THE SPECTRA AND MOLECULAR VIBRATIONS OF GLYOXAL.

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The correlation of spectroscopic data with measurements of heat capacity provides valuable information about the possible occurrence of internal molecular rotation about the carbon-carbon bond in such molecules as ethane.[1] Whereas in the latter molecule internal rotation appears to be largely restricted, the data suggest that it occurs freely in dimethyl acetylene.[2] Comparison of a series of related molecules might indicate the factors upon which the height of the potential barrier to internal torsion depends. Measurements on glyoxal have therefore been made. The chemical properties and instability of this substance make it unsuitable for the measurement of heat capacity, and at first appeared to preclude the measurement of either the Raman spectrum or the infra-red absorption spectrum. Despite experimental difficulties, however, the infra-red absorption between $1 \cdot 15 \, \mu$ has been measured, and fluorescence measurements have to some extent replaced Raman data. In addition, the ultraviolet absorption spectrum of glyoxal is of exceptional interest. There are two systems of bands between 4780-3400 A. and 3200-2300 A. respectively. The first system comprises a series of bands in which the rotational structure is comparatively easily resolved. With a molecule having such large moments of inertia this is surprising, and suggests that a detailed analysis of the spectrum might be profitable. Moreover, the only other extensive and conclusive analysis of the ultraviolet bands of a polyatomic molecule which appears so far to have been made refers to the closely related molecule formaldehyde.[3] From a photochemical standpoint the correlation of the fluorescence of glyoxal with the second ultraviolet band system is of foremost interest.

During the progress of the present work Lu Valle and Schomaker [4] described electron diffraction measurements on glyoxal and dimethyl glyoxal from which it was concluded that each of these molecules has a planar " trans " structure. These authors also suggest that there may be a barrier of about 12 kcal. to internal rotation.

1. The Ultraviolet Absorption Spectrum.

This has been studied previously by Henri,[5] and by Lüthy,[6] and has been referred to by Snow and Eastwood.[7] On the basis of the intensity distribution Lüthy suggested one vibration interval for the band system

[1] Kistiakowsky, Lacher and Stitt, *J. Chem. Physics*, 1930, **7**, 289.
[2] Osborne, Garner and Yost, *ibid.*, 1940, **8**, 131.
[3] Dieke and Kistiakowsky, *Physic. Rev.*, 1934, **45**, 4.
[4] *J. Am. C. S.*, 1939, **61**, 3520.   [5] *Structure des Molecules*, Paris, 1925.
[6] *Z. physikal. Chem.*, 1923, **107**, 285.
[7] *Proc. Roy. Soc., A*, 1935, **149**, 446.

at longer wave-lengths. His conclusions fall into line with those suggested below, but the dispersion used by him was inadequate for a detailed analysis, and to some extent his measurements are misleading.

Two spectrographs were used, for the preliminary work the first order of a 10-foot concave grating giving about 5·8 A. per mm., and later the second and third orders of a 21-foot concave grating giving about 1·2 A. per mm. and 0·8 A. per mm. respectively. The absorption cells used were a glass tube 50 cm. in length with quartz or glass ends cemented on, and an all-quartz cell 1 metre in length, the pressures varying from 1-150 mm. The glyoxal was usually prepared by heating commercial paraglyoxal with excess phosphorus pentoxide, the product being condensed in a trap surrounded by a freezing mixture and subsequently fractionated in vacuo. Some specimens were prepared by passing ethylene over a mixture of selenium dioxide and phosphorus pentoxide.[8] This method, although the more costly, gives a cleaner and more satisfactory product which shows less tendency to polymerise on keeping. The continuous source was a tungsten arc for the longer wave-length regions and a hydrogen discharge tube for the shorter wave-length range. Disturbing orders were avoided in the work with the gratings by use of filters where necessary. Wavelengths were measured from superposed iron arc spectra.

As stated above, there are two regions of absorption, *c.* 4780-3400 A. and 3200-2300 A. The bands of the shorter wave-length region are diffuse under high dispersion and at the lowest pressures, and have the appearance of predissociated bands. Attempts to excite fluorescence by irradiation with wave-lengths of the mercury arc less than 3650 A. failed, which agrees with this conclusion. A detailed vibrational analysis of this band system has not been made.

The system between 4780-3400 A. consists of discrete bands which, although to a large extent overlapping and extremely complicated, reveal a definite arrangement. In agreement with their discrete nature, it was found that irradiation with 3650 A. leads to rapid polymerisation. The intense absorption begins at 4550 A. and in contrast with what is usually found with polyatomic molecules, the extinction coefficient decreases progressively on passing to shorter wave-lengths. The bands appear to be of two types, α and β, and perhaps a third, γ. These are not necessarily, though they may prove to be, connected with the *A, B* and *C* type bands of Badger and Zumwalt,[9] which refer to oscillations involving a change in electric moment parallel to the least, intermediate, or major axis of the molecule. The α type bands have superficially an appearance not unlike that of electronic bands of a diatomic molecule showing strongly degrading *P* and *R* branches, upon which is superposed symmetrically an array of fainter and much more closely packed lines. The β type bands consist of one (or more) very strong broad line, similar to an intense *Q* branch, with attendant irregularly spaced fainter lines as a background. The γ type bands are similar to the β type bands, but there are small differences. It is hoped to discuss the details of this rotational structure in a later paper. For the present, the approximate apparent origin of each band will be used for the purpose of vibrational analysis. A complete analysis of the very complex system has not so far been achieved, and photographs and microphotometer tracings of the entire system will not at present be given. We are here most directly concerned with the magnitudes of the vibration frequencies in the electronic ground state. Finer details relating to vibrational intervals in

[8] Riley and Friend, *J. Chem. Soc.*, 1932, 2342.
[9] *J. Chem. Physics*, 1938, **6**, 711.

the excited electronic state are therefore of less immediate value.   Fig. 1 shows the arrangement of the most important bands at the long wave-length end of the spectrum.   The intense on-set of absorption occurs at 4550 A., band K_1 of the type α.   Similar bands K_2, K_3, K_4 occur at 4279 A., 4040 A. and c. 3825 A.   These bands give a progression of intervals 1390, 1380 and $\sim$ 1400 cm.$^{-1}$, and indicate a vibration frequency of c. 1390 in the upper electronic state.   To some extent the arrangement of bands seen over the region of the first of these three intervals is repeated in the other two intervals.   The band K_1 at 4550 A. is the first of a close group of four moderately strong α type bands K_1, K_1', K_1'', K_1''' lying at 4550, 4527, 4507 and 4485 A., with separations of about 100 cm.$^{-1}$, and diminishing progressively in intensity with decreasing wave-length.   The band K_2 similarly has at least two corresponding associated bands K_2', K_2'' with intervals of about 100 cm.$^{-1}$.   The corresponding features of the region around the bands K_3 and K_4 are more obscure.

At 4400 A. in the middle of the K_1-K_2 interval lies an intense band L_1 of the β type.   The interval K_1-L_1 is 750 cm.$^{-1}$.   To the high frequency side of L_1 is a succession of similar β type bands L_1', L_1'', L_1''', L_1'''' at 4381 A., 4363 A., 4344 A. and 4327 A., the intensity decreasing uniformly

FIG. 1.

with decreasing wave-length.   The intervals L_1-L_1', L_1'-L_1'', etc., are each close to 100 cm.$^{-1}$, and each of the L_1 bands has a satellite of its Q branch about 50 cm.$^{-1}$ to the high frequency side of the latter.

These results suggest vibration frequencies in the excited state of approximately 100, 750 and 1390.   To the shorter wave-length side of 4279 A. the bands overlap severely, but many of them can be interpreted using these same frequencies, and the interval 100 is prominent.

Two moderately weak bands of the β type occur at 4315 A. and 4298 A., separated by 100 cm.$^{-1}$.   The interval between 4550-4315 A. corresponds to 1190 cm.$^{-1}$, and this may also be a frequency in the excited state. Each of the bands at 4315 A. and 4298 A. has a satellite at higher frequencies like the bands L_1, L_1', etc.   At 4226 A., 4209 A. and 4191 A. lie three more moderately weak bands, perhaps γ type, the intervals being again close to 100 cm.$^{-1}$.   The interval between 4550-4226 A. corresponds to 1690 cm.$^{-1}$.   Although we may expect a carbonyl group frequency in the ground state to be about 1700, this will probably be modified appreciably in the excited state, and a more probable interpretation of the interval 1690 is (1190 + 500), suggesting another excited state frequency of about 500.   At 4455 A., 4446 A. and 4436 A. lie three bands, for which an interpretation is less obvious.   There is little difference in intensity between the three bands, which are of the α type and separated

by intervals close to 50 cm.$^{-1}$. Of the three, that at 4446 A. seems slightly the strongest. The interval 4550—4455 A. corresponds to 460 cm.$^{-1}$, agreeing roughly with the previous interval of 500, but if this interpretation is correct, it is difficult to understand the two intervals of 50 cm.$^{-1}$.

To summarise therefore, there appear to be definite excited state frequencies of 100, 750 and 1393 ; other possible intervals are 1193 and 500. In addition, an interval of about 50 cm.$^{-1}$ occurs repeatedly. This must surely be too small to be associated with any vibrational motion, even a torsional oscillation, of a molecule with moderately light nuclei like glyoxal. Its significance must be left in doubt. The rotational structure suggests that the frequencies 100 and 1393 (and possibly 500) may be associated with vibrations in a different symmetry class from the vibration of frequency 750 (and possibly 1190).

To the long wave-length side of 4550 A. lie a series of bands from which we may hope to discover the magnitude of the vibration frequencies in the electronic ground state. At 4579 A., 4602 A. are two weak α type bands, which are designated α_1 and α_2 respectively. It seems natural to explain α_1 and α_2 as arising from absorption from levels in the ground state of 140, and 250, *i.e.* to assume a ground state frequency of about 140 with high anharmonicity factor. According to the Boltzmann factor however, the population of molecules in a level at 140 cm.$^{-1}$ should be moderate at room temperatures, and although quantitative estimates of the relative intensities cannot be made, we might expect α_1 to be the more intense compared with K_1 than it appears. In the same way we might expect the intensity of α_2 to be noticeably less than that of α_1, which does not appear to be the fact. Again, the relative intensities of α_1 and α_2 would lead us to expect a third band, α_3, some 100 cm.$^{-1}$ lower in frequency than α_2. No such band has been found, but a much weaker α type band occurs at 4614 A., 60 cm.$^{-1}$ to the low frequency side of α_2. If this band is to be ascribed to α_3 and belong to the progression α_1, α_2, α_3, the vibration 140 must have a high anharmonicity. At 4667 A. is an α type band designated as β_1, and the interval β_1-K_1 suggests a ground state frequency of 550 cm.$^{-1}$. The intensity of the band β_1 is roughly that to be expected from considerations of the Boltzmann factor. Two other feeble α type bands occur at 4640 A., 4627 A. The intervals 4667—4640 A. and 4640—4627 A. correspond to 123 and 70 cm.$^{-1}$ respectively. Taken as a whole, the most probable explanation of these bands seems to be that there are ground state frequencies of *c.* 135 and 550; and that the lower of these has a high anharmonicity factor and a large coupling factor with other vibrations. The vibration of magnitude 135 may have the character of a torsional oscillation.

Using high pressures of vapour, other much weaker β type bands are seen at 4777, 4752, 4728 and 4710 A., designated by γ_1, γ_2, γ_3 and γ_4. The intensity diminishes uniformly in passing from γ_1 to γ_4. The interval γ_1-K_1 gives a ground state frequency of about 1050 cm.$^{-1}$; and the intervals γ_1-γ_2 (120), γ_2-γ_3 (110), and γ_3-γ_4 (80) may be connected with the successive levels of the low frequency vibration in the excited state, in agreement with the above.

For the ground state, therefore, we have frequencies *c.* 135, 550, and 550, the first two probably belonging to a different symmetry class from the third ; 135 may be correlated with 100 in the excited state, 550 with 460 or 550, and 1050 with 750.

2. The Infra-red Spectrum.*

No previous measurements of the infra-red spectrum have been re-corded. The instrument used in the present work was a Hilger large aperture spectrometer D 88, with interchangeable prisms of rock salt, fluorite, and quartz. Details of the experimental arrangements have been described elsewhere.[10] The absorption cells were 21 cm. in length and 24 mm. in diameter, with rock salt plane ends. Pressures of glyoxal up to 200 mm. were used, but erratic polymerisation made exact measurement of the pressure impossible.

The transmission curves over the entire region, and the slit widths, used, are shown in Fig. 2, and Table I lists the wave-lengths of the absorption maxima.
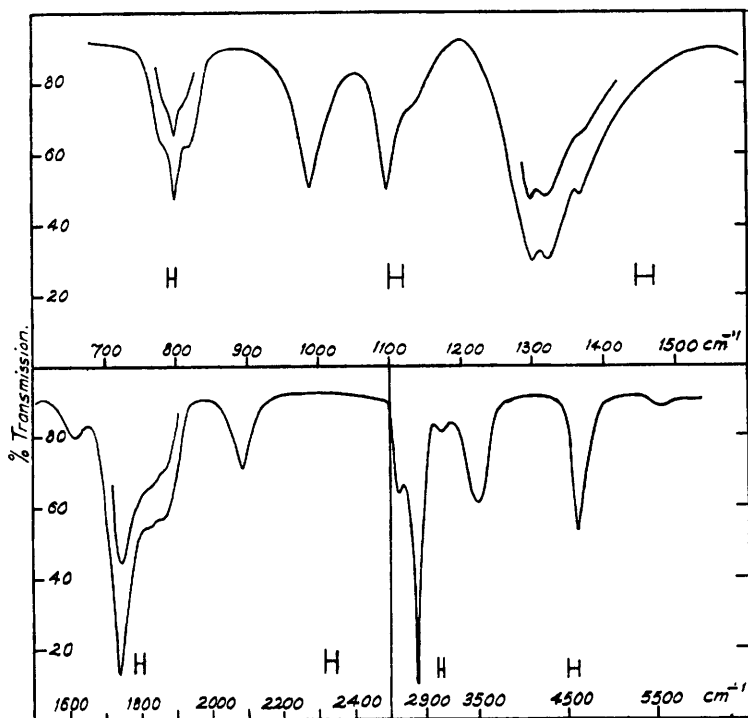

FIG. 2.

The band at $12 \cdot 5 \, \mu$ shows a central peak at 800 cm.$^{-1}$, and has shoulders on each side of this peak. It is probable that the two maxima at 1305, 1326 cm.$^{-1}$ are connected with a single band with centre at $c.$ 1315; a spacing of the " branch " maxima of 20 cm.$^{-1}$ may seem somewhat large for so large a molecule, but it is not at all inconsistent with the nature of some of the ultraviolet bands.

In considering the assignment of these absorption bands to normal modes or combination tones we may first consider the possible configurations of the glyoxal molecule and the selection rules relating to each of them. The molecule may have a planar " trans " structure I

* With A. E. Rout.   [10] Trans. Faraday Soc., 1940, 36, 797.

(Fig. 3), a planar " cis " form II, or a non-planar configuration III in which the two CHO groups lie in planes at right angles to each other. In principle of course, the planes of these two end groups may not be at right angles, but at an oblique angle ; this will not, however, materially affect our subsequent arguments. In addition to the above three possible structures, another is possible in which unrestricted rotation of the two CHO groups about the C—C bond may occur. Structure I belongs to the symmetry group C_{2h}. It has a twofold axis of rotation C_2^z, a plane of symmetry σ_z, and a centre of symmetry. There will be twelve normal modes, six permitted to appear in the infra-red spectrum. In Table II the symmetry properties and forms of these vibrations are summarised. It is seen from the selection rules that no first overtones of any vibration will be allowed in the infra-red, and the only binary combinations allowed will be those involving a vibration which is in-active in the infra-red as a fundamental with one which is active.

TABLE I.

Wave-length (μ).	Wave Number (cm.$^{-1}$).	Intensity.
12·5	800	medium
10·16	985	medium
9·11	1098	medium
c. 8·7	c. 1150	weak
7·66	1305	strong
7·54	1326	strong
? 7·25	1379	weak
6·22	1608	very weak
5·78	1730	very strong
c. 5·39	c. 1850	medium
c. 5·5	c. 1818	medium
4·81	2080	medium
3·76	2660	medium
3·53	2833	very strong
3·25	3077	very weak
2·90	3448	medium
2·18	4587	medium
1·81	5525	very weak

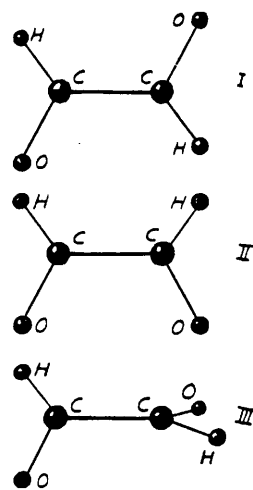

FIG. 3.

Superficially at least there are some indications that the infra-red data agree with the symmetry C_{2h}. Thus, the first overtone of ν_9, which occurs as a very intense fundamental at 2833, is apparently not observed, although the combination $(\nu_9 + \nu_1)$ appears at 5525. Other facts are not, however, in agreement with this. The six fundamentals permitted to appear in the infra-red include a CH valency vibration ν_9, a CO valency vibration ν_{10}, and the torsional vibration ν_6 ; ν_9 and ν_{10} can at once be attributed to 2833 and 1730 ; the ultraviolet data given above suggest that ν_6 may have a value of about 135, and even if it does not have this value it will almost certainly be less than 500 cm.$^{-1}$. In this case only three fundamentals should be observed in the infra-red below about 1500 cm.$^{-1}$ in the region studied. That more than three such fundamentals appear is for several reasons almost certain. Thus, if no first overtones are to appear, 1098 cannot be interpreted as the harmonic of 550, a frequency observed in the ultraviolet spectrum. There will then be four bands of at least moderate intensity, namely 800, 985, 1098, and

1315.   While intensity in itself is no criterion of a fundamental, these frequencies are best interpreted as such.   If only three of the frequencies observed below 1500 cm.$^{-1}$ are fundamentals, the remainder must be explained as combination tones and at least one of the four strong bands just mentioned must be explained as a combination of two frequencies, each lying below 800 cm.$^{-1}$.   We shall then have fixed eleven fundamentals (two at about 1730, two at about 2800, 135, 550, 1050, three of the group 800, 985, 1098 and 1315, and at least one other below 800). A careful study of the results of such an assignment shows that it could not satisfactorily account for the array of combination tones observed. The facts therefore suggest that if the selection rules remain unbroken, some other symmetry exists in the normal state of the molecule, which will permit a greater number of observed fundamentals.

There is, however, one possible reason for expecting the selection rules to break down.   The low value of the torsional fundamental ν_6 would imply that this vibration may be considerably excited at ordinary

TABLE II.

Symmetry Class.	Symmetry with respect to			Permitted in		Total.	Form.
	C_2^z.	σ_z.	i.	Raman.	Infra-red.		
A_g .	s	s	s	Yes	No	5	ν_1 CH valency. ν_2 CO valency. ν_3 CC valency. ν_4 CHO deformation. ν_5 CHO rocking.
A_u .	s	as	as	No	Yes	2	ν_6 torsional. ν_7 CHO bending.
B_g .	as	as	s	Yes	No	1	ν_8 CHO bending.
B_u .	as	s	as	No	Yes	4	ν_9 CH valency. ν_{10} CO valency. ν_{11} CHO deformation. ν_{12} CHO rocking.

temperatures, leading to a noticeable angular range of oscillation between the planes of the two CHO groups.   With such a distortional oscillation there may be a considerable departure from the selection rules which apply only to a strictly planar form.   There is, then, no strong reason for excluding the symmetry type I, but the alternatives should nevertheless be considered.

Before considering such alternatives it is profitable to examine the assignment of the various magnitudes to the different vibrational forms. This is to some extent unaffected by the symmetry type.   The vibrations have been designated ν_1-ν_{12} in Table 2.   As stated above, the infra-red data give $\nu_9 = 2833$, $\nu_{10} = 1730$, and also we may tentatively assume $\nu_6 = 135$.   The following magnitudes may also be fundamentals: 550, 1050, 800, 985, 1098, 1315 ; to which will be added $\nu_1 \sim 2700$ and $\nu_2 \sim 1730$, the twelfth frequency being still undetermined.   If the molecule does not have the symmetry C_{2h} we cannot apply the appropriate selection rules, but a consideration of the frequencies of related

compounds is helpful. Raman data for aldehydes [11] in general show that a characteristic frequency of the aldehyde group is about 1390 cm.$^{-1}$, associated with a planar deformation. In addition, we shall expect ν_3, which is essentially the C—C bond vibration, to be about 1000 cm.$^{-1}$ and the pair ν_5 and ν_{12} will be roughly equal in magnitudes. Also, the bending frequencies ν_7 and ν_8 will probably have values lower than all others except the torsional mode. The Raman spectrum of the closely related molecule butadiene [12] gives frequencies 513, 906, 1204, 1277, 1436, 1634, 3000 and 3090.

A study of these facts leads to the plausible assignment shown in Table III; 1315 might be assigned to either of the deformations ν_4 and ν_{11}. It has been written as ν_4 and the weak band at 1150 which is not easily interpreted as a combination has been tentatively ascribed to the second deformation ν_{11}. The combination tones are then interpreted as in Table IV.

As already seen, there might be objections to the molecular symmetry C_{2h}. The second structure II falls in the symmetry group C_{2v}, and has a twofold rotation axis $C_2{}^z$ and two planes of symmetry σ_x and σ_y. The vibrations split into four classes :—

TABLE III.

$\nu_1 \sim 2700$	$\nu_7 = 800$
$\nu_2 \sim 1730$	$\nu_8 = 550$
$\nu_3 = 985$	$\nu_9 = 2833$
$\nu_4 = 1315$	$\nu_{10} = 1730$
$\nu_5 = 1050$	$\nu_{11} = 1150?$
$\nu_6 = 135$	$\nu_{12} = 1098$

TABLE IV.

Wave Number.	Interpretation.	Calculated Wave Number.
? 1379	? $(\nu_7 + \nu_8)$	1350
1608	$\begin{cases} 2\nu_7 \\ (\nu_5 + \nu_8) \end{cases}$	$\begin{cases} 1600 \\ 1600 \end{cases}$
$\sim$ 1850	$\begin{cases} (\nu_5 + \nu_7) \\ (\nu_4 + \nu_8) \end{cases}$	$\begin{cases} 1850 \\ 1850 \end{cases}$
$\sim$ 1818	$(\nu_3 + \nu_7)$	1785
2080	$(\nu_3 + \nu_{12})$	2083
2660	$\begin{cases} (\nu_4 + \nu_7 + \nu_8) \\ (\nu_{10} + \nu_6 + \nu_7) \\ 2\nu_4 \end{cases}$	$\begin{cases} 2665 \\ 2665 \\ 2630 \end{cases}$
3077	$\begin{cases} (\nu_2 + \nu_4) \\ (\nu_{12} + 2\nu_3) \end{cases}$	$\begin{cases} 3045 \\ 3068 \end{cases}$
3448	$\begin{cases} (\nu_2 + \nu_4) \\ (\nu_{12} + 2\nu_3) \end{cases}$	$\begin{cases} 3460 \\ 3460 \end{cases}$
4587	$(\nu_9 + \nu_{10})$	4563
$\sim$ 5525	$(\nu_9 + \nu_1)$	5533

A_1. Symmetries with respect to $C_2{}^z, \sigma_x, \sigma_y$: s, s, s ; 5 vibrations. Raman and infra-red active. (CH valency, CO valency, CC valency, CHO deformation, CHO rocking.)

A_2. Symmetries with respect to $C_2{}^z, \sigma_x, \sigma_y$: s, as, as ; 2 vibrations. Raman active. (Torsional, CHO bending.)

B_1. Symmetries with respect to $C_2{}^z, \sigma_x, \sigma_y$: as, as, s ; 1 vibration. Raman and infra-red active. (CHO bending.)

B_2. Symmetry with respect to $C_2{}^z, \sigma_x, \sigma_y$: as, s, as ; 4 vibrations. Raman and infra-red active. (CH valency, CO valency, CHO deformation, CHO rocking.)

[11] Kohlrausch and Köppl, Z. physikal. Chem., B, 24, 370.
[12] Dadieu and Kohlrausch, Ber., 1930, 63, 1657.

There will therefore be ten vibrations permitted in the infra-red absorption spectrum. This is more in agreement with the number of bands observed, and an assignment of the magnitudes to the different types of vibration can be made which is precisely similar to that given above. This cannot, however, be taken to imply the correctness of the symmetry C_{2v} for the third non-planar structure III is without symmetry (group C_1), and all the vibrations will be permitted as fundamentals in the infra-red, and the numerical magnitudes can be assigned to the various vibration types exactly as before.

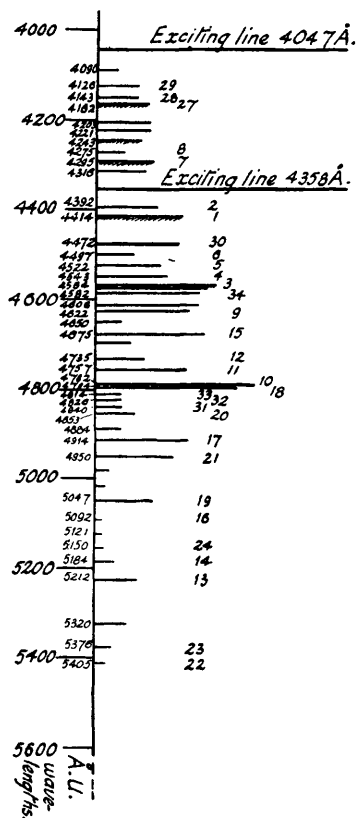The structure II might be considered improbable on other grounds. Thus the two oxygen atoms (and the two hydrogen atoms) might be expected to repel each other, and non-planar structures of a similar type to III have been suggested for hydrazine,[13] hydrogen peroxide and nitrogen tetroxide.[14] On the other hand, Pauling has suggested [15] that in conjugated systems such as glyoxal the molecule probably tends to remain planar. If the molecule has a structure III in which the planes of the two CHO groups are perpendicular to each other, it will be a symmetrical rotator ($I_B = I_C \pm I_A$), so that if the rotational structure of the ultraviolet bands can be fully analysed, some evidence should be obtained about this. This analysis is being attempted. Certainly, some of the extremely widely spaced rotational structure suggests that the excited state of the molecule must possess one very small moment of inertia. This could only be true of form I. We might consequently be led to infer a difference in geometrical form between the ground state (say C_1) and the excited state (say C_{2h}). If such a change occurred, it would not be surprising that the torsional vibration is so prominently excited in the ultraviolet absorption spectrum. It cannot, however, be said that the data enable us at present to decide unequivocally between the several possibilities.

FIG. 4.

3. The Fluorescence Spectrum.

As explained above, glyoxal absorbs from 4550 A. to shorter wave-lengths. Fluorescence was excited by irradiation with the wave-lengths 4358 A. and 4047 A. emitted by a mercury arc with suitable filters. The

[13] Penney and Sutherland, *J. Chem. Physics*, 1934, **2**, 492.
[14] Harris and King, *ibid.*, 1934, **2**, 51.
[15] *The Nature of the Chemical Bond*, p. 203.

glyoxal vapour was admitted to a cell with plane glass windows, placed before the slit of a glass prism spectrograph of high aperture and resolving power, and dispersion of 60 A. per mm. at 5000 A.   Pressures up to about 200 mm. were used.   An intense blue-green fluorescence was observed, stretching from the exciting lines to shorter wave-lengths, and consisting of a very complex system of bands, with one very intense band at 4782 A. The fluorescence appears to be independent of pressure, and is not

FIG. 5.

appreciably quenched by the addition of excess nitrogen.   Every band was unresolved and therefore diffuse and broad ; and in addition the relative intensities observed are somewhat misleading, since some of the bands at the higher frequencies correspond to wave-lengths which are absorbed by the vapour.   For example, there is a strong region of absorption just to the long wave-length side of 4358 A.   For these reasons the measured wave-lengths of the fluorescence bands cannot be
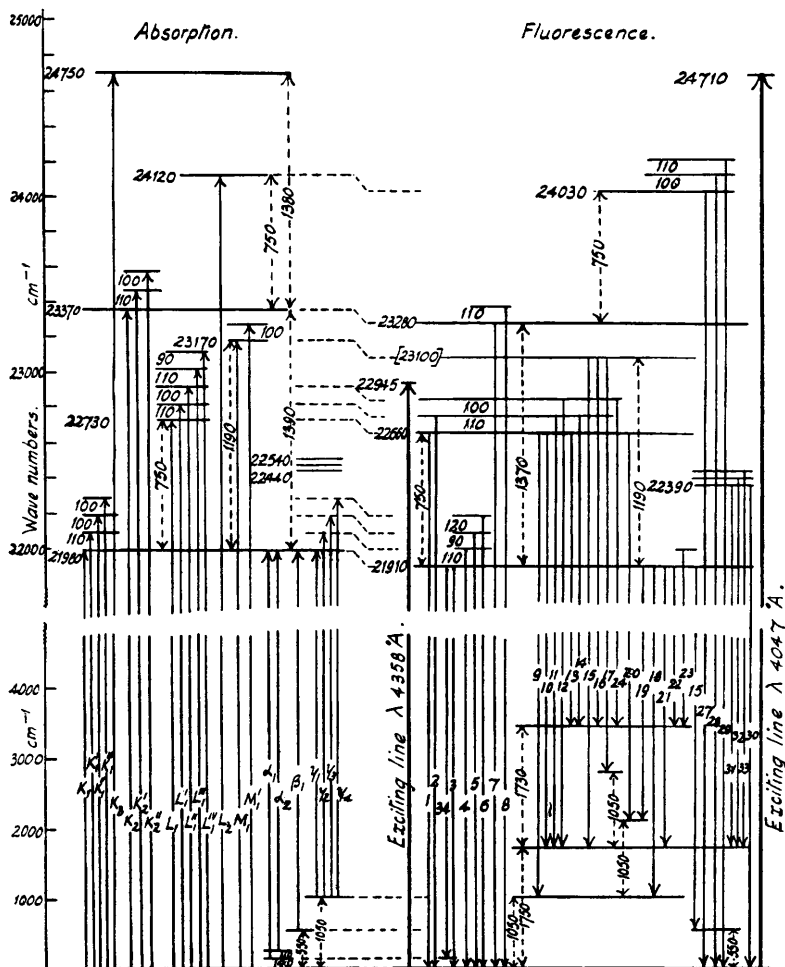
regarded as accurate to more than 2 A., and in some cases to less than this, which implies a possible error in the frequency intervals of about $\pm$ 10 cm.$^{-1}$.   Fig. 4 shows the arrangement of the bands, from which it can be seen that no simple progression is noticed such as occurs in the fluorescence of formaldehyde.   The increased number of vibration frequencies in the present case might be expected to lead to a more complex spectrum.   It has not been possible to make an unambiguous analysis of the band system, but if certain assumptions are made about the re-distribution and de-localisation of vibrational energy in the excited electronic state, a noticeable correlation can be obtained between most of the fluorescence emission bands and the absorption bands.   In Fig. 5 the two sets of transitions are shown together.   It is seen that in interpreting the fluorescence bands vibrational levels are assumed which agree well with those previously determined, in particular 550, 1050 and 1730 in the ground state, and the small value of about 100 cm.$^{-1}$ in the excited state.   It is peculiar that all the levels in the excited state deduced from the fluorescence data appear to lie about 70-90 cm.$^{-1}$ below the corresponding levels deduced from the ultraviolet data.   No explanation of this can at present be given.

4. Force Constants and Molecular Structure.

The normal vibration frequencies of formaldehyde and deuteroformaldehyde have recently been fixed by measurements of Ebers and Nielsen.[16]   A potential energy function for these molecules of the simple valency force field type and involving four constants was found by them to reproduce the values of the five planar frequencies fairly closely.   A consideration of the extra interaction terms constants found suitable with other related molecules suggests a plausible fifth constant by use of which complete agreement might be obtained.   For the calculation of the nine planar vibration frequencies of glyoxal a simple valency force field function will involve five constants, but since the pairs of localised C—H and C—O vibrations are each almost entirely controlled by a single constant the number of distinct frequencies is effectively seven. Two interaction terms could then, in theory, be introduced and might lead to a satisfactory solution.   It was originally hoped to compare the force constants in formaldehyde and glyoxal in this way.   The above assignment of the numerical magnitudes to the several normal modes cannot, however, be regarded as sufficiently convincing to justify detailed calculations of this kind, especially since the molecular form is uncertain.   An examination of the normal frequencies of acetaldehyde suggests that in this molecule the frequency which is largely determined by a vibration of the carbon-carbon bond has a magnitude of 914 cm.$^{-1}$. If for glyoxal, as suggested above, the corresponding frequency ν_3 is 985, we may infer a relative strengthening of the carbon-carbon bond in this molecule, which would be expected if it is a resonance hybrid.   The electron diffraction data of Lu Valle and Schomaker are said to suggest an abnormally low C—C bond length.   The concurrent weakening of the carbon-oxygen bonds is less apparent in the relative magnitudes. of the relevant frequencies.   In this respect the distances suggested by the electron diffraction measurements also do not reveal any abnormality.

[16] *J. Chem. Physics,* 1938, **6**, 311.

Summary.

The ultraviolet absorption spectrum of glyoxal vapour has been measured.   There are two band systems : between 3200—2300 A. is a system of diffuse predissociated bands ; irradiation of the molecule with frequencies in this region does not lead to fluorescence.   From 4780—3400 A. is a system of fine structured bands for which a partial vibrational analysis has been made ;   this suggests frequencies in the ground state of 135, 550 and 1050 cm.⁻¹.   Some features of the rotational structure of certain of the bands have been indicated.

The infra-red absorption spectrum has been measured between 1-15 μ. The bands observed have been discussed in relation to selection rules for different possible types of molecular symmetry, and a plausible assignment of the magnitudes to fundamental vibrations of the several geometric forms has been made.   Possible fundamentals are 135, 550, 800, 985, 1050, 1098, ? 1150, 1315, 1730, 2700 and 2833.   Although the data do not lead to an unambiguous decision between the several possible molecular structures, the planar " trans " form is not excluded.   The possibility of a change in molecular symmetry on electronic excitation is considered.

The fluorescence spectrum emitted in the blue and green when glyoxal vapour is irradiated with wave-lengths 4047 A. and 4358 A. has been measured and correlated with the absorption spectrum.

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