' and ν_6'', are active in fluorescence, and the fundamentals, anharmonic terms, and zero-order frequencies are noted in Table 4. The anomalies in the anharmonic terms (*e.g.*, $x_{66}^{\text{D·CDO}}$ is $> x_{66}^{\text{H·CHO}}$) are due to the substitution of band centres for the true gyrovibronic origins, and the product-rule calculation has a small defect (0·6%) for the same reason. The explanation of the poorer development of the

TABLE 3. *Band centres in the fluorescence spectrum of formaldehyde.*

	H·CHO Intensity ^{a}	H·CHO cm.$^{-1}$	D·CDO Intensity ^{a}	D·CDO cm.$^{-1}$		H·CHO Intensity ^{a}	H·CHO cm.$^{-1}$	D·CDO Intensity ^{a}	D·CDO cm.$^{-1}$
Assigt.					Assigt.				
$\alpha_{1,-3}$	—	—	b	30,852 ^{c}	$\gamma_{7,0}$	—	—	5	22,283·2
$\alpha_{1,-2}$	0	29,359 ^{c}	0	29,708 ^{c}	$\alpha_{3,2}$	3	21,293·6	3	22,173·8
$\alpha_{1,-1}$	2	28,207	3	28,550 ^{c}	$\alpha_{5,1}$	—	—	6	22,029·0
$A_0 = \beta_{0,0}$	b	28,312·7	00	28,377	$\alpha_{7,0}$	—	—	6	21,898·6
$\beta_{2,-1}$ / $\alpha_{1,0}$	5	$\{27,173 \ ^c$ / $27,035·9 \ ^c\}$	4 / 5	27,690·0 ^{c} / 27,372·4 ^{c}	$\delta_{8,0}$	—	—	3	21,673·8
$\beta_{0,1}$	1	27,569·1 ^{c}	—	—	$\beta_{2,3}$	—	—	2	21,499·2
$\alpha_{1,\pm 1}$	2	26,469·0	—	—	$\beta_{4,2}$	1	20,271	2	21,339·5
$\alpha_{3,-1}$	—	—	5	26,704·1	$\beta_{6,1}$	—	—	5	21,200·8
$\beta_{2,0}$	4	25,990·9 ^{c}	6	26,515·4 ^{c}	$\beta_{8,0}$	—	—	4	21,074·7
$\beta_{4,-1}$	—	—	4	25,848·0	$\gamma_{7,1}$	—	—	1	20,628·0
$\alpha_{1,1}$	6	25,296·8	5	25,679·2	$\alpha_{3,3}$	—	—	1	20,528·2
$\alpha_{3,0}$	4	24,721·3	7	25,523·7	$\gamma_{9,0}$	—	—	2	20,506·3
$\gamma_{5,-1}$	—	—	2	25,257·2	$\alpha_{5,2}$	—	—	2	20,374·8
$\beta_{2,1}$	6	24,258·5	6	24,823·7	$\alpha_{7,1}$	—	—	2	20,242·5
$\beta_{4,0}$ / $\alpha_{1,2}$	10	$\{23,687·0$ / $23,578·7\}$	9 / 3	24,675·1 / 24,003·0	$\alpha_{9,0}$	—	—	1	20,121·8
$\gamma_{5,0}$	—	—	3	24,084·2	$\beta_{6,2}$	—	—	0	19,553
$\alpha_{3,1}$	6	22,996·6	9	23,840·2	$\beta_{8,1}$	—	—	1	19,422
$\alpha_{5,0}$	—	—	10	23,698·4	$\gamma_{9,1}$	—	—	00	18,864
$\delta_{6,0}$	—	—	4	23,462·7	$\alpha_{5,3}$	—	—	0	18,750
$\beta_{2,2}$	4	22,547·2	3	23,153·6	$\alpha_{7,2}$	—	—	0	18,609
$\beta_{4,1}$	4	21,970·9	9	22,999·5	$\alpha_{9,1}$	—	—	1	18,479
$\beta_{6,0}$	—	—	10	22,863·5	$\alpha_{11,0}$	—	—	00	18,366
$\alpha_{1,3}$	3	21,880·6	3	22,345·5	$\beta_{8,2}$	—	—	0	17,788
					$\beta_{10,1}$	—	—	1	17,673

^{a} Visual estimates on a scale of 10. ^{b} Band observed in absorption only. ^{c} Observed in fluorescence and as a temperature-sensitive band in absorption.

A $-$ sign preceding the second subscript in the notation (col. 1) indicates a quantum change of the excited state carbonyl vibration, $\nu(CO)$; a $\pm$ sign indicates a quantum change in both upper and lower states.

TABLE 4. *Ground-state fundamentals and zero-order frequencies.*

	H·CHO Fluorescence spectrum	H·CHO Infrared spectrum	D·CDO Fluorescence spectrum	D·CDO Infrared spectrum
ν_2	1744·7	1743·6 ^{a}	1704·1	1700 ^{a}
x_{22}	$-10·3$	—	$-9·0$	—
ω_2^0	1755·0 $\pm$ 1·2	—	1713·1 $\pm$ 1·4	—
ν_6	1163·6	1165 ^{a}	934·7	933·8 ^{b}
x_{66}	$-2·3$	—	$-3·1$	—
ω_6^0	1165·9 $\pm$ 0·6	—	937·8 $\pm$ 0·6	—
x_{26}	$-6·5$	—	$-7·0$	—

ω_6^0 (HCHO)/ω_6^0 (DCDO) $= 1·244 \pm 0·003$; calc. 1·252.

^{a} Herzberg, " Infra-red and Raman Spectra," van Nostrand, New York, 1945, p. 300. ^{b} Table 6.

spectrum of normal formaldehyde than of that of the deuterated molecule is twofold. First, the most probable transition combining a pyramidal excited state with a planar ground state must involve a greater quantum change of ν_6''(D·CDO) than of ν_6''(H·CHO) owing to the larger vibrational amplitude of the light molecule. This effect is very pronounced, the active vibrational levels running much higher with [$^2H_2$]formaldehyde.

Secondly, with [1H2]formaldehyde the accidental near-coincidence between $2\nu_2''$ (3490 cm.$^{-1}$) and $3\nu_6''$(3492 cm.$^{-1}$) produces systematic overlapping in the bands of the α and β systems. The coincidence does not lead to a perturbation (the symmetry properties of the levels are different) but when the bands are weak the adjacent transitions are difficult to pick out. Several transitions of [1H2]formaldehyde are, in fact, visible below 20,000 cm.$^{-1}$ but it has not been possible to disentangle and assign the band centres with any certainty.

The dependence of intensity on the quantum change of ν_2'' and ν_6'' is shown, for [2H2]formaldehyde, in Table 5. The entries in the horizontal rows refer alternately to β

TABLE 5. *Intensity distribution in the fluorescence bands of* [2H2]*formaldehyde.*

$n_6'' =$	0	1	2	3	4	5	6	7	8	9	10	11
				β and α bands								
$n_2'' = -1$	—	3	4	5	4	—	—	—	—	—	—	—
0	00	5	6	7	9	10	10	6	4	1	—	00
1	—	5	6	9	9	6	5	2	1	1	1	—
2	—	3	3	3	3	2	0	0	0	—	—	—
3	—	3	2	1	—	0	—	—	—	—	—	—
				δ and γ bands								
$n_2'' = 0$	—	—	—	—	—	3	4	5	3	2	—	—
1	—	—	—	—	—	—	—	1	—	00	—	—

(n_6'' even) and α (n_6'' odd) bands; the smoothness of the intensity distribution shows that the $|\psi_{\text{ev}}|^2$ function must have nearly the same shape in the upper levels of both systems. Compared with the α and β systems, the strongest transitions of the γ and δ series are to appreciably higher levels of ν_6''.

(3) *The Fluorescence Spectrum : Rotational Structure.*—(a) [1H2]*Formaldehyde.* The $\alpha_{1,0}$ band of [1H2]formaldehyde (Fig. 4a) was discussed in an earlier paper.[14] The prominent lines in the sub-bands of the violet region are rR heads, the rQ branches being by comparison much less prominent owing to the red shading of the band; the pattern is not repeated on the red side of the band origin because of the intrinsic weakness of the pR branches. The K-numbers of the violet sub-bands deduced in the previous paper have been confirmed by high-dispersion measurements,[8c] and the conclusion that sub-bands with *even K''* are *strong* proves that the lower state of the transition is B_1 or B_2. From the appearance of the first violet sub-band, in the region where the limiting symmetric top formulæ are inadequate, it is almost certain that the band is type B. Finally, the high-dispersion measurements establish that the band is really double; Coriolis coupling of the fundamentals $\nu_5''(b_1)$ and $\nu_6''(b_2)$ mixes the characters of the two levels and the band marks an unresolved pair of transitions to the b_2 components in each of the resultant states (Fig. 3). As in quite recent papers the lower level of $\alpha_{1,0}$ has been identified with the vibrationless ground state [8b] and with the upper level of the fundamental $\nu_5''(b_1)$,[10,15] it is worth emphasising that the evidence for its assignment to a b_2 state is overwhelming.

The transitions to higher vibrational levels of ν_6'' show that there is systematic coupling between the overtones $n\nu_5''$, $n\nu_6''$ with n odd, and between the overtone and combination levels $2n\nu_6''$, $n\nu_5'' + n\nu_6''$ with n integral (but excluding zero). The first type of coupling affects the lower levels of the α, and the second the lower levels of the β bands; in both cases the product of the symmetry species of the coupled levels is A_2 and the coupling perturbs the normal dependence of the rotational energy levels on K''. In this respect the rotational structure of the fluorescence bands closely resembles the ν_5,ν_6 infrared fundamental.

In the β system of fluorescence bands, sub-bands with *odd K''* are *strong* and the lower state is therefore A_1 or A_2, in agreement with purely vibrational evidence (Section 2) which requires A_1 lower states. This point is illustrated for the $\beta_{2,0}$ band in Fig. 4c, where it can be seen that the $K'' = 1$ sub-band (split by the asymmetry into two heads 6 cm.$^{-1}$ apart) is strong. As the spacing of the sub-bands is abnormal, indicating Coriolis coupling,

[14] Brand, *Trans. Faraday Soc.*, 1950, **46**, 805.
[15] Walsh, *J. Chem. Phys.*, 1952, **20**, 1502.

it is inferred that each of the β bands marks a double transition terminating on mixed A_1 and A_2 lower states, the higher-frequency component being to the even-numbered (mainly A_1) overtones of v_6''.

(b) [²H₂]*Formaldehyde.* To number the sub-bands of the $\alpha_{1,0}$ band of [²H₂]formaldehyde it is necessary first to know the numbering of the v_5, v_6 ground-state fundamental which hitherto has not been analysed. For the fundamental, neglecting the effect of asymmetry (valid for $K' \ll 3$) and assuming the same rotational constants in the upper and lower states, Nielsen's equation [16] for the sub-band frequencies is :

$$v_{0(5,6)}^{sub} = (v_5 + v_6)/2 + \zeta^2 A - (A - D) \pm 2(A - D)K'^2 \pm [(v_5 - v_6)^2/4 - (2A\zeta K')^2]^{\frac{1}{2}} . \quad (1)$$

The first $\pm$ symbol in equation (1) refers to transitions with $\Delta K = \pm 1$, and the second distinguishes the two states arising from the rotational coupling. Apart from the complex

FIG. 4.
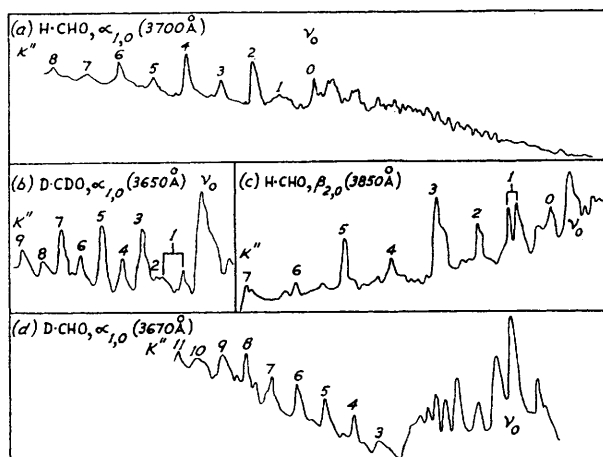
region between the origins, the $+$ and $-$ signs are taken in phase, $++$ in the violet sub-bands and $--$ in the red. In these branches the sub-band frequencies can be expressed as sums and differences : [17]

$$(v_{++} + v_{--})/2 = (v_5 + v_6)/2 + \zeta^2 A - (A - D) \quad . \quad . \quad . \quad . \quad (2)$$

and

$$[(v_{++} - v_{--})/2 - 2K'(A - D)]^2 = (v_5 - v_6)/2 + 4A^2\zeta^2 K'^2 \quad . \quad . \quad (3)$$

where in each case v_{++} and v_{--} refer to sub-bands with the same K'. The analysis requires prior knowledge of A and D which in this paper are calculated from the rotational constants for [¹H₂]formaldehyde; [3] as this demands an appeal to the molecular geometry only for the smaller constant D, the values are probably accurate to 0·02 cm.⁻¹. A least-squares treatment of the experimental frequencies [18] using equations (2) and (3) leads to the results in Table 6;* agreement with the value of v_6'' deduced from the fluorescence spectrum (Table 4) is satisfactory.

The procedure for numbering the sub-bands of the $\alpha_{1,0}$ band is as follows. As the upper state of the v_5, v_6 fundamental is identical with the lower state of $\alpha_{1,0}$, the Kth R sub-head of the parallel transition connecting the vibrationless ground state with the upper level of $\alpha_{1,0}$ (*i.e.*, the absorption band a_0) is found by adding the frequency of the

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* Eqns. (1)—(3) enable the two origins of the v_5, v_6 band to be calculated, without discriminating between them. The identification of v_6'' with the 934 cm.⁻¹ frequency follows from the product rule (Table 4).

[16] Nielsen, *J. Chem. Phs.*, 1937, **5**, 818.
[17] Davidson, Stoicheff, and Bernstein, *ibid.*, 1954, **22**, 289.
[18] Ebers and Nielsen, *ibid.*, 1938, **6**, 311.

TABLE 6. *Analysis of the ν_5, ν_6 (ground state) fundamental of $[^2H_2]$formaldehyde.*

A = 4·705, D = 1·001 cm.$^{-1}$.[a]

K'		3	4	5	6	7	8	9
				Frequency, cm.$^{-1}$				
ν_{++}	obs.[b]	1014·4	1023·3	1033·3	1043·4	1053·8	1066·4	—
	calc.	1013·3	1023·2	1033·3	1043·7	1055·5	1065·9	1076·9
ν_{--}	obs.[b]	906·4	893·3	887·8	875·9	864·9	852·9	841·3
	calc.	905·6	895·9	886·7	875·2	864·3	853·2	841·9
Intensity		s	w	s	w	s	w	s

$\nu_6 = 933\cdot8$ cm.$^{-1}$, $\nu_5 = 990\cdot4$ cm.$^{-1}$, $\zeta = 0\cdot498$.

[a] Calculated from the rotational constants of $[^1H_2]$formaldehyde.   [b] Ebers and Nielsen, ref. 18.

—— sub-band of ν_5, ν_6 with $K'' = K$ to the rR head of the sub-band of $\alpha_{1,0}$ with $K' = K$ (Table 7). Because the sum must be consistent with the measured frequency of band a_0, only one set of numbers for the sub-bands of $\alpha_{1,0}$ is acceptable (Fig. 4*b*). Moreover, for not too large or too small values of K, the sub-heads of the parallel band obey the usual equation for a symmetric top, *viz.*,

$$\nu_R^{sub} = \nu_R^0 + [(A' - D') - (A'' - D'')]K^2 \quad . \quad . \quad . \quad . \quad (4)$$

The least-squares value of $[(A' - D') - (A'' - D'')]$, one point seriously off line being neglected, is in Table 7. A direct analysis of the rotational structure of a_0 was not undertaken, partly because the band was seriously overlapped by a strong neighbour (A_0) and partly because the dispersion of the quartz spectrograph was inadequate in this region.

TABLE 7. qR *Sub-heads in the* a_0 *absorption band of* $[^2H_2]$*formaldehyde.*

K	4	5	6	7	8	9	10
			Frequency, cm.$^{-1}$				
$\alpha_{1,0}$, rR Head	27,400·9	27,410·3	27,419·8	27,429·5	27,439·0	27,448·1	27,457·3
ν_5, ν_6, pQ Branch [a]	906·4	893·3	887·8	875·9	864·9	852·9	841·3
ν_R^{sub}	28,307·3	28,303·6	28,307·6	28,305·4	28,303·9	28,301·0	28,298·6
Intensity	s	w	s	w	s	w	s

$[(A'' - D'') - (A' - D')] = 0\cdot11_9 \pm 0\cdot03$ cm.$^{-1}$.

[a] Ebers and Nielsen, ref. 18.

The intensity alternation in the $\alpha_{1,0}$ band of $[^2H_2]$formaldehyde, compared with $[^1H_2]$formaldehyde, is reversed by the change in nuclear statistics. Asymmetry is apparent in the sub-bands with $K'' < 2$, the probable assignment of the various maxima being indicated in Fig. 4*b*. The splitting of the $K'' = 1$ sub-band is in better agreement with the calculated value if the band is type B rather than type C. Coriolis coupling in the lower state doubles each of the transitions in fluorescence (Fig. 3), as already described for $[^1H_2]$formaldehyde. The rotational structure is well marked in the fluorescence spectrum to about 22,000 cm.$^{-1}$, but at lower frequencies, and especially below 20,000 cm.$^{-1}$ where the bands are very weak, only the band centres and one or two rotational sub-maxima are visible. Among the well-developed bands it is easily verified that the α and γ bands have the same intensity alternation as $\alpha_{1,0}$, and that the β and δ bands have qualitatively the same rotational structure but with the intensity alternation reversed. The previous conclusion, that the α and β bands have respectively B and A lower states, is therefore confirmed completely.

(c) $[^2H_1]$*Formaldehyde.* The microphotometer record of the $\alpha_{1,0}$ band of $[^2H_1]$formaldehyde is reproduced in Fig. 4*d*. The intensity distribution is different from the corresponding bands of the symmetrically substituted formaldehydes, the apparent band centre (or strongest " line," ν_0) being farther to the red, and the violet sub-bands weaker than with either of the other isomers. The explanation, however, is simply that the $\nu_5''(a')$ fundamental of $[^2H_1]$formaldehyde is lower in frequency than $\nu_6''(a'')$,[17] the order in which the pair of transitions of the composite ultraviolet band appear in the spectrum being reversed. The band centre still marks the transition terminating in emission on the $\nu_6''(a')$ component of the coupled state, as in the spectra of the symmetrical isomers; but

the violet sub-bands now belong to the transition combining the upper state with the essentially $v_5''(a')$ component of the lower state, and their origin is some 25 cm.$^{-1}$ higher in frequency than the band centre. The violet sub-heads are numbered by the method described for [$^2H_2$]formaldehyde, using the analysis of the v_5,v_6 fundamental recently published by Davidson *et al.*[17]

(4) *Rotational Constants of the Excited State.*—Although the rotational constants of several excited vibronic levels of [$^1H_2$]formaldehyde are known from high-dispersion measurements (cf. Table 1), values for at least two isotopically substituted species are required for a full structure determination. In the present analysis, the first step is to evaluate $[(A' - D') - (A'' - D'')]$ using equation (4) and the particular combination of infrared and ultraviolet frequencies represented (for D·CDO) in Table 7. The double prime then refers to the vibrationless ground state, and the single prime to the lowest vibrational level of the excited state (0$^+$ in Fig. 3). As the ground-state constants are completely known only for [$^1H_2$]formaldehyde, $D_{[v]}''$ for [$^2H_2$]formaldehyde and $A_{[v]}''$ and $D_{[v]}''$ for [$^2H_1$]formaldehyde were calculated from the probable molecular geometry ($r_{CH} = 1\cdot08_9$, $r_{CO} = 1\cdot21_5$ Å, $\widehat{HCH} = 120°$), the estimated uncertainty being about 0·03 cm.$^{-1}$ in $A_{[v]}''$ and proportionately less in $D_{[v]}''$.*

The values of the constant $(A_{[v]}' - D_{[v]}')$ found by this treatment are in Table 11.

Approximate values of $D_{[v]}'$ were obtained as follows. Under medium dispersion the rR-branches of the perpendicular fluorescence bands abruptly lose sharpness and much of their intensity when, by the cancellation of lines ($J \ll K$), the higher sub-bands fail to form heads. For the $\alpha_{1,0}$ band of [$^1H_2$]formaldehyde this is observed for $K'' \gg 7$, and it follows that the inflection of the R-branches occurs with $J'' = 7$. This is known from high-dispersion measurements to be correct [8c] and the method can be applied with some confidence to the isotopic formaldehydes. Convergence in the rR-branches is controlled by $(D_{[v]}'' - D_{[v]}')$, the value of J'' nearest to the inflection being given by

$$2/(2J'' + 3) \approx (D_{[v]}'' - D_{[v]}')/D_{[v]}'' \quad . \quad . \quad . \quad . \quad . \quad (5)$$

When applied to the $\alpha_{1,0}$ bands, $D_{[v]}''$ in equation (5) refers to the upper level of the v_5,v_6 fundamental. If the difference between this level and the vibrationless ground state is neglected, the value of $D_{[v]}''$ calculated from the molecular geometry can be substituted in equation (5); $D_{[v]}'$ is then found directly from the spectra (Table 11).

The rotational constants found by these methods do not, of course, approach the accuracy of high-dispersion measurements. For the time being, however, they represent a coherent set of values for the three isotopically substituted formaldehydes.

DISCUSSION

(5) *Selection Rules for Transitions between a Planar Ground State and a Non-planar Excited State.*—The ground state of an isotopically symmetrical formaldehyde is C_{2v}. On the assumption that the C–H bonds are equivalent, the non-planar state is C_s, the potential field retaining the higher symmetry (C_{2v}) on account of the inversion. In both states the molecule is a near-prolate symmetric top ($I_a \ll I_b$, I_c) and the rotational levels can be classified by the approximate quantum number K : this is a useful classification experimentally for, under medium dispersion, the transitions with different K are resolved whereas those with different J are not.

The overall selection rules [19] are

$$\Delta J = 0, \pm 1, \quad + \longleftrightarrow -, \quad s \longleftrightarrow s, \quad a \longleftrightarrow a$$

In the C_s state the inversion doubling gives rise to pairs of levels wherein one sub-level is $+$ and the other $-$ with respect to inversion. The corresponding s,a characters are found from the expression

$$P(\psi) = I(\psi) \cdot C_2{}^b(\psi_r) \cdot \sigma_{ac}(\psi_{ev}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

---

* With these parameters the calculated value of $(A_{[v]}' - D_{[v]}'')$ for [$^2H_1$]formaldehyde is $5\cdot49_8$ cm.$^{-1}$. Experimental measurement [17] gives $5\cdot47 \pm 0\cdot3$ cm.$^{-1}$.

[19] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945, p. 50.

where $I(\psi)$ and $P(\psi)$ denote the operations of inversion and permutation of identical nuclei, the factor $C_2^b(\psi_r)$ rotates the molecule by π about the b-axis, and $\sigma_{ac}(\psi_{ev})$ reflects the electronic co-ordinates and the nuclear displacements in the plane of the a,c axes. The last two factors contribute a product of ± 1 depending on the species of the rotational and vibronic wave-functions. It follows immediately from equation (6) that the rotational manifold of one inversion doubling sub-level of an A' vibronic state has the identical $+,-$ and s,a characters as an A_1 ground vibronic state, the other having the characters of a B_2 state. Similarly, the A'' inversion doublets have collectively the same characters as the A_2 and B_1 ground vibronic states. This result might have been foreseen intuitively for, as the non-planar equilibrium configuration is straightened out, the inversion doublets must go over into a quantum of the $v_6(b_2)$ fundamental of the planar molecule.

Transitions allowed by the overall selection rules are listed in Table 8. The transitions in cols. 1—3 are free from any restriction, but those in col. 4 are forbidden by the rotational selection rules for an asymmetric top; they will not appear if the species of the rotational wave-function is pure, but may do so if mixing occurs by a suitable perturbation. The rules in Table 8 are formally the same as those governing the combination of two C_{2v} states. Owing to the different statistical weight of the s and a levels, the sub-bands of a transition will display the usual alternation of intensity with K, whether the inversion doubling is resolved or not.

TABLE 8.

ΔK odd ($\perp$)				ΔK even ($\parallel$)	
c-axis		b-axis		a-axis	forbidden
$A_1 \longleftrightarrow A'(-)$	$A_1 \longleftrightarrow A''(-)$	$A_1 \longleftrightarrow A'(+)$	$A_1 \longleftrightarrow A''(+)$
$A_2 \longleftrightarrow A''(-)$	$A_2 \longleftrightarrow A'(-)$	$A_2 \longleftrightarrow A''(+)$	$A_2 \longleftrightarrow A'(+)$
$B_1 \longleftrightarrow A''(+)$	$B_1 \longleftrightarrow A'(+)$	$B_1 \longleftrightarrow A''(-)$	$B_1 \longleftrightarrow A'(-)$
$B_2 \longleftrightarrow A'(+)$	$B_2 \longleftrightarrow A''(+)$	$B_2 \longleftrightarrow A'(-)$	$B_2 \longleftrightarrow A''(-)$

The symbols $(+)$ and $(-)$ following the C_s species classification distinguish the *vibronic* sub-levels arising from the inversion doubling. $(+)$ States correlate with the A states of the rotational sub-group (C_2) of the planar molecule, and $(-)$ with B.

For $[^2H_1]$formaldehyde, the non-planar state has no symmetry element (C_1). If the inversion doubling is resolved, however, one sub-level will behave as A' and the other as an A'' vibronic state of the point-group C_s. The intensity alternation vanishes, as can be seen from Fig. 4d.

(6) *Vibrational Analysis.*—The analysis in terms of a pyramidal excited state offers no serious difficulty. The crucial point is the interpretation of four low-lying levels of the excited state, which are now assigned in pairs to the inversion doubling the sub-levels of the zeroth (0+, 0⁻; cf. Walsh [10]) and first (1+, 1⁻) vibrational levels of the fundamental $\gamma(CH_2)$ (Table 9). The vibration frequency is found approximately from the separation of the centres of the inversion doublets.

TABLE 9.

Upper level of fluor. system		α	β	γ	δ
Height (cm.⁻¹)	H·CHO	0	124 *	540	947
	H·CDO	0	93	458	794
	D·CDO	0	67	385	671
Assigt. γ (CH₂)		0+	0⁻	1+	1⁻

* The gyrovibronic origin of A_0 (Table 1) and the R-head of band a_0 (ν_R^0; eqn. 4) are separated by $28,312\cdot7 - 28,198\cdot0 = 115\cdot7$ cm.⁻¹. To find the separation of the *origins* we add $8\cdot8$ cm.⁻¹, representing the calculated interval between the R-head and gyrovibronic origin of a_0. The corresponding values for the isotopic formaldehydes are uncorrected.

The transitions connecting the ground A_1 vibronic state with the 0⁻ and 1⁻ upper vibronic levels are known [3] to be type B, and the species of the upper levels is therefore $A''(-)$ (Table 8). Similarly, the transitions between the B_2 ground vibronic states and the 0+ and 1+ levels almost certainly are also type B, and the $(+)$ upper levels must be $A''(+)$. Granted this, the species of the upper state orbital wave-function is A''. The fact that $\parallel$ transitions connect the A_1 ground state with the 0+ and 1+ upper states is supplementary evidence of their $(+)$ character [if they were $(-)$ levels the transitions

would be forbidden by the strict $s \longleftarrow|\longrightarrow a$, $+ \longleftarrow|\longrightarrow +$, and $- \longleftarrow|\longrightarrow -$ prohibition], but the full explanation is not quite straightforward for the $A''(+) \longleftarrow A_1$ transitions are forbidden by the asymmetric top rules (Table 8). As the combination $A'(+) \longleftarrow A_1$ is allowed by both the asymmetric top and the overall selection rules it seems likely that the predominantly $A''(+)$ states have some admixed $A'(+)$ character; and although the identity of the perturbation is uncertain it may be connected with the state which induces predissociation in the absorption bands at higher frequencies.

In an $A'' \longleftarrow A_1$ transition the quantum change of the $\gamma(CH_2)$ vibration is unrestricted by the selection rules. The $\nu_6(b_2)$ ground state vibration is unlimited as to *even* quantum changes, the odd levels being allowed to combine with $(+)$ upper states and the even levels with $(-)$. Apart from this peculiar restriction, the spectral activity of both vibrations is controlled by the Franck–Condon principle.[20] Experimentally, the two vibrations are active in a strikingly different way for, whereas the ground-state vibration changes by as many as 10 quanta, the $\gamma(CH_2)$ fundamental is active only in the zeroth and first levels. This is largely the Franck–Condon effect. If the transitions in fluorescence are considered first, it is clear that the overlap between the vibronic level of the bent upper state and the ground state is greatest when several quanta of $\nu_6(b_2)$ are excited. With [$^2H_2$]formaldehyde the intensity maximum corresponds to $n_6'' = 5$ or 6 in transitions from the 0^+ and 0^- levels (α and β bands), and to $n_6'' = 6$ or 7 in transitions from the higher 1^+ and 1^- levels (γ and δ bands : Table 5). The similarity in intensity distribution among the α and β bands follows naturally from the fact that the pair of upper levels is simply an inversion doublet. In absorption, however, the position is different because, owing to the inversion doubling, the overlap between the wave-functions of the vibrationless ground state and the levels of $\gamma(CH_2)$ in the excited state does not pass through a maximum; rather it decreases progressively from the zeroth level of $\gamma(CH_2)$ upwards, and only the transitions to the zeroth and first levels are recorded in the spectrum.

The a' excited-state fundamentals of the symmetrically substituted formaldehydes are assembled in Table 10, together with incomplete results for [$^2H_1$]formaldehyde. The product-rule ratio is not entirely satisfactory, for the defect is in the wrong direction; probably the evaluation of $\gamma(CH_2)$ from the centres of the inversion doublets is rather a poor approximation to the zero-order frequency. The present measurements do not give a direct indication of the multiplicity of the excited state, but the oscillator strength of the spectrum of an ether solution[21] is about 5×10^{-4} and it seems certain that there is no multiplicity change in the transition. The excited electronic wave-function can therefore be specified as $^1A''$. The electronic origins, measured to the centre of the 0^+ and 0^- inversion doublet, are noted in Table 10.

TABLE 10. *Electronic origin and a' fundamentals of excited formaldehyde.*

	H·CHO	H·CDO	D·CDO
ν_0	28,252	28,303	28,343
$\nu(CH)$	2875	—	2078
$\delta(CH_2)$	1322	1071	989
$\nu(CO)$	1182	1188	1176
$\gamma(CH_2)$	682	579	494

$$\Pi\{\nu(D\cdot CDO)/\nu(H\cdot CHO)\} = 0.39 \text{ (calc. : } 0.41).$$

(7) *Stereochemistry of the Excited State.*—(a) *The asymmetry parameter.* The asymmetry parameter, $\delta = (B - C)/(A - C)$, of the excited state of the absorption bands analysed by Dieke and Kistiakowsky[3] is 0.0145. (The states in question include the 0^- and 1^- levels discussed in Section 6; between one level and another there is a small variation of δ which probably does not exceed the experimental error.) This value is appreciably smaller than in the ground state ($\delta = 0.0195$; Lawrance and Strandberg[22]) and is actually too low to be consistent with a planar upper state. Dieke and Kistiakowsky explained the defect by a rotational perturbation, but the assumption of a non-planar upper state removes the

[20] Herzberg and Teller, *Z. phys. Chem.*, 1933, B, **21**, 410.
[21] Reiche and Meister, *Ber.*, 1935, **68**, 1465.
[22] Lawrance and Strandberg, *Phys. Rev.*, 1951, **83**, 363.

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difficulty altogether. The variation of the asymmetry parameter with Δ, the angle between the plane of the CH_2 nuclei and the C–O axis, is shown in Fig. 5 for trial structures wherein the geometrical parameters were chosen to fit the experimental rotational constants. The recorded value of δ corresponds to $\Delta = 25$—$30°$.

(b) *The inversion doubling splitting.* An independent value of Δ can be found [23] from the inversion doubling splitting, $\Delta\nu = 0^- - 0^+$, and the fundamental frequency $\gamma(CH_2)$. The potential, assumed harmonic, is given by

$$V = \tfrac{1}{2}k_\Delta(\Delta - \Delta_e)^2 \qquad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Δ_e being the equilibrium value of Δ. k_Δ is approximately a valence force constant if the equilibrium configuration is not too strongly bent. The potential defined by equation (7) leads to a double-minimum function with a cusp at the centre; the real barrier must be rounded and somewhat lower, but the error is probably not serious because the amplitude

FIG. 5.
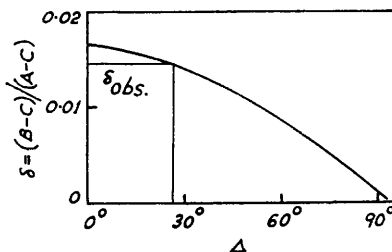
of the vibrational wave-function is small in this region. Two assumptions which further simplify the calculation are : first, that the $\gamma(CH_2)$ vibration does not interact appreciably with the other a' normal modes; and, secondly, that the normal co-ordinates for the motion of the hydrogen nuclei are parallel to the plane of symmetry of the molecule. Here also the assumptions are reasonable if the equilibrium state is not too strongly bent. To correct in part for the approximations, values of k_Δ are calculated separately from the frequencies $\gamma(CH_2)$ and $\gamma(CD_2)$ by the expression

$$4\pi^2c^2\nu^2 = \frac{k_\Delta}{r_{CO}r_{CH}\cos\theta}\left[\frac{r_{CO}}{r_{CH}\cos\theta}\left(\frac{1}{2m_H} + \frac{1}{m_C}\right) + \frac{2\cos\Delta}{m_C} + \frac{r_{CH}\cos\theta}{r_{CO}}\left(\frac{1}{m_C} + \frac{1}{m_O}\right)\right]; \quad 2\theta = \widehat{HCH}$$

Hence, $k_\Delta(H\cdot CHO) = 1\cdot24 \times 10^{-12}$ and $k_\Delta(D\cdot CDO) = 1\cdot02 \times 10^{-12}$ erg rad.$^{-2}$. $\Delta\nu$ was calculated for trial values of Δ by the Wentzel–Kramers–Brillouin equation, as described by Weston.[24] For $\Delta = 27° 30'$ the theoretical and observed splittings are

		H·CHO	D·CDO
$\Delta\nu$ (cm.$^{-1}$)	{ Calc.	125	68
	{ Obs.	124	67

Treatment of the k_Δ's as independent parameters implicitly leads to different barrier heights for the normal and dideuterated molecules. The theoretical barriers ($\Delta = 27\tfrac{1}{2}°$) are

$$V_0(H\cdot CHO) = 720 \text{ cm.}^{-1}; \quad V_0(D\cdot CDO) = 590 \text{ cm.}^{-1}$$

The average value, 650 cm.$^{-1}$, represents the extra stability conferred on the excited state by virtue of its non-planarity.

(c) *The rotational constants.* The experimental constants of the 0^+ level of the excited state are consistent with the assumption of a non-planar configuration, but are not sufficiently accurate of themselves to exclude a planar configuration. Four parameters define the geometry of the excited state, the C–H and C–O bond lengths, the $\widehat{HCH}$ interbond

[23] Costain and Sutherland, *J. Phys. Chem.*, 1952, **56**, 321.
[24] Weston, *J. Amer. Chem. Soc.*, 1954, **76**, 2645.

angle, and the angle Δ. For $\Delta = 27\frac{1}{2}°$ satisfactory agreement with the experimental constants is found (Table 11) with $r_{CO} = 1.32_2$ Å, $r_{CH} = 1.09$ Å, and $\widehat{HCH} = 120°$ The values of Δ and $\widehat{HCH}$ determine $\widehat{HCO} = 116\frac{1}{2}°$. Some mutual adjustment of r_{CH} and either the $\widehat{HCH}$ or the $\widehat{HCO}$ bond angle is certainly possible, but the agreement obtained with [²H₁]formaldehyde is a fairly sensitive indication that the parameters are essentially correct.

TABLE 11. *Rotational constants of excited formaldehyde.*

	Calculated [a]			Observed [b]		
	H·CHO	H·CDO	D·CDO	H·CHO	H·CDO	D·CDO
$A_{[v]}' - D_{[v]}'$	7·835	5·262	3·621	7·85	5·26	3·61
$D_{[v]}'$	1·067	0·959	0·878	1·065 [c]	0·97	0·88
δ	0·0145	—	—	0·0145 [d]	—	—

[a] $r_{CH} = 1.09$ Å, $r_{CO} = 1.32_2$ Å, $\widehat{HCH} = 120°$, $\widehat{HCO} = 116\frac{1}{2}°$. [b] For the 0^+ excited state level (Section 4). [c] Dyne, ref. 8(c). [d] For the 0^- excited state level (Dieke and Kistiakowsky, ref. 3).

(8) *Electronic Configuration of the Excited State.*—The configuration of the electronic ground state of formaldehyde is usually written [25]

$$KK(O, 2s; \ a_1)^2(\sigma_{CH}; \ a_1)^2(\sigma_{CH}; \ b_1)^2(\sigma_{CO}; \ a_1)^2(\pi_{CO}; \ b_2)^2(n_O; \ b_1)^2 : \ A_1 \ . \quad (8)$$

the symbol n_O denoting the higher non-bonding orbital, approximately O, $2p$, centred on the oxygen nucleus. The lowest unoccupied orbital of planar formaldehyde is $(\pi^*_{CO}; \ b_2)$, the configuration of the first excited state of the C_{2v} molecule being [25]

$$\ldots\ldots(\pi_{CO}; \ b_2)^2(n_O; \ b_1)(\pi^*_{CO}; \ b_2) : \ A_2 \ . \quad\quad\quad (9)$$

Higher excited states have been assigned speculatively to the configurations (10) and (11).

$$\ldots\ldots(\pi_{CO}; \ b_2)^2(n_O; \ b_1)(\sigma^*_{CO}; \ a_1) : \ B_1 \ . \quad\quad\quad (10)$$

$$\ldots\ldots(\pi_{CO}; \ b_2)(n_O; \ b_1)^2(\pi^*_{CO}; \ b_2) : \ A_1 \ . \quad\quad\quad (11)$$

At equilibrium, however, the first excited state is not planar. When the molecule bends, the gap between the energies of the π_{CO} and π^*_{CO} orbitals narrows and their contribution to bonding (and antibonding) across the C–O link diminishes. In a strongly bent configuration ($\widehat{HCH} \approx \widehat{HCO} \approx 109°$) these orbitals are equivalent to a pair of non-bonding orbitals, approximately sp^3, one localised on the oxygen nucleus and the other on carbon; the former is more tightly bound and correlates with the π_{CO} orbital of the planar molecule. The A' configurations of the strongly bent molecule are represented in order of increasing energy by (12)—(14), (12) being the (unstable) ground state of pyramidal formaldehyde.

$$\ldots\ldots(n_O; \ a')^2(n_O; \ a'')^2 : \ A' \ . \quad\quad\quad\quad (12)$$

$$\ldots\ldots(n_O; \ a')(n_O; \ a'')^2(n_C; \ a') : \ A' \ . \quad\quad\quad (13)$$

$$\ldots\ldots(n_O; \ a'')^2(n_C; \ a')^2 : \ A' \ . \quad\quad\quad\quad (14)$$

The lowest A'' state of the bent molecule arises by promotion of an $(n_O; \ a'')$ electron to the $(n_C; \ a')$ orbital (vacant in the C_s ground state). The configuration is

$$\ldots\ldots(n_O; \ a')^2(n_O; \ a'')(n_C; \ a') : \ A'' \ . \quad\quad\quad (15)$$

The correlation with the configurations of C_{2v} formaldehyde is shown in Fig. 6.

The state at 28,250 cm.$^{-1}$ obviously correlates with the $A_2 - A''$ state of Fig. 6. It is, however, not so strongly bent as the hypothetical configuration (15) and is energetically more stable than either (9) or (15). The C–O bond is nominally a five-electron bond, three of the electrons occupying the π_{CO}–n_O and π^*_{CO}–n_C orbitals in which the capacity for bonding and antibonding has been weakened by the change of shape. Approximately, the antibonding electron cancels the bonding power of one of the electrons in the bonding orbital,

[25] McMurry, *J. Chem. Phys.*, 1941, **9**, 231.

and the C–O bond in excited formaldehyde should, therefore, be weaker and somewhat longer than a 3-electron bond in a planar molecule. The bond length (1·32 Å) fulfils this expectation quite well.

	MeOH	H·CHO $^eA''$	CO_3^-	$H·CO_2^-$
No. of electrons	2	—	$2\frac{2}{3}$	3
r_{CO} (Å)	1·434 ^{a}	1·32$_2$	1·31 ^{b}	1·27 ^{d}
			1·24—1·26 ^{e}	1·24—1·26 ^{e}

^{a} Ivash and Dennison, *J. Chem. Phys.*, 1953, **21**, 520. ^{b} Elliot, *J. Amer. Chem. Soc.*, 1937, **59**, 1380. ^{c} Brown, Peiser, and Turner-Jones, *Acta Cryst.*, 1949, **2**, 167. ^{d} Zacharisen, *J. Amer. Chem. Soc.*, 1940, **62**, 1011. ^{e} Sugawara, Kakado, and Nitta, *X-sen Kondantai*, 1951, **6**, 85.

The factor governing the geometry of the A'' state is the energy of the singly-occupied π_{CO}–n_C orbital.[10] If the π_{CO} and π^*_{CO} orbitals of the planar molecule uncouple, this orbital falls in energy and becomes increasingly non-bonding; but the uncoupling is not automatically profitable for, although the highest occupied orbital (π^*_{CO} in the planar configuration) is graded down in energy, the remaining orbitals are graded up. In a non-conjugated system, however, the uncoupled form is preferred when the number of

FIG. 6.
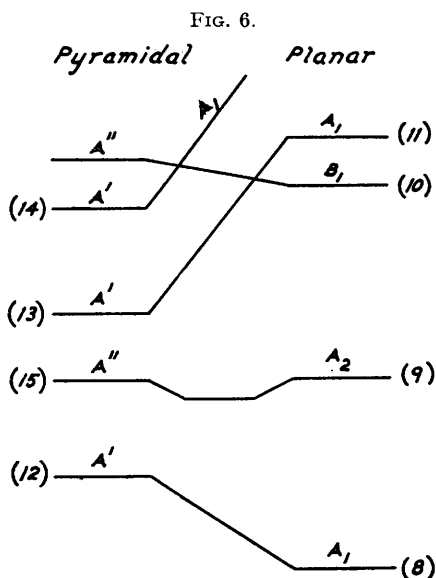
The energies of the electronic configurations of C_{2v} formaldehyde are arranged in the order deduced semi-theoretically by McMurry.[25] The position of the higher A'' electronic configuration of the pyramidal molecule relative to the adjacent A' configurations is uncertain.

electrons is sufficient to fill the non-bonding orbitals. [Comparison of –C≡C– (*linear*) with ⟋N=N⟍ and ⟋O–O⟍ (*bent*) directly illustrates the principle of this effect.] In the $A_2 - A''$ configuration of formaldehyde, where the outermost π^*_{CO}–n_C orbital is singly occupied, the energy balance is critical; the result is a compromise in which the high-energy π^*_{CO} orbital of the planar structure is avoided without the hybridisation change to (15) being complete.

A possible analogy is with the ground state of nitrogen dioxide ($\widehat{ONO} = 134°$; Moore [26]) or with the $^2A_1$ excited state of NH_2 ($\widehat{HNH} \approx 160°$; Herzberg and Ramsay [27]), both odd-electron molecules. The result is not general, however, and in other cases (*e.g.*, the A_u state of acetylene [28]); the hybridisation change is well defined.

[26] Moore, *J. Opt. Soc. Amer.*, 1953, **43**, 1045.
[27] Herzberg and Ramsay, *Discuss. Faraday Soc.*, 1953, **14**, 11.
[28] Ingold and King, *J.*, 1953, 2702.