1010. *Excited States of Glyoxal.*

By Gerald W. King.

The (0–0) bands in the absorption spectra of glyoxal and dideuteroglyoxal, at approximately 4550 Å, have been photographed with a 20 ft. Ebert grating spectrograph. A rotational analysis of their observed structure is suggested, according to which glyoxal has a planar, centrosymmetric *trans*-configuration in each electronic state of the transition and the excited state has A_u electronic symmetry. Assuming values for the C–H bond length and angle, we have obtained values for the ∠CCO and the sum of the C–C and C–O bond lengths for the vibronic states of the molecule concerned in the transition. The rough values for individual bond lengths deduced do not agree with the predictions of simple molecular-orbital theory concerning the dimensions of the excited state.

Monomeric glyoxal vapour possesses a system of weak, discrete absorption bands between 5000 Å and 3700 Å.[1, 2] These appear diffuse towards shorter wavelengths. The spectrum has also been obtained in emission.[3, 4] Brand[1] has suggested a convincing analysis of these bands, based on their appearance when photographed with use of a prism spectrograph of moderate resolving power.

There is little evidence as to the precise structure of the molecule in the ground state. Infrared[5] and electron-diffraction[6] indicate a planar, *trans*-configuration, of C_{2h} symmetry. On this assumption, the electron-diffraction measurements have given the following dimensions:

$$r_{CC} = 1{\cdot}47 \pm 0{\cdot}02\ \text{Å};\ r_{CO} = 1{\cdot}20 \pm 0{\cdot}01\ \text{Å};\ \angle\text{CCO} = 123 \pm 2°$$

---

[1] Brand, *Trans. Faraday Soc.*, 1954, **50**, 431.
[2] Thompson, *ibid.*, 1940, **36**, 988.
[3] *Idem, J. Chem. Phys.*, 1939, **7**, 855.
[4] Gaydon, *Trans. Faraday Soc.*, 1947, **43**, 36.
[5] Cole and Thompson, *Proc. Roy. Soc.*, 1949, *A*, **200**, 10.
[6] LuValle and Shomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 3520.

with the assumed values $r_{CH} = 1{\cdot}09$ Å and $\angle CCH = 114°$. In addition, it is reasonable to assume that the ground state electronic configuration is ^1A_g, all the electrons being paired in orbitals of lowest energy. (*trans*-Glyoxal has the same symmetry classifications as has *trans*-acetylene; for tables showing the electronic and vibrational symmetry species, their direct products, and the overall symmetry classifications of the rotational energy levels, see ref. 7.)

Brand's analysis shows that, given a planar ground state of this symmetry, then the excited state of the electronic transition is also *trans*- and planar, with A_u symmetry. However this assignment largely depends upon the apparent polarisation of the transition moment of certain vibrational bands; that is, whether they are type A, B, or C bands polarised respectively along the *a*, *b*, or *c* momental axes of the molecule. In particular, there is one strong band (at 21,973 cm.$^{-1}$ in glyoxal and at 22,013 cm.$^{-1}$ in dideuteroglyoxal) which appears strongly both in absorption and emission and is very probably the (0–0) origin band of the electronic transition. The polarisation of this band immediately gives the symmetry of the electronically excited state. This band will be referred to as the A_0^0 band, following Brand's nomenclature. On either side of it are the bands K_0^0 and L_0^0, which can be assigned to (1—0) and (0—1) transitions, involving excitation of one quantum of the out-of-plane hydrogen bending vibration of symmetry B_g. The analysis requires the A_0^0 band to be a perpendicular type C band and the two forbidden bands K_0^0 and L_0^0 to be mainly parallel type A bands with a small perpendicular component.

Some of the absorption bands of both glyoxal and dideuteroglyoxal, in particular the A_0^0 bands, have been investigated here under high resolving power, in order to determine their polarisation directly from their rotational structures and also, by analysis of these, to determine the dimensions of the molecule in the ground and the excited state. The bands have a complex rotational structure; it must be emphasised that the analysis offered here is one that is consistent with their appearance under the resolution that has been achieved.

EXPERIMENTAL

Dideuteroglyoxal was prepared by Riley and Friend's method [8] from tetradeuteroethylene, made from pure samples of 1 : 2-dibromodeuteroethylene prepared by Wilson and Wylie.[9] 3 c.c. of dry and freshly purified dioxan were moistened with 1 drop of 99·6% deuterium oxide and added to approximately 2 g. of dry " AnalaR " 16—24 mesh zinc dust. 3 c.c. of dibromodeuteroethylene were added and the reactants slowly heated in a glycerol bath. A slow current of dry nitrogen at atmospheric pressure swept the generated deuteroethylene through a trap at −78° into a trap cooled by liquid nitrogen, where it condensed. After 2 hr. this trap was isolated and evacuated, and its contents allowed to evaporate into an evacuated 8 l. glass storage reservoir. The deuteroethylene was purified by passing it repeatedly at low pressure through a trap at −78°.

Dideuteroglyoxal was prepared by distilling the deuteroethylene several times *in vacuo* through a hard-glass tube packed loosely with selenium dioxide and powdered phosphoric oxide (1 : 1 w/w). Initially this tube was heated electrically to about 200°. This temperature was not exceeded during reaction, otherwise excessive charring occurred. After several vacuum resublimations to remove traces of selenium and phosphoric oxide, the product was distilled into a trap at −78° sealed to a fused silica absorption cell 50 cm. long.

The apparatus (all glass) was baked out under vacuum beforehand. Reactants were added in a countercurrent of dry nitrogen.

Glyoxal was made directly from cylinder ethylene by the same method. In each case, the product was stable indefinitely when stored under vacuum at −78°.

In the dideuteroglyoxal spectrum there were no discrete bands which could be assigned to either the monodeutero- or dihydrogen-glyoxal, different samples possessing identical absorption.

---

[7] Ingold and King, *J.*, 1953, 2708.
[8] Riley and Friend, *J.*, 1932, 2342.
[9] Wilson and Wylie, *J.*, 1941, 596.

However, owing to the extended and complex structure of the bands, they may have contained weak unrecognised lines due to hydrogenic impurities.

Absorption spectra were photographed in the first order of a 20 ft. Ebert grating spectrograph [10] with, as light source, a high-pressure xenon arc with a 2 mm. thickness of Chance Bros. glass type OY10 as a filter. Spectra were recorded on Kodak L.15 plates; iron-arc comparison spectra were superposed immediately before or after each exposure. The glyoxal was kept at some fixed temperature between −20° and −30° during exposures. The cell itself was at 20°; some spectra were also recorded with the cell cooled to −20° by external circulation of cold alcohol, but no measurable variation in intensity distribution was observed. The cell could not be heated above room temperature, owing to the rapid polymerisation of the glyoxal which occurred.

The plate dispersion in the absorption region was approximately 0·65 Å/mm. and the resolving power was 150,000. This corresponded to a minimum separation between resolvable lines of approximately 0·04 mm. Lines were measured from the plate in both directions, a travelling microscope reading to 0·01 mm. being used, and mean values taken. The wavelengths of iron-arc reference lines were fitted to a calculated dispersion curve for the spectrograph,[11] which was then used to calculate absorption line wavelengths. These were then converted into vacuum wave numbers.

DISCUSSION

Rotational Energy Levels.—The planar glyoxal molecule is a near-prolate asymmetric top, with moments of inertia $I_a \ll I_b < I_c$. The asymmetry parameter $\kappa = (2B - A - C)/(A - C) \simeq -0{\cdot}99$ in the ground state, A, B, and C being corresponding rotational constants.

There is probably no gross change of shape of the molecule upon electronic excitation. Otherwise, by the Franck–Condon principle, long progressions in that excited-state vibration which tends to bring this state into the shape of the ground state should be observed, as in acetylene.[7] If the excited state were non-planar, then its energy levels would " split " into two components, leading to an apparent doubling of spectral lines; if this splitting were large, two sets of vibrational levels, with different vibronic (vibrational–electronic) origins, would appear; if it were small, the doubling would appear in the rotational structure. Neither effect was observed. Brand's vibrational analysis, and our rotational analysis, are both consistent with a planar excited state. Of the four possible electronic symmetry states of an excited state of C_{2h} symmetry, transitions to two of them, of symmetries A_u and B_u, are allowed. The former transition is polarised along the c-axis, the latter in the (a, b) plane.

The energy levels of a prolate symmetric top ($I_b = I_c$, $\kappa = -1$) are given by

$$E(J, K) = BJ(J + 1) + (A - B)K^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where J and K are quantum numbers associated with the total angular momentum and its component along the a-axis respectively, with $J \geqslant K$.

A slightly asymmetric top has similar energy levels, but all levels with $K > 0$ are " split " into two components, the splitting being greatest for levels of low K-value. When the splitting is negligibly small, a good approximation to the energy levels is given by

$$E(J, K) = DJ(J + 1) + (A - D)K^2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $D = \frac{1}{2}(B + C)$.

The energies of levels of low K can only be obtained by a perturbation treatment or by other approximate methods. Here, a Mathieu function approximation was used. This method is based on the similarity between the matrix equations which give characteristic

---

[10] King, *J. Sci. Instr.*, in the press.

[11] Callomon, *Canad. J. Phys.*, 1956, **34**, 1046.

values for Mathieu's differential equation and those giving the energy levels of an asymmetric rotor.[12] There exist comprehensive tables of these characteristic values.[13] In order to compare observed and calculated rotational structure, it was not necessary to calculate energy levels to the degree of accuracy envisaged by Golden;[12] his first- and second-order correction terms were ignored, and his expression for the energy levels approximated still further by the equation;

$$E(J, K) = CJ(J+1) + (A-D)b_K(s) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $b_K(s)$ is the characteristic value giving rise to the requisite odd or even solution of Mathieu's equation, with

$$s = (B-C)/(A-D)[J(J+1) - \{1 + 1/2J(J+1)\}] \quad . \quad . \quad . \quad (4)$$

By use of these equations large numbers of energy levels could be calculated rapidly to a suitable degree of accuracy.

Rotational Structure of Bands.—When the symmetric-top approximation to the energy levels is valid for both combining states, selection rules predict that each $(K' - K'')$ transition * should consist of a P, Q, and R branch, due to the accompanying changes in quantum number J (except in the $K'' = 0$, $\Delta K = 0$ transition, where the Q branch is missing). Each of these " sub-bands " can be referred to an origin, which is where the hypothetical $J'' = 0$, $\Delta J = 0$ Q-line would occur. The frequencies of these sub-band origins are given by the equations:

$$\nu_0 = \nu_{00} + \{(A' - D') - (A'' - D'')\}K^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

for parallel-type bands with $\Delta K = 0$, and

$$\nu_0 = \nu_{00} + (A' - D') \pm 2(A' - D')K + [(A' - D') - (A'' - D'')]K^2 \; . \quad (6)$$

for perpendicular-type bands with $\Delta K = \pm 1$ respectively, ν_{00} being the vibrational origin of the band. The restriction $J \geqslant K$ on the energy levels causes certain lines to be missing in each sub-band; for example, in a perpendicular-type transition, the line R(K) is the R line nearest to the origin of the Kth sub-band.

For transitions between levels of low K number in a slightly asymmetric top, such patterns as are given by the above equations will disappear, owing to the splitting and displacement of the energy levels from their equivalent symmetric-top values.

The line intensities within a band are obtainable from the tables given by King, Hainer, and Cross.[14] These values must be combined with appropriate Boltzmann factors for the population of the ground-state levels involved, and also with statistical weight factors for the nuclear spins of the atoms in the molecule, as in acetylene.[7]

Observed Structure of the A_0^0 *Bands.*

Plate 1 shows the rotational structure of the A_0^0 band of glyoxal near the band origin. A central intensity minimum † occurs. To the short wavelength side of this, a series of heads labelled $K_2, K_3, \cdots$ each degraded towards the red, extend with increasing separation. A considerable amount of fine structure can be observed between these heads: similarly

---

* When describing transitions by pairs of symbols in parentheses, the upper state is placed first; primes and seconds refer to the upper and the lower state respectively.

† Absorption lines are shown black. " Intensity " refers to intensity of absorption.

[12] Golden, *J. Chem. Phys.*, 1948, **16**, 78.

[13] National Bureau of Standards, " Tables Relating to Mathieu Functions," Columbia Univ. Press, 1951.

[14] Cross, Hainer, and King, *J. Chem. Phys.*, 1944, **12**, 210.

spaced structure, of higher intensity of absorption, is also found on the long-wavelength side of the intensity minimum.

Plate 2 is a similar reproduction of the A_0^0 band of dideuteroglyoxal. Again, heads degraded towards the red extend in regular sequence towards short wavelengths. In both spectra these heads extend a considerable distance beyond the region shown; their frequencies are listed in Table 1. At wavelengths longer than those shown, both spectra consist of complex mazes of overlapping lines, which contain no prominent features and could not be analysed.

TABLE 1. *Frequencies* (*cm.*$^{-1}$) *and assignments of sub-band heads in the* A_0^0 *bands of glyoxal and dideuteroglyoxal.*

Glyoxal	Dideuteroglyoxal	K''	Glyoxal	Dideuteroglyoxal	K''
21,996·85	22,029·68	4	22,041·53	22,057·08	12
22,001·66	32·62	5	48·10	61·08	13
6·66	35·74	6		65·20	14
11·89	39·00	7		69·47	15
17·08	42·36	8		73·82	16
23·06	45·86	9		78·34	17
28·96	49·45	10		83·02	18
35·12	53·21	11			

The frequencies of the two sets of heads in Table 1 could be fitted to eqn. (6) with $\Delta K = +1$. In a perpendicular transition, these heads could be either the unresolved Q-branches of low J'' numbering, or else R-heads of the sub-bands. They were taken to be the latter, for the following reasons. First, the intensities of the observed heads remain considerable up to high values of K''; whereas the theoretical intensities of Q-branches drop rapidly as K'' increases. Secondly, the heads remain sharp at high K'' values, whereas missing lines would be expected to give unresolved Q-maxima rounded edges in these circumstances. Thirdly, Q-maxima would be expected to persist with considerable intensity, and with small deviation from their positions as calculated from eqn. (6), back to the band origin ν_{00}; whereas in both spectra, the positions of intensity maxima become very irregular at wavelengths longer than those of the points labelled $K'' = 4$. As will be shown below, comparison of calculated and observed positions of the heads justifies their assignment as R-heads.

The next problem was to assign the correct K'' numbering to these heads, since the values of the rotational constants in eqn. (6) depend on this assignment. On fitting the head frequencies in Table 1 to a quadratic equation by a least-squares approximation [15] and evaluating from this the constants in eqn. (6), we found three sets of rotational constants for each molecule which lay within the error limits permitted by the electron-diffraction ground-state dimensions and their associated errors. These are shown in Table 2, and correspond to the three possible numberings of the sub-band heads labelled α, β and γ. The α-numbering is shown beside the frequencies listed in Table 1. Furthermore, it was not possible to associate, say, the α-numbering for glyoxal with the β-numbering for dideüteroglyoxal, since such combinations were found to correspond to highly improbable sets of molecular dimensions.

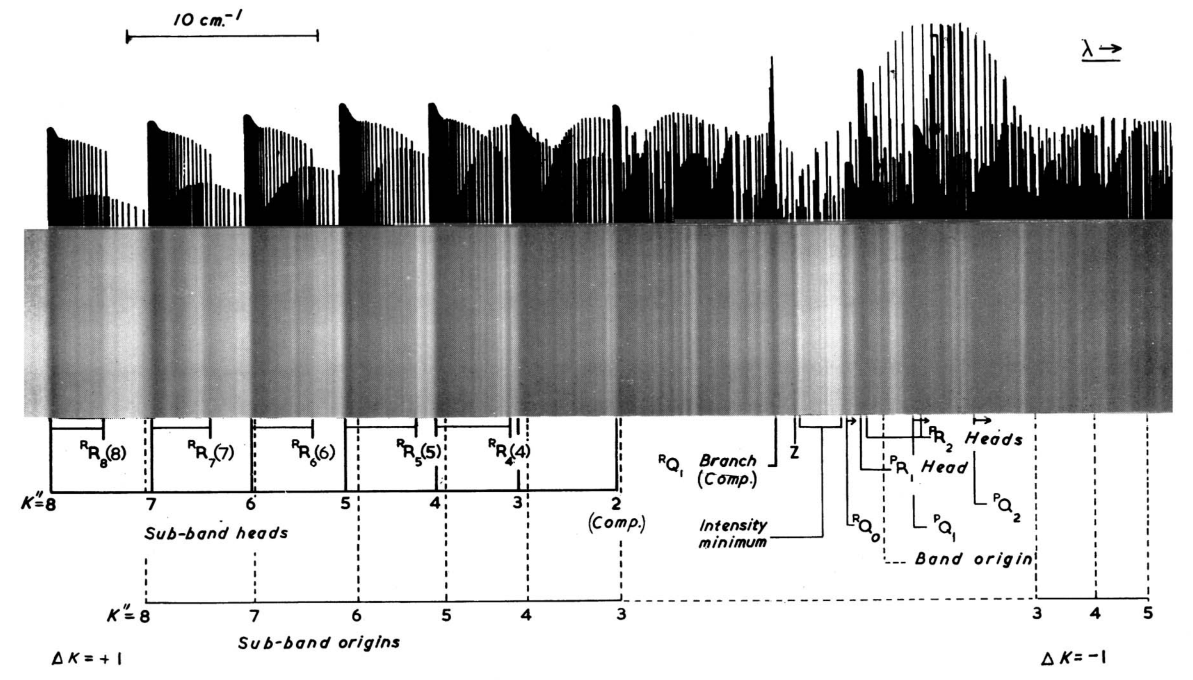
The quadratic equations for the band heads for each molecule predict that the heads themselves will converge to a head. This " head of heads" can be clearly seen for dideuteroglyoxal in Plate 2. It cannot be distinguished in the glyoxal spectrum; calculation shows that here there are fewer sub-band heads to absorb light at the actual convergence limit frequency than there are in the case of dideuteroglyoxal.

Theory predicts that in sub-bands of high K'' numbering in a perpendicular transition, only the R branches have appreciable intensity. It is possible to pick out series of lines assignable as R branches in several of the sub-bands of the glyoxal spectrum. In Plate

---

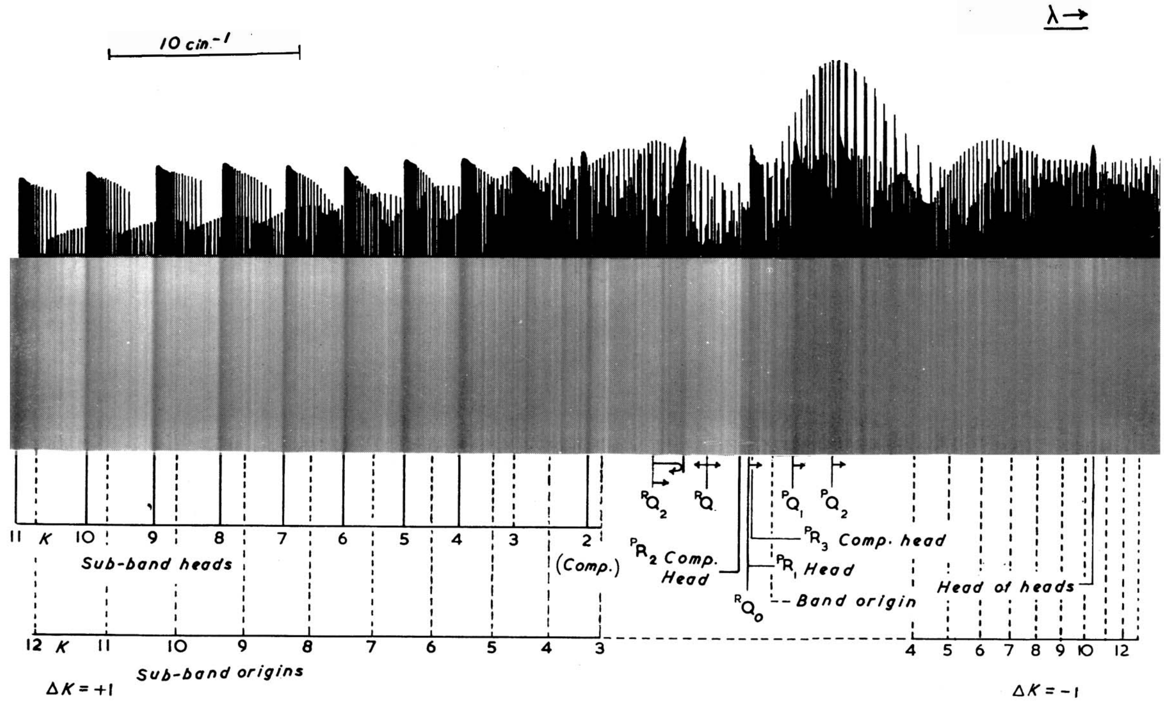
[15] Birge, *Rev. Modern. Phys.*, 1947, **19**, 298.

PLATE 1. A_0^0 *band of glyoxal.*



[To face p. 5058

PLATE 2. A_0^0 band of *dideuteroglyoxal.*



1 these are seen as groups of fairly intense lines to the long-wavelength side of the heads labelled $K_4, K_5, \cdots$. Such series were not defined clearly in the dideuteroglyoxal spectrum, since it is overlapped in the appropriate spectral region by the rotational structure of another band with its origin at approximately 22,116 cm.$^{-1}$. The frequencies of groups of resolved R lines in the glyoxal spectrum are given in Table 3. The lines listed were only just resolvable and could not be measured with extreme accuracy; however, some information could be gleaned from them. Other groups of R lines associated with sub-band heads of higher K'' numbering could be distinguished on the plates, but were not clearly resolvable.

TABLE 2. *Rotational constants (cm.$^{-1}$) obtained by least-squares approximation of heads in Table 1 to equation (6).*

(CHO)$_2$				(CDO)$_2$			
Head Numbering	$(A'' - D'')$	$(A' - D')$	S.D.	Head Numbering	$(A'' - D'')$	$(A' - D')$	S.D.
(α) $K'' = 4$—13	1·7657	1·8795	±0·0073	(α) $K'' = 4$—18	1·1396	1·2033	±0·0045
(β) $K'' = 5$—14	1·6518	1·7657	±0·0081	(β) $K'' = 5$—19	1·0758	1·1396	±0·0049
(γ) $K'' = 3$—12	1·8796	1·9934	±0·0065	(γ) $K'' = 3$—17	1·2033	1·2671	±0·0041

Also, for (CHO)$_2$, $(A' - D') - (A'' - D'') = 0·11387 \pm 0·00061$ cm.$^{-1}$; for (CDO)$_2$, $= 0·06375 \pm 0·00028$.

The J numbering of the R lines in each sub-band depends on the K numbering of the sub-band head; that is, on which of the assignments α, β, or γ in Table 2 is taken as correct. However even with this ambiguity, it was possible to calculate from the figures in Table 3 that the origin of each sub-band lay some 5 cm.$^{-1}$ to the red of the corresponding sub-band head. This implied that the Q-branch of the K''th sub-band was buried beneath the R-head of the (K''-1)th sub-band; and it can be seen from Plate 1 that the R-heads possess a diffuse and extended intensity at low K'' values, where the intensity of the underlying Q-branch would be expected to be appreciable.

TABLE 3. *Frequencies of* R-*lines in glyoxal sub-bands.*

$J'' =$ K''	4	5	6	7	8	9	10	11	12	13	14	15
4	21,993·01	93·35	93·62	93·84	94·16							
5		21,998·00	98·33	98·63	98·82	99·06						
6			22·003·35	03·60	03·83	04·08	04·26	04·46	04·66	04·86	05·02	05·23
7				22,008·79	09·06	09·27	09·48	09·69	09·87	10·10	10·30	

Some preliminary calculations were then carried out. Planar molecular models were assumed for the ground and excited states, with dimensions that yielded rotational constants approximately corresponding to the values for the α, β, and γ assignments of Table 2, and which yielded values of D_H'' and D_H' appropriate to a sub-band head-origin separation of approximately 5 cm.$^{-1}$ and a spacing between R-lines approximating to that observed. Using these models, we calculated the frequencies and positions of all lines near the band origin for a type-C transition for both glyoxal and dideuteroglyoxal; the Mathieu function approximation was used to obtain the energy levels.

In all the calculated glyoxal spectra, the stronger lines formed a clear overall pattern of intensity, which showed that the band origin ν_{00} lay some 3—4 cm.$^{-1}$ to the red of the central intensity minimum. This overall pattern was very similar in all three sets of calculated spectra, a fact which enabled the K-numbering of the sub-bands to be fixed definitely but, conversely, made it difficult to use the observed pattern of lines to obtain accurate values of the rotational constants.

The approximate position of the band origin, and the approximate head-origin separation in the sub-bands being known, the α-numbering of the sub-band heads in Table 2 can be assigned as correct. This immediately gives the J numbering of the R lines in the sub-bands.

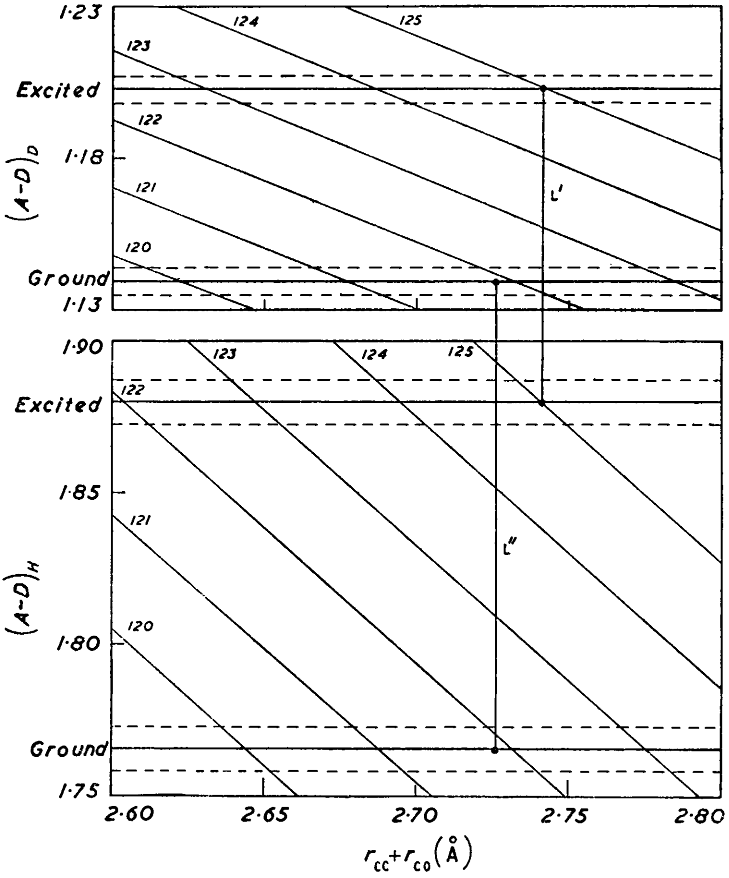
For the symmetric-top approximation, the separation of the line R(J) from the corresponding sub-band head is given by the equation:

$$\Delta\nu_J = (\Delta\nu_H - 2D') - (3D' - D'')J - (D' - D'')J^2 \quad . \quad . \quad . \quad (7)$$

where $\Delta\nu_H$ is the head-origin separation in the sub-band. The accurate positions of the sub-band heads were calculated by using the α-numbering in Table 2, and the separations of the R lines in Table 3 from the corresponding heads in each sub-band were fitted to eqn. (7) by least-squares approximation. This gave a value of D_H'' and D_H' for each sub-band considered. These were combined to give mean values for the two constants, giving each individual value a weighting inversely proportional to the sum of the squared residuals in the corresponding calculation. This gave:

$$D_H' = 0{\cdot}1479 \pm 0{\cdot}0095 \qquad D_H'' = 0{\cdot}1520 \pm 0{\cdot}0095 \text{ cm.}^{-1}$$
$$(D_H' - D_H'') = -0{\cdot}00413 \pm 0{\cdot}00070 \text{ cm.}^{-1}$$

FIG. 1. *Nomograph for calculation of dimensions of glyoxal. The sloping lines correspond to different values of ∠CCO. The broken lines show the limits of error of the observed values of* (A — D).



The Calculation of Molecular Dimensions.—If values are assumed for the C–H bond length and angle, the other molecular parameters r_{CO}, r_{CH}, and ∠CCO can now be calculated for each state of the molecule. It is also necessary to assume that, for the planar molecule in its lowest vibrational state, $I_c = I_a + I_b$; that is, the inertial defect is set equal to zero.

Various molecular models were assumed, and their rotational constants calculated by Hirschfelder's method.[16] The derivatives of $(A - D)_H$, $(A - D)_D$, and D_H were determined with respect to each of the three parameters r_{CO}, r_{CH}, and ∠CCO. These derivatives could be taken as constant over the range of dimensions which it was necessary to consider.

It was found that $d(A - D)_H/dr_{CC}$ and $d(A - D)_H/dr_{CO}$ were almost equal in sign and magnitude; this was also true in the case of dideuteroglyoxal. Hence calculated values of $(A - D)_H$ and $(A - D)_D$ were each plotted as a function of $(r_{CC} + r_{CO})$, giving series of straight lines corresponding to different values of ∠CCO, as shown in Fig. 1. There existed, for each electronic state, one value of $r_{CC} + r_{CO}$ (the lines L′ and L″) and of the angle which corresponded to the observed values of $(A - D)_H$ and $(A - D)_D$ (Table 4).

FIG. 2. *The errors associated with the determined bond lengths.*

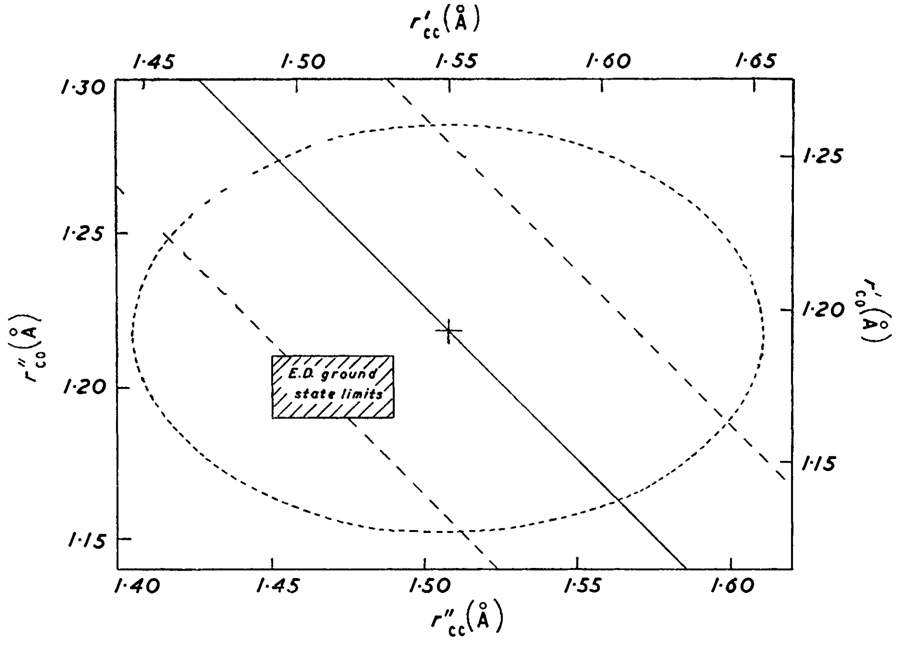


TABLE 4. *Parameters of the ground and the excited state.*

	$r_{CC} + r_{CO}$	∠CCO
Ground	2·726 ± 0·062 Å	121·9 ± 1·3°
Excited	2·742 ± 0·062 Å	125·0 ± 1·3°

The quoted deviations are determined from Fig. 1.

TABLE 5. *Bond lengths* (*very approximate*) *in the ground and the excited state.*

	r_{CC}	r_{CO}
Ground	1·50 Å	1·22 Å
Excited	1·55 Å	1·19 Å

Since the derivatives dD_H/dr_{CC} and dD_H/dr_{CO} differ considerably in magnitude, it was now possible to obtain individual values for the C–C and C–O bond lengths in each electronic state (Table 5), the observed D_H values being used together with the figures in Table 4. *It*

---

[16] Hirschfelder, *J. Chem. Phys.*, 1940, 8, 431.

is important that these individual bond lengths should not be regarded as being particularly accurate. Their individual standard deviations are of the order of 0·1 Å, and have little meaning. The permitted values for the individual bond lengths, however, are always correlated, in a sense, by the permitted values for their sums in Table 4.*

The deviations involved are shown in Fig. 2. The shaded rectangle shows the limits of error of bond lengths from the electron diffraction measurements. The straight line shows the most probable value of $r_{CO} + r_{CO}$; the broken lines flanking it show the corresponding standard deviations. The area contained within the ellipse gives the uncorrelated individual values of r_{CO} and r_{CO} that are possible. The ellipse is centred here on the most probable values for the bond lengths given in Table 5. In the ground state, the possible electron-diffraction values lie within the ellipse, and also lie largely within the area bounded by the broken lines. The same diagram, apart from the shaded rectangle, also applies to the excited state if a different set of co-ordinates are used, as shown.

In all these calculations, it was assumed that $r_{CH} = 1{\cdot}071$ Å and ∠CCO = 120°.

Calculated Appearance of Bands.—The bond angles in Table 4 and lengths in Table 5 † were used to calculate the theoretical structure of the $A_0{}^0$ bands of the two isotopic species. The results are shown at the tops of Plates 1 and 2, where the line strengths of all the individual lines present in the regions shown up to $J'' = 40$ are plotted against frequency. The Mathieu-function approximation was used in calculating the energies of rotational levels with $K < 4$, and the symmetric-top approximation was used for the others. In diagrams of this nature it is not possible to show readily the integrating effect which the use of a spectrograph of finite resolving power has upon the observed lines in a spectrum; however, in the diagrams, the intensities of sub-band heads, and of Q-branches at low J'' values, where many closely-spaced lines are present, have been deliberately increased. The bands are labelled in accordance with symmetric-top nomenclature.[17] Near the band origins, the splitting of energy levels in each state often leads to a splitting of the (symmetric-top) branches into two components, and only one of these may form a head, as shown.

The overall patterns of the observed and calculated spectra are in good agreement. There is too much overlapping of series of lines to be able to make detailed assignments of the observed fine structure of the bands. Generally, intensity maxima are predicted at the positions in which they are observed in the regions around the band origins. It is noteworthy that the ${}^{R}Q_1$ branch component is shaded towards the blue in both the calculated and the observed glyoxal spectrum, and that one ${}^{R}Q_2$ branch component forms a head shaded towards the blue in the dideuteroglyoxal spectrum, as indicated by the curved arrow. There is one apparent minor head, marked Z, in the glyoxal spectrum, which cannot be accounted for; it may be due to some weak $\Delta K = 2$ transition, or else to a P-branch forming a head at a high J'' numbering.

Rotational Structure of Other Bands.—If two transitions have a vibronic state in common, then rotational analysis should yield a common $(A - D)$ value for this state. It is theoretically possible to use this fact to deduce the correct K'' numbering of sub-bands. This was not practicable here, since the deviations in the first-order terms in the quadratics for the sub-band heads were too large in comparison with the second-order terms. Many vibrational bands were overlapped by other bands, so that only a few sub-band heads could be measured, giving correspondingly large deviations for the rotational constants. The $C_0{}^0$ band, at 22,487 cm.$^{-1}$, was fairly well defined; by Brand's analysis, this is a perpendicular band with the same ground state as the $A_0{}^0$ band. One K numbering of

---

* If it is assumed that the quoted electron-diffraction C–C and C–O bond lengths are correct, then the following set of approximate excited state dimensions can be deduced: $r'_{CO} = 1{\cdot}56$ Å, $r'_{CO} = 1{\cdot}14$ Å, ∠CCO = 126·3°.

† The values used have been rounded off to 2 decimal places in Table 5.

[7] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, 1945, p. 426.

the $C_0{}^0$ sub-band heads gave: $(A'' - D'')_H = 1{\cdot}793 \pm 0{\cdot}025$ cm.$^{-1}$; $(A' - D')_H = 1{\cdot}911 \pm 0{\cdot}025$ cm.$^{-1}$; $(A' - D')_H - (A'' - D'')_H = 0{\cdot}1184 \pm 0{\cdot}0029$ cm.$^{-1}$. The value for $(A'' - D'')$ can be compared with that for the $A_0{}^0$ band.

Under high resolution, the $K_0{}^0$, $K_1{}^0$, and $K_2{}^0$ bands are clearly parallel-type bands, as required by the vibrational analysis. Each has a weak perpendicular component. The parallel component in each consists of a series of heads, each shaded toward the red, extending towards the blue from a strong intensity maximum. These heads could be fitted to eqn. (5) to give reasonable values of the rotational constant function therein; for example, the $K_0{}^0$ bands in each spectrum gave $(A' - D')_H - (A'' - D'')_H = 0{\cdot}109$ cm.$^{-1}$ and $(A' - D')_D - (A'' - D'')_D = 0{\cdot}062$ cm.$^{-1}$. However the complete analysis of these bands is another problem.

Conclusion.—The observed structure of the $A_0{}^0$ bands of both isotopic species is consistent with a planar, centrosymmetric *trans*-configuration in both the ground and the excited state, with a perpendicular type C transition between them. The main postulates upon which Brand based his vibrational analysis are confirmed, and hence if the $A_0{}^0$ band is the (0–0) band, the excited state has A_u electronic symmetry.

Fairly accurate values for the ∠CCO and the sum of the C–C and C–O bond lengths can be obtained from the analysis of the rotational structure; but there is considerable uncertainty in the individual values to be assigned to the bond lengths in the ground and the excited state. This is partially due to the fact that analysis of the rotational structure of bands yields information about the three principal moments of inertia of the molecule, and the geometry of the glyoxal molecule is such that substitution of the hydrogen atoms by deuterium does not greatly alter the momental parameters. However, the ground-state dimensions that have been derived are in approximate agreement with those obtained by electron diffraction. In the excited state, the ∠CCO increases by some 3°, compared with the ground state, and the indications are that the C–C bond may increase slightly in length, and the C–O bond decrease by a smaller amount.

The electronic transition investigated in this paper is very weak ($f \sim 0{\cdot}00004$ in solution)[18] and is ascribed to the promotion of one of the non-bonding oxygen electrons, which in the ground state fill two almost degenerate molecular orbitals, into a π-type orbital. There are two such configurations of A_u electronic symmetry; in one of them, the promoted electron is in a π-orbital that is essentially bonding between the carbon atoms and antibonding between the carbon and oxygen atoms; the other is antibonding with respect to both the C–C and C–O bonds. In neither state would it be expected that the C–O bond decreases in length relative to the ground state, if this in fact occurs. Neither does such a decrease agree with Brand's assignment of the (mainly) C–O stretching frequency of symmetry A_g dropping from approximately 1740 to 1390 cm.$^{-1}$ upon electronic excitation.

However, simple molecular-orbital pictures may not be appropriate here.[19] Thus they ignore the charge redistribution which takes place, electronic charge being transferred from the oxygen atoms towards the centre of the molecule in the course of the transition. This, also, must affect the bond lengths, and might tend to shorten the C–O bonds and increase the C–C bond in the excited state.

The author thanks Professor D. P. Craig, Dr. J. C. D. Brand, and Dr. J. H. Callomon for comments and suggestions.

William Ramsay and Ralph Forster Laboratories,
University College, London, W.C.1.

[*Received, July 24th*, 1957.]

---

[18] McMurry, *J. Chem. Phys.*, 1941, **9**, 241.
[19] Orgel, *J.*, 1955, 121.