206. *The Absorption Spectrum of Keten in the Far Ultra-violet.*

By W. C. Price, J. P. Teegan, and A. D. Walsh.

The absorption spectrum of keten has been photographed in the far ultra-violet. Between 1830 and 1300 A. it bears a certain resemblance to that of ethylene, shown in (*a*) the vibrational patterns of the successive electronic states, (*b*) the proportionate reduction of the vibrational frequencies of the excited states from the ground state values, and (*c*) the term values of corresponding bands that are Rydberg in type. A Rydberg series leading to a limit of 9·60(5) ± 0·02 v. has been found : it arises from the excitation of an electron from a π-orbital localised in the C–C bond. The considerable decrease in first ionisation potential relative to ethylene is mainly caused by a particular stability of the higher excited states and of $(CH_2{:}CO)^+$. This is explicable by the assumption of conjugation between the π-C:C and the $2p\pi$-O orbitals in the excited states and in $(CH_2{:}CO)^+$, *i.e.*, the tendency of the $2p\pi$-O electrons to occupy the place vacated in the C:C-π-orbital. Stabilisation of the ground state by conjugation between the bonding π-C:C and non-bonding $2p\pi$-O orbitals appears to be small in comparison with that of the excited and the ionic states arising from this cause.

A transition caused by excitation of an electron in the CO group of the molecule occurs between 2150 and 1950 A.

Previous studies have been made of the spectra, in the far ultra-violet, of ethylene (Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207) and carbon dioxide (Price and Simpson, *ibid.*, 1939, *A*, **169**, 501). The present paper reports a study of the spectrum of keten, which is closely related to ethylene and is isoelectronic with carbon dioxide.

Experimental.—Our plates were obtained with a 1-m. normal incidence spectrograph, the grating being of glass with *ca.* 30,000 lines to the inch, giving a dispersion of *ca.* 8 A./mm. The large volume of the spectrograph (*ca.* 40 l.) minimised absorption by the products of photodecomposition, the accumulation of which was prevented by continuously pumping the material through the system : our plates showed no strong absorption due to either ethylene or carbon monoxide.

The keten was kindly provided by Professor G. Herzberg. It had been freshly prepared by pyrolysis of acetone and was purified by distillation *in vacuo*.

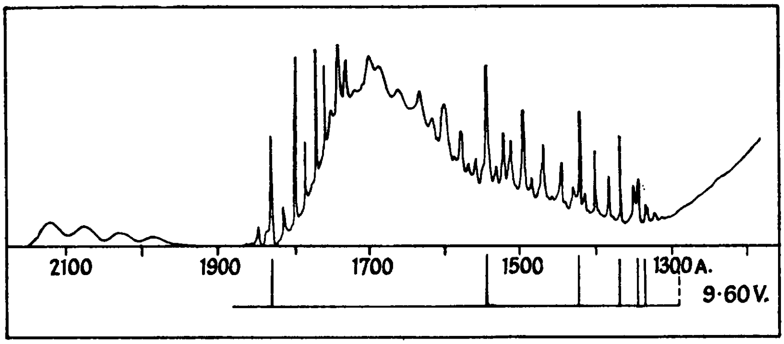
Description of the Spectrum.—In the near ultra-violet region, the absorption spectrum of keten consists of diffuse bands between 3850 and 2607 A. (Lardy, *J. Chim. physique*, 1924, **21**, 353). This represents a shift of about 200 A. to long wave-lengths relative to the corresponding bands in ketones. There are no sharp bands in this region, and the molecule exhibits no fluorescence (Norrish, Crone, and Saltmarsh, *J.*, 1933, 1533; *J. Amer. Chem. Soc.*, 1934, **56**, 1644).

Approaching the far ultra-violet region from the long wave-length end, the spectrum begins with four diffuse bands in the region 2150—1950 A. (Fig. 1). These occur at higher pressures than are necessary to bring out the bands at shorter wave-lengths reported below, and the system appears to be analogous to that occurring in aldehydes and ketones in the 2000—1600-A. region. The four bands have a frequency separation of ~1100 cm.$^{-1}$ ($_1\Delta_2 \sim 1093$ cm.$^{-1}$; $_2\Delta_3 \sim 1093$ cm.$^{-1}$; $_3\Delta_4 \sim 1170$ cm.$^{-1}$). It is unlikely that this represents a parallel-type vibration of the C:CO chain similar to the frequency appearing in the 1745—1600-A. absorption of ethylene, for the only plausible ground-state fundamental vibration of this type in keten has a frequency of 1120 cm.$^{-1}$ and, to judge by the ethylene spectrum, one would expect a considerably greater reduction of this in the excited state than from 1120 to ~1100 cm.$^{-1}$. There is little doubt that the 1100-cm.$^{-1}$ band corresponds to the frequency of *ca.* 1200 cm.$^{-1}$ found in the 1820—1650-A. region for acetaldehyde (Walsh, *Proc. Roy. Soc.*, 1946, *A*, **185**, 176) and in the 1960—1850-A. region for acetone (Lawson and Duncan, *J. Chem. Physics*, 1944, **12**, 329). In the latter case there is evidence that it represents the totally symmetrical hydrogen-bending frequency of the CH_3 group, which is 1357 cm.$^{-1}$ in the ground state. Similar frequencies occurring in the spectra of the methyl halides can be assigned unequivocally to similar CH bending vibrations (Price, *ibid.*, 1936, **4**, 1939). Thus the 1100-cm.$^{-1}$ separation of keten most probably represents the symmetrical CH deformation frequency which has been assigned the value 1386 cm.$^{-1}$ in the ground state (Halverson and Williams, *ibid.*, 1947, **15**, 552).

At shorter wave-lengths there appears a strong continuum of absorption with its maximum at *ca.* 1700 A.* The long-wave-length side of this is overlapped by a number of discrete bands starting at 1830 A. and proceeding to shorter wave-lengths. The strongest band is at 1802 A. The whole pattern, especially the occurrence of the bands in pairs, bears a considerable resemblance to that of the 1745-A. transition of ethylene.

FIG. 1.

The far ultra-violet spectrum of keten.



(*Note : absorption intensities are qualitative.*)

The bands at 1830, 1802, and 1792 A. are sharp on their short-wave sides and degrade to long wave-lengths. Similarly, the ethylene 1745—1600-A. bands are degraded to the red; but, in contrast, the acetaldehyde 1800-A. bands are degraded to short wave-lengths. Table I shows the frequencies of the main bands of the keten 1830—1730-A. region. The pairs of bands lie *ca.* 860 cm.$^{-1}$ apart, the members of each pair being separated by *ca.* 300 cm.$^{-1}$. The separation of consecutive pairs in ethylene is *ca.* 1370 cm.$^{-1}$, this representing the totally symmetrical valence frequency of the C:C bond reduced from its value of 1623 cm.$^{-1}$ in the ground state. The corresponding valence frequencies of the C:CO chain in the ground state of keten are 1120 and 2153 cm.$^{-1}$ (Halverson and Williams, *loc. cit.*). It appears fairly certain that it is the 1120-cm.$^{-1}$ frequency which is concerned here. The reduction of this to *ca.* 860 cm.$^{-1}$ is, proportionately, about the same as the corresponding reduction for ethylene. The members of the pairs of bands in the ethylene spectrum are separated by 470 cm.$^{-1}$. This separation was interpreted originally as one quantum (Price and Tutte, *loc. cit.*) and later two quanta (Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265) of a twisting vibration of the CH_2 groups thought to be 825 cm.$^{-1}$ in the ground state. The spectrum of deuteroethylene shows that for ethylene it is a vibration mainly involving motion of the hydrogen atoms. An equally plausible interpretation

---

* There is a possibility that in part the continuous absorption between 1800 and 1550 A. is due to water vapour, since (*a*) water vapour has a continuum of absorption in this region, and (*b*) bands on our plates at less than 1250 A. look like those of water vapour at these wave-lengths.

of the vibration is that it represents two quanta of the $H_2C{:}C$ bending vibration (949·2 cm.$^{-1}$ in the ground state). This would also be equivalent to a totally symmetrical vibration which is the necessary condition for it to appear in absorption from a vibrationless ground state. The only ground-state frequency of the keten molecule to which the separation of 300 cm.$^{-1}$ in the excited state could correspond seems to be two quanta of a bending vibration of the C:CO chain. If the molecule had cylindrical symmetry, there would be two degenerate vibrations of this type. The presence of the hydrogen atoms removes this degeneracy and results in two frequencies of rather similar magnitude. In the ground state these have been assigned the values 529 and 588 cm.$^{-1}$ (Halverson and Williams, *loc. cit.*). If the 300-cm.$^{-1}$ separation represents two quanta of one of these, the reduction is, proportionately, about the same as for ethylene.

Several rather diffuse bands occur in the region 1630—1550 A. They lie within the short-wave part of the 1700-A. continuum and also on the short-wave side of it. The main bands are separated by ~1000 cm.$^{-1}$ with weaker bands ~500 cm.$^{-1}$ to the short-wave side of each. Table II records the separations observed. It is suggested below that these two frequencies are due to the same modes of vibration as are responsible for the long and the short spacing of the 1830-A. system (*i.e.*, probably a valence vibration of the $C{=}CO$ group and two quanta of a bending vibration of this group, respectively).

TABLE I.

Separations of bands in the 1830—1730-A. *region* (*frequencies in cm.*$^{-1}$).

54,680	55,058	55,510	55,810	56,370	56,642	57,347
378		300		272		
830		860		977		

TABLE II.

Separations of bands in the 1630—1550-A. *region* (*frequencies in cm.*$^{-1}$).

61,550	61,844	62,369	62,900	63,364	63,914	64,365
494		531		550		
1019		995		1001		

TABLE III.

Vibrational structure of the 1545-A. *transition* (*frequencies in cm.*$^{-1}$).

64,760	65,368	65,785	66,395
608		610	
1025			

TABLE IV.

Vibrational structure of the 1493-A. *transition* (*frequencies in cm.*$^{-1}$).

66,984	67,611	68,009	68,749	69,094	69,704
627		740		610	
1025		1085			

TABLE V.

Vibrational structures of the 1421-A. (70,371 *cm.*$^{-1}$) *and* 1370-A. (72,983 *cm.*$^{-1}$) *systems.*

70,371	70,963	71,394	72,064	72,466	72,983	73,594	73,993	74,604
592		670			611		611	
1023		1072			1010			

At 1545 A. a strong band initiates another electronic transition. The frequencies of the vibrational bands of this are recorded in Table III. A moderately strong band at 1493 A. appears to start a further electronic transition. In both cases (Tables III and IV) the frequencies involved appear to be *ca.* 1025 and *ca.* 620 cm.$^{-1}$. A similar vibration pattern appears in further transitions starting at 1421 and 1370 A. Table V records some of the structure of these transitions.

The similarity of pattern between these successive systems indicates that similar electronic transitions are involved. The frequencies of this pattern maintain their magnitudes in the successive higher states. This in turn means that the upper orbitals of the 1545-, 1493-, 1421-, and 1370-A. transitions are all so large compared with the molecular dimensions (see Fig. 2, discussed later) that further excitation makes no difference to the binding between the atoms of the molecule. These transitions are clearly Rydberg transitions and they show the crowding together and the diminution in intensity as one passes towards shorter wave-lengths that are characteristic of such bands. They eventually fuse into a continuum of absorption just below 1300 A. and it is clear that an ionisation potential of the molecule occurs at about this wave-length. It is in fact possible to pick out the members of a Rydberg series represented by the formula

$$\nu_0^n = 77{,}491 - \frac{R}{(n - 1{\cdot}07)^2}, \quad n = 3, 4, 5 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

Table VI records the observed and calculated frequencies of the members.

TABLE VI.

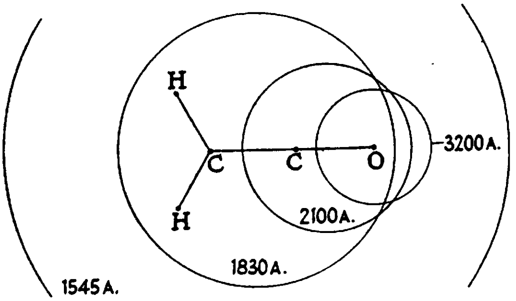
The observed and calculated frequencies of the Rydberg bands of series (1).

n.	$\nu_{obs.}$, cm.$^{-1}$.	$\nu_{calc.}$, cm.$^{-1}$.	ν ethylene, cm.$^{-1}$.	ν ethylene $-$ ν keten, cm.$^{-1}$.
3	54,680	48,039	57,340	2660
4	64,760	64,710	71,790	7030
5	70,371	70,388	77,600	7229
6	72,983	72,975	80,215	7232
7	74,367	74,371	81,625	7258
8	75,179	75,206		

Discussion.—The limit of series (1) is 9·60(5) ± 0·02 v. The series obviously corresponds to the main series found in the spectrum of ethylene (Price and Tutte, *loc. cit.*). Not only are the vibrational patterns similar, but the higher members have practically identical term values. The first member of the series is a very poor fit in the formula, but, because of its obvious resemblance to the first Rydberg transition of ethylene, there is little doubt of its classification.

FIG. 2.

The figure indicates the dimensions of the excited orbitals of the 3200-, 2100-, 1830-, *and* 1545-A. *bands of keten.*



The short vibrational progressions associated with the members of series (1) show that the bands refer to excitation of an electron from a weakly-bonding orbital. The orbital concerned is undoubtedly of a π-type and, just as with ethylene, the series may be interpreted as $\pi \longrightarrow ns$. Since the bands of series (1) represent excitation of an electron from an orbital compounded from atomic L-shell orbitals, it is clearly better to make the upper orbital of the first member of the series have the principal quantum number 3 rather than 2. For this reason, the quantum defect of series (1) has been written as 1·07 instead of 0·07. The corresponding quantum defect for ethylene is 1·09.

The reason for the poor agreement of $\nu_{obs.}$ and $\nu_{calc.}$ for the first member of series (1) is obviously that the size of the upper orbital for that member is not sufficiently large for the nuclear framework to be regarded, in comparison, as a single atom. In order that the effects of the molecular dimensions on the excited orbital may be readily understood it is valuable to calculate approximate radii for the excited orbitals and to insert them on a scale diagram of the molecule. These radii are calculated on the assumption that the term values of the states are inversely proportional to the effective radii ($V \propto 1/r$). The ionisation potential and combination radii of the electron in the ground state, together with the term value of the excited state, provide the necessary data. This has been done in Fig. 2 for the main bands of keten. The 3200-A. system of keten probably arises from the excitation of a non-bonding electron on the oxygen atom. If a radius of 0·6 A. and an ionization potential of *ca.* 11 v. for the 2pπ-oxygen electron are used, the effective radius of the excited state is calculated as 0·93 A. centred on the oxygen atom. Similarly for the band system around 2100 A., if this is interpreted as the transition of an electron from the C=O bonding orbital to an antibonding upper orbital ($\pi + \pi \longrightarrow \pi - \pi$). The excited orbital may be regarded, in an oversimplified way, as a circle of radius about 1·5 A. having its centre in the C=O bond. The upper orbitals of the 183 -, 1545,- 1493-, 1421-, and 1370-A. bands are indicated by circles centred on the C=C bond wit radii 2·2, 4·0, 4·9, 7·2, and 11·4 A. respectively. It can easily be seen that while the 3200- and the 2100-A. upper orbitals are within the molecular dimensions and must therefore be regarded as upper orbitals of intra-valence shell transitions, that of the 1830-A. band is just starting to clear the structure though it still occupies much space that might cause it to give rise to appreciable antibonding effects. These antibonding effects will tend to raise the height of the excited state above the value predicted by the Rydberg series and this is what is found ($\nu_{\text{obs.}} - \nu_{\text{calc.}} = 6641$ cm.$^{-1}$). The analogous band in ethylene at 1745 A. has an orbital of somewhat the same dimensions relative to its molecular structure (effective radius 2·1 A. centred on the double bond). It also deviates from the series formula by an amount that is comparable ($\nu_{\text{obs.}} - \nu_{\text{calc.}} = 2680$ cm.$^{-1}$), though somewhat smaller because of the less extended structure of ethylene relative to keten. The orbital of the 1545-A. band of keten is well clear of the molecular structure and can have but little effect on the binding of the molecule.

The slightly antibonding character of the first Rydberg orbitals relative to the higher ones is also brought out by the way the vibration frequencies change with the excitation. As the upper orbital of a member of series (1) changes from one comparable in size with the nuclear framework (the 1830-A. transition) to one large in comparison with it (the 1545-A. transition), the main frequencies of the vibrational pattern characteristic of the members rise from *ca.* 300 and *ca.* 860 cm.$^{-1}$ to *ca.* 620 and *ca.* 1025 cm.$^{-1}$. The 1630—1550-A. system (effective radius = 3·2 A.), although not a member of series (1),* shows intermediate frequency values. In the transitions at wave-lengths shorter than 1545 A., the vibrational frequencies remain roughly constant. In other words, (*a*) the transitions at 1545 A. and to shorter wave-lengths all have upper orbitals so extended that the excited electron has practically no effect on the binding between the atoms of the keten molecule, and (*b*) the 1830-A. transitions are to upper orbitals which possess some small anti-bonding character. (*b*) is further supported by the observed degradation to the red of bands in the 1830-A. system.

Just as for keten, the second member of the main Rydberg series found for ethylene has a long spacing greater than that of the first member; and subsequent members show spacings practically identical with those of the second member. The increase of the short spacing in keten from *ca.* 300 cm.$^{-1}$ to *ca.* 620 cm.$^{-1}$ shows that the interpretation of this spacing as representing a single quantum of the 529- or the 588-cm.$^{-1}$ ground-state vibrations is unlikely, but is compatible with the interpretation of the spacing as representing two quanta of such a vibration, as required by the selection rule.

In the spectrum of ethylene the first member (at 1745 A.) of the strongest Rydberg series is superimposed on a weaker region of continuous absorption reaching a maximum at 1630 A. A similar situation occurs for keten, the maximum of the continuous absorption being at 1700 A. The shift is about what is expected in view of the shifts of corresponding Rydberg series members in this wave-length region (Table VI). In ethylene it has been suggested that this transition is to be labelled $N \rightarrow V$ in the terminology of Mulliken (*J. Chem. Physics*, 1939, **7**, 14, 20) (cf. Walsh, *Ann. Reports*, 1947, **44**, 32).

Although the keten series (1) corresponds to the main Rydberg series of ethylene, its members are shifted considerably to long wave-lengths relative to the corresponding ethylene bands. The shifts are given in Table VI. As the upper orbital decreases in dimensions from the $n = 7$ to the $n = 6$ to the $n = 5$ member, the shift from ethylene to keten remains approximately constant. Actually it decreases slightly. From the $n = 5$ to the $n = 4$ member it decreases more rapidly and from the $n = 4$ to the $n = 3$ member it decreases most markedly. This is connected with the change of nature of the upper orbital from extra- to intra-valence shell type.

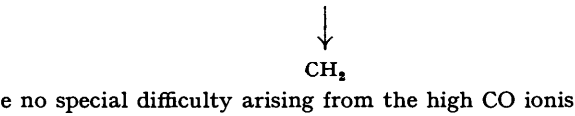
---

* It probably inaugurates a weaker Rydberg series analogous to one of the weaker series found for ethylene. The 1493-A. transition may be the second member.

It indicates that the main influence causing the ionisation potential of keten to be so much less than that of ethylene only comes into play when a π-electron is excited to an orbital large compared with the dimensions of the molecule. In other words it is a particular stability of $(CH_2{:}CO)^+$ rather than an instability of $CH_2{:}CO$ that causes the low ionisation potential. Stability of $(CH_2{:}CO)^+$ is probably due to the tendency of the 2pπ-O electrons to occupy the place vacated by the electron removed from the C:C bond : *i.e.*, delocalisation appears to be a much more important phenomenon in the higher excited states of $CH_2{:}CO$ and in $(CH_2{:}CO)^+$ than in the lower states. It is relevant here to point our that, in spite of the marked shift of the ionisation potential from ethylene to keten, (*a*) the force constants controlling stretching of the C:C bonds in ethylene and keten have been reported as identical (Linnett, *Quart. Reviews*, 1947, **1**, 85), (*b*) the C:C lengths in the two molecules are the same as determined by spectroscopic measurements (see Allen and Sutton, *Acta Crystall.*, 1950, **3**, 46) and (*c*) Kistiakowsky and Rosenberg find the rates of reaction of CH_2 with C_2H_4 and with $CH_2{:}CO$ to be almost identical (*J. Amer. Chem. Soc.*, 1950, **72**, 321) although the activation energy for reaction of a free radical or acceptor body with a π-electron system is usually less the lower the π^{-1} ionisation potential (see, *e.g.*, Chamberlain and Walsh, *Trans. Faraday Soc.*, 1949, **45**, 1032). There are therefore indications that, as regards the ground states, the C:C-π-orbital is not far from being equally tightly bound in keten and in ethylene. If so, delocalisation in the ground state of keten is probably small. Presumably it occurs to a limited extent but is largely balanced in its effect on the C:C orbital, by the inductive effect of the O atom, and the " acetylenic " nature of the central C atom in keten (Walsh, *J. Amer. Chem. Soc.*, 1946, **68**, 2408).

The electron impact value for the first ionisation potential of allene is at 9·9 v. (Delfosse and Bleakney, *Physical Rev.*, 1940, **58**, 787), and thus lies between the values for keten and ethylene (10·50 and 9·60 v., respectively). The big decrease from ethylene to keten we have explained as probably due to conjugation between the C·C-π- and the O-2pπ-electrons in the $(CH_2{:}CO)^+$ ion. The smaller decrease from ethylene to allene is then easily explicable as caused by the reduced conjugating power of a CH_2 group relative to that of an O atom. Similar stabilisation effects in ionic states have been suggested by Price (*Chem. Rev.*, 1947, **41**, 257) to be the most frequent cause of the reduction of the ionisation potentials of particular electron groups in molecules.

Judging from the spectra of aldehydes and ketones the Rydberg bands of the 2pπ-O-electrons of keten should have appeared in the region below 1700 A. Failure to detect these calls for an explanation. It is suggested that the ionisation potential of these electrons is considerably greater in keten than, for example, in acetaldehyde where the value is 10·23 v. (Walsh, *Trans. Faraday Soc.*, 1945, **41**, 498). This indeed is to be expected from the reduced polarity of the CO bond of keten relative to that of acetaldehyde (Walsh, *J. Amer. Chem. Soc.*, 1946, **68**, 2408). This reduced polarity can be regarded theoretically as due to the digonal nature of the central carbon atom in keten and is supported by experimental evidence from a variety of sources (Walsh, *ibid.*, p. 2408). It has also to be remembered that any conjugation that occurs between the π-C:C-electrons and the 2pπ-O-electrons (the former corresponding to the lower ionisation potential) will push the C:C levels up and the O levels down. Similar effects occur in vinyl chloride (Price and Tutte, *loc. cit.*; Walsh, *Trans. Faraday Soc.*, 1945, **41**, 35), and in monochlorobenzene (Price and Walsh, *Proc. Roy. Soc.*, 1947, *A*, **191**, 22). On the other hand, the ionisation potential of the 2pπ-O-electrons in keten should be lower than that in carbon dioxide (13·79 v.) in view of the lowered electronegativity of a CH_2 group relative to an oxygen atom. If the value turns out to be about 12 v., then the Rydberg bands would fall considerably to the short wave-lengths of the C:C double-bond Rydberg bands. In fact they are probably obscured by bands which appeared on our plates but which were due to water present as an impurity. That the lowest ionisation potential of the keten molecule should be that of the π-orbital of the C:C bond helps to explain the reaction of methylene with the keten molecule. The reaction may be pictured (Walsh, *J.*, 1947, 89) as



$$\begin{tikzcd}[column sep=small] CH_2 + CH_2{=}C{=}O \arrow[r] & CH_2{=}C{=}O \arrow[r] \arrow[d] & C_2H_4 + CO \\ & CH_2 & \end{tikzcd}$$

There seems to be no special difficulty arising from the high CO ionisation potential in the explanation of the long-wave shift of the near ultra-violet bands of keten (~3200 A.). The relatively positive character of the CO group will increase the binding of both the ground and the low excited state, and the latter will be still further stabilised by the tendency of the C:C-π-

electrons to occupy the place in the 2pπ-O orbital vacated by the excited electrons, *i.e.*, for the C:C orbital to become more delocalised in the excited state. The long-wave-length shift can thus be accounted for.

One of us (W. C. P.) acknowledges assistance by the U.S. Office of Naval Research under Task Order IX of Contract N6—ori 20 with the University of Chicago. Another (J. P. T.) thanks the Commissioners for the Exhibition of 1851 for the award of an Overseas Scholarship (for Eire), during the tenure of which this work was carried out. We are also grateful to the Royal Society and to the Chemical Society for grants for equipment, and to Professor C. A. Coulson for discussion in connection with this paper.

DEPARTMENT OF PHYSICS, KING'S COLLEGE,
UNIVERSITY OF LONDON.
DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEEDS.

[*Received, November 27th,* 1950.]