The absorption spectra of sulphur dioxide and carbon disulphide in the vacuum ultra-violet

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[Plates 3, 4]

In the near ultra-violet the absorption spectrum of sulphur dioxide has been investigated to a greater extent than that of any other triatomic molecule. The excellent work of Clements (1935) on the temperature dependence of the bands has enabled the ν_0 of the upper state to be definitely fixed. It has resulted in a satisfactory analysis of the so-called low-frequency system (i.e. bands appearing at high pressures which are due to transitions from various initial vibrating states), and has yielded a plausible arrangement of part of the high-frequency system (bands appearing at low pressures and temperatures, and probably corresponding to transitions from vibrationless ground states to the various vibrational levels of the upper state). Asundi and Samuel (1935) have put forward an alternative analysis of these bands, but we do not favour it on the grounds that it disregards the results of temperature experiments, contains many violations of Herzberg and Teller's selection rules (1933), and interprets several strong bands as transitions from initial vibrational states in spite of prohibitive Boltzmann factors. A photograph of the spectrum is shown in fig. 1b, Plate 3. The bands are very strong and appear at pressures of about 1/2 mm. in a path length of 1 m. Another system several times stronger than the previous one starts in the region of 2350 A. It has been investigated by several experimenters, but the only attempt at an analysis has been made by Chow (1933a, b). One of the difficulties that has troubled previous experimenters is that the bands continue to shorter wave-lengths past the transmission limit of quartz, and thus go outside the range of their instruments. We have therefore photographed the bands with a vacuum grating spectrograph, and in this way have obtained the absorption spectrum of sulphur dioxide down to about 1000 A. The technique used in obtaining the absorption spectra has been described previously (Collins and Price 1934). The Lyman continuum was employed as the continuous background against which the absorption was observed.
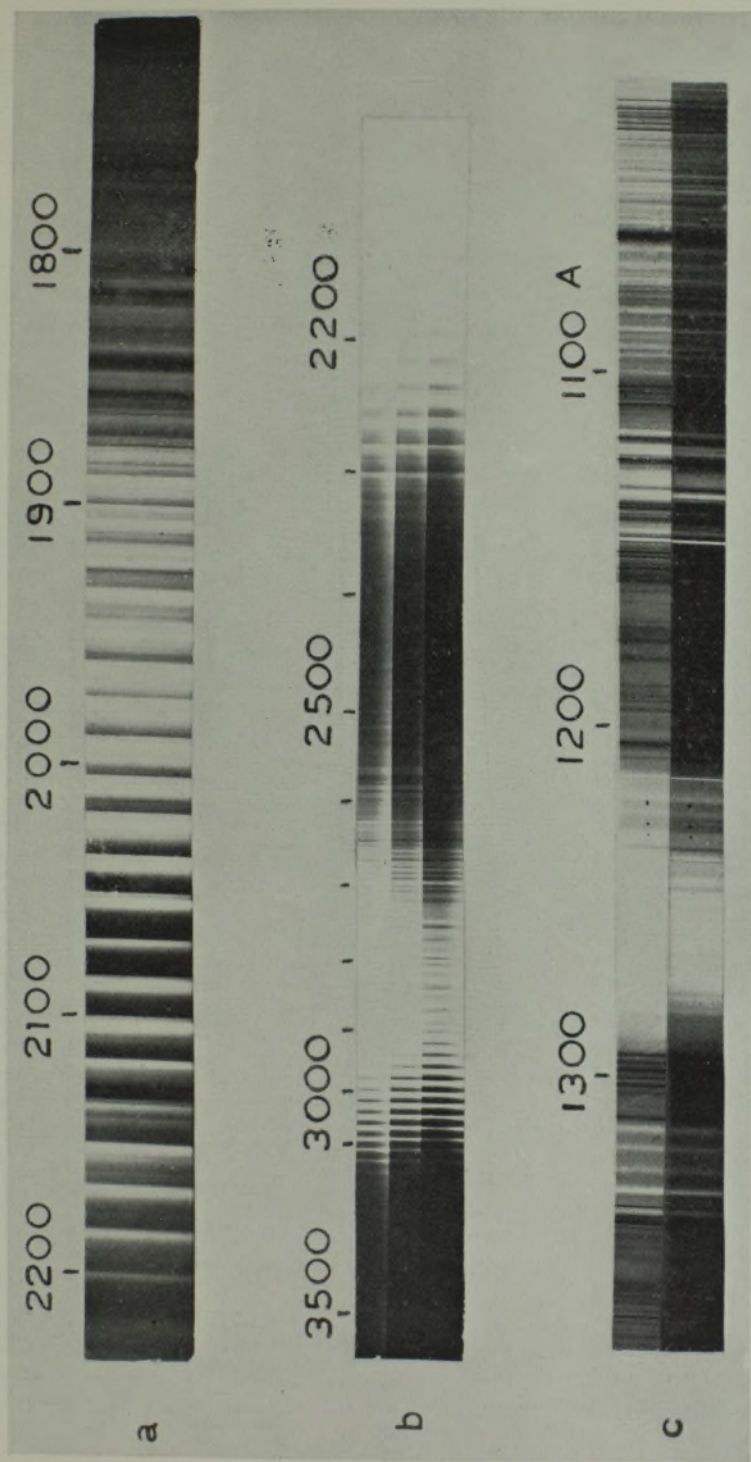
[272]

Fig. 1

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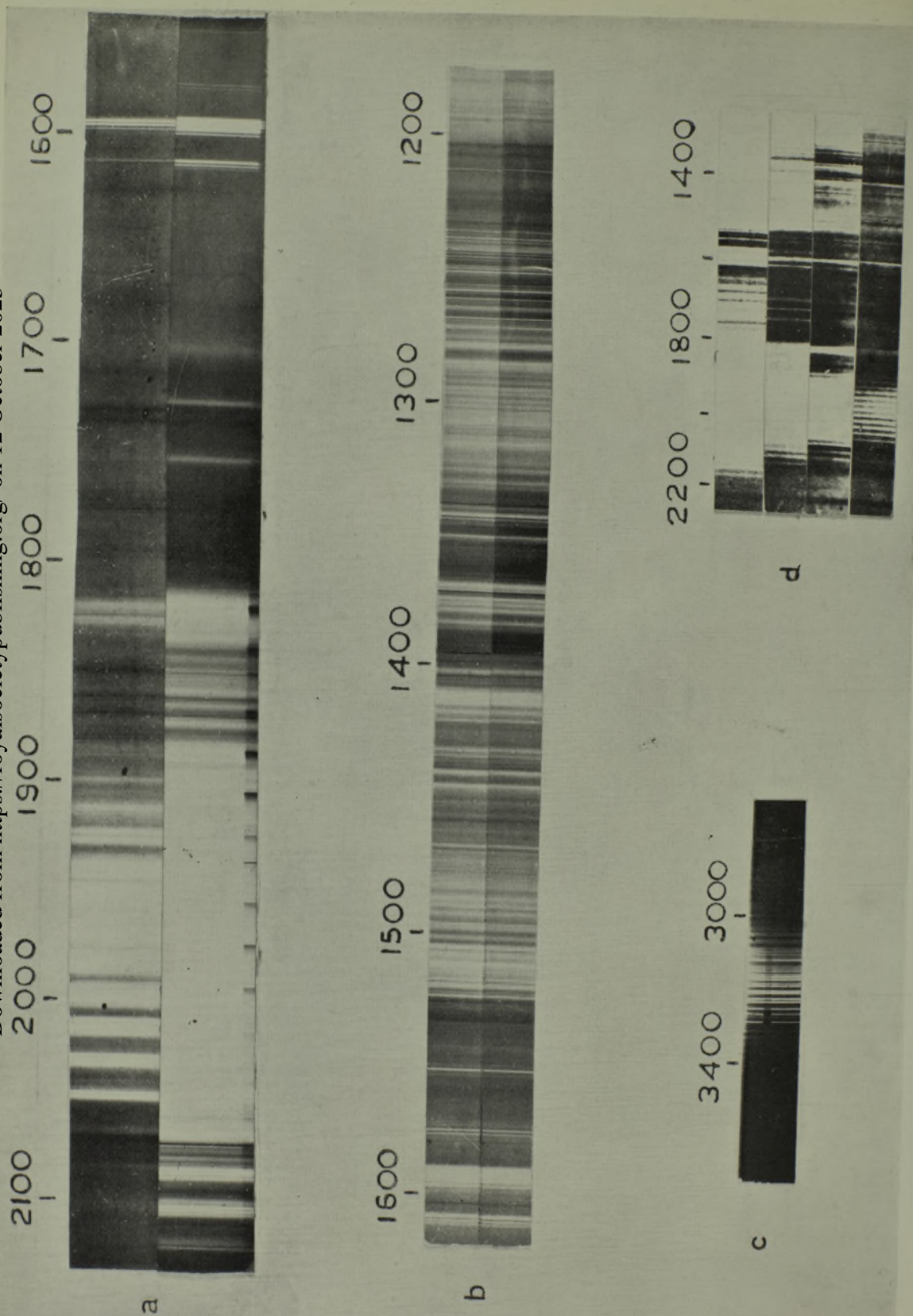Proc. Roy. Soc., A, vol. 165, Plate 4

FIG. 3

A photograph of the 2350–1800 A system of bands is given in fig. 1*a*, Plate 3. They are shaded towards the red, and many of them possess more than a single head. As far down as 1950 A some degree of regularity is apparent in the spectrum.† Beyond this the bands depart from a regular spacing, and tend to split up into several components in a rather peculiar way. Between 2300 and 1950 A we find about twenty bands forming a progression with an average spacing of 380 cm.$^{-1}$ (see Table I). The separation between consecutive members, which is taken between the centres of gravity of the various bands, is found to remain constant within quite narrow limits. After trying to fit the bands into many alternative schemes it has been concluded that a simple progression with a 380 cm.$^{-1}$ difference accounts most satisfactorily for all the strong bands which appear in this region. The separation 380 cm.$^{-1}$ most probably corresponds to the deformation frequency ν_2, which has a value of ~524 cm.$^{-1}$ in the ground state. It shows little tendency to fall off to a smaller value in going to shorter wave-lengths, and as the work of Clements (1935), Lotmar (1933), and Chow (1933*a, b*) indicates that the anharmonic constant for the 524 cm.$^{-1}$ frequency is extremely small, the similar behaviour shown by the 380 difference would seem to lend support to the suggestion that it also corresponds to the ν_2 mode of vibration. On account of the irregularities and the extremely small value of the anharmonic constant no attempt has been made to express the bands by a formula. Temperature variation experiments, which will be published separately, indicate that the 43,100 cm.$^{-1}$ band is the first member of the progression.

There are two main difficulties which the above interpretation of the bands encounters. The first is that there is a periodic fluctuation in the intensity of the bands. Starting with the band at 2206 A, and proceeding to shorter wave-lengths, the intensity of the main members gradually increases up to the fourth and then drops suddenly to the fifth. Subsequently it rises again to the eighth, and drops at the ninth. There is a further rise to the twelfth, and drop at the thirteenth, and this is repeated at the sixteenth and seventeenth bands respectively. Now all these strong bands almost certainly originate on the vibrationless ground state. If the bands form a single progression, it might be expected from analogy with the diatomic case, using the Franck-Condon principle, that the intensity of the bands would increase uniformly to a maximum, and die away on either side of

† We do not find any very definite evidence for the sudden onset of predissociation at this wave-length as reported by Henri (1931). Certainly there is some general diffuseness, but the increase in multiplicity and the departure from regularity are the most striking features of these shorter wave-length bands.

this. However, if the transition probabilities are worked out by wave mechanical methods, it can be predicted that subsidiary maxima may accompany the main one (Hutchisson 1930, 1931). This is found to occur for instance in the Dieke and Hopfield bands of hydrogen. The peculiar intensity fluctuations may therefore have some explanation on such a basis. Other more likely causes will be discussed later.

TABLE I. FREQUENCIES IN THE 380 CM.$^{-1}$ PROGRESSION OF THE 2300–1800 A SYSTEM IN SO_2

I	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$	I	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
0	43,100	—	7	47,220	380
1	43,470	370	9	47,590 M	370
1	43,840	370	9	47,980 M	390
1	44,220	380	7	48,355	375
2	44,600	380	9	48,730	375
3	44,980	380	9	49,120	390
5	45,350 M	370	10	49,500 M	380
7	45,740	390	10	49,890	390
8	46,110	370	10	50,280	390
8	46,470	360	10	50,670	390
5	46,840 M	370	10	51,030	360

$M \equiv$ mean values.

The second difficulty is that the internal structure of the individual bands varies considerably. This gives rise to some apparent irregularities in the measured spacing. Some of the bands are double, while others seem to possess only a single head though the structure is not in general so simple as this remark would imply. The sulphur dioxide molecule is an asymmetric top rotator, and the bands belonging to it should therefore be expected to have a complicated rotational structure which will depend to some extent on the vibrational state of the molecule. We have found it misleading to compare the structures of two bands which appear on the same plate with very different intensities. In fact, if these bands are examined on two plates, which are taken at such pressures that the weaker band on the high-pressure plate appears at the same strength as the stronger band on the low-pressure plate, then it is generally found that the difference in structure is not nearly so marked.

Chow in his analysis has resorted to the device of splitting up the system into three neighbouring electronic states in order to arrange the bands. However, we consider it desirable, for reasons which will be apparent later when the bands are compared to those at longer wave-lengths and to similar systems in carbon disulphide, to interpret them as a single system.

Minor irregularities in the separations and structures are explained as due to the influence of neighbouring states. Clements (1935) uses such an explanation to account for the deviations which occur in his ν_2 (220 cm.$^{-1}$) progression. In referring to the disturbance in the neighbourhood of the band "O", he states that "perhaps this is due to an interaction of the normal modes of vibration in the upper state, since ν_1 and ν_2 and even multiples of ν_3 belong to the same representation of the symmetry group". With increasing amplitudes of the molecule corresponding to the higher vibrational quantum numbers, the interaction may be supposed to increase, so that this explanation may be called upon to account for the much greater irregularities which occur around 2600 A. The breadth and diffuseness of the bands in the region 2800–2500 A has been tentatively attributed by Franck, Sponer and Teller (1932) to collision broadening, they pointed out that energy considerations prevented it from being due to predissociation. The chief difficulty with their explanation is that it requires the molecule in the excited state to have a collision radius 15 times greater than in its normal state.

The short wave-length bands of the 2300–1800 A system behave in a rather similar way to the corresponding members of the 3300–2600 A system. It would clearly be advantageous to have a common explanation for both, especially as the corresponding bands in carbon disulphide also seem to exhibit the same kind of peculiarity. It has been remarked by Mulliken that there must be considerable interaction between the various modes of vibration of a polyatomic molecule, and that the variables referring to the normal modes cannot in general be completely separable. Effects resulting from this will become increasingly important with the increase in the number of vibrational quanta present. Any particular vibrational band A of an electronic state in a polyatomic molecule is liable to be perturbed by a state B provided the symmetries of the vibronic wave functions of both states belong to the same species (Mulliken 1937). B would, of course, be built up from a different combination of the proper frequencies of the electronic state and the magnitude of the perturbation would depend on the proximity of the energy values of A and B. Such a perturbation could be used to account for the variation in intensity observed among the lower members. For example, let us consider a polyatomic molecule which has a low vibrational frequency (e.g. 300 cm.$^{-1}$) the others being high (1000 cm.$^{-1}$) and for simplicity further assume that both 300 and 1000 cm.$^{-1}$ frequencies are totally symmetrical. In a long progression of the 300 frequency, one might expect the tenth member to be perturbed by the third member of the 1000 frequency, provided that the

anharmonic constants were not too large. If the higher frequency happened to be roughly a multiple of the lower one, in this case for example 900 or 1200 cm.$^{-1}$, then a periodic perturbation would be apparent in the progression of the smaller vibration. Thus the variation in intensity with every fourth member in the 2300–1800 A system may be due to a perturbing frequency in the upper state of about 1500 cm.$^{-1}$, which belongs to the same vibrational species as ν_2, e.g. probably ν_1. Similarly, it seems possible that the 1320 cm.$^{-1}$ upper state frequency of Clements (1935) arises from a regular perturbation frequency of this magnitude rather than from one which is really present in the spectrum. If this is not so, it is necessary to assume that the 1320 is an exact multiple of the 220 cm.$^{-1}$ frequency, in the same way that it would be necessary for one frequency to be four times the other to account for the periodicity of the 2300–1800 A system. The much more violent disturbances which occur below 1950 A in the latter system may result from the fact that for such high vibrational states more combinations of the normal frequencies can have energy values laying close to the unperturbed state, and are thus able to affect it. Such an explanation might well account for the complexities of the short wave-length bands of both the 3300–2600 A and the 2300–1850 A systems.

The assignment of both the 220 cm.$^{-1}$ difference in the 3300–2600 A system and the 380 cm.$^{-1}$ difference in the 2300–1850 A system to the angle vibration of sulphur dioxide, can be supported to some extent by the consideration of a simplified potential energy diagram. Possible U/θ curves for the ground, first excited and second excited states of sulphur dioxide are shown schematically in fig. 2, θ being the $\widehat{OSO}$ angle. To obtain some idea of the absorption spectrum arising from transitions between the lowest level of the ground state vertical lines a, b, c, and α, β, γ are drawn from $a\alpha$ (the zero point energy $\frac{1}{2}\nu_2$) cutting the upper potential curves in $b\beta$ and $c\gamma$. The vertical distances between b and β, and c and γ give a measure of the frequency range over which the absorption spectrum is likely to extend. It can be seen from the figure that a much greater frequency spread is to be expected for the state in which the vibration frequency is little diminished, than for that in which it is considerably reduced.† The 3300–2600 A system in which ν_2 has fallen to the low value of 220 cm.$^{-1}$ has a frequency range of only 6000 cm.$^{-1}$; on the other hand, the 2300–1850 A system extends over the much greater spread of 13,000 cm.$^{-1}$. It therefore appears that the correlation of the 220 and

† The above argument is only valid when the potential curves of both the upper states have changed considerably from that of the ground state. This seems certainly to be true in the case under discussion.

380 cm.$^{-1}$ frequencies is supported in some measure by the frequency range over which their respective states extend.

The probable explanation of the origin of the bands seems to be that they are due to the transitions of a relatively non-bonding electron localised on an oxygen atom (i.e. the "lone pair" $2p_0$) into excited orbitals which are anti-bonding in that they weaken the angular restoring forces.† Since the excited orbital of the longer wave-length system is not so attenuated as that of the shorter wave-length system, but is closer in and concentrated between
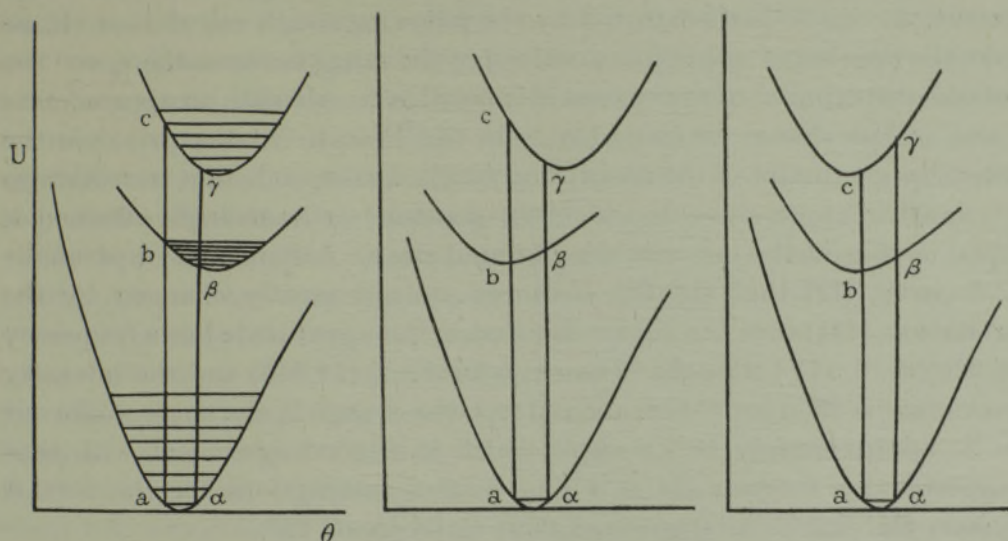

Fig. 2. Schematic U/θ curves for SO_2.

the atoms, its anti-bonding power is likely to be the larger one, if all the other factors are the same. A similar explanation seems to account for the breadths of the analogous systems in carbon disulphide. Mulliken's discussion of the electronic structure of sulphur dioxide (Mulliken 1935 c) shows that the most loosely bound electrons are slightly anti-bonding and would, in fact, be strongly so were it not for the triangular configuration of the molecule. The preference is given to the non-bonding electrons as originators of the absorption, because of the apparent absence of strongly excited valence frequencies in the upper state. The alternative explanation that the excitation is that of a bonding (valence) electron to an anti-bonding orbital, after the manner of the Schumann-Runge bands of oxygen, would probably have to be applied if the molecule happened to be linear.

The $\widehat{OSO}$ angle as determined in the ground state from electron diffraction measurements is $124 \pm 15°$ (Brockway 1936). Jonescu (1933) from a partial

† This does not necessarily mean that θ_0 increases.

rotational analysis reports the $\widehat{OSO}$ angle in the first excited state to be 96°. This computation assumes that the SO distances are not greatly altered by the excitation. Such an assumption could not in general be valid. However, according to the proposed analysis the so-called valence vibrations do not appear strongly in the spectrum. This suggests that the valence fields are not much changed by the excitation, and Jonescu's assumptions might be expected to hold roughly. Certainly the fact that he is able to deduce the $\widehat{OSO}$ angle in the ground state to be 120° supports them to some extent. It can be further tested by the following rough calculation. If we take the number of ν_2 quanta contained in the range between the ν_0 and the intensity maximum of the system it is possible to calculate an approximate value of the change in the angle. On the Franck-Condon principle the intensity maximum of the absorption bands corresponds to a transition to a vibrating upper state in which the greatest, or least angle attained is equal to that in the non-vibrating ground state. Assuming (I) a parabolic U/θ curve, (II) that the SO distances are not greatly changed by the excitation, (III) that the angle vibration in the upper state has a frequency of 220 cm.$^{-1}$, (IV) that the distance between ν_0 (31,945) and the intensity maximum is 3300 cm.$^{-1}$ (i.e. about $15\nu_2$), the change in the angle works out to be approximately 28°, a result which is in good agreement with that suggested by Jonescu (24°). Using similar assumptions for the 2000 A system the change in angle works out to be about 22°.

One of the most definite characteristics of both the 3000 and 2000 A systems of sulphur dioxide is that they are shaded towards the red. For molecules of the asymmetric top type, it is not in general possible to draw any conclusion concerning the change of a particular moment of inertia from this fact, without a more detailed analysis of the structure, such as has presumably been carried out by Jonescu. However, since the moments of inertia of sulphur dioxide in the normal state are roughly 12, 73, and 85×10^{-40} g.cm.^{2}, it can be regarded approximately as a symmetrical top rotator, in which one moment of inertia is very considerably less than the other two. The gross structure in this case would be expected to consist of a number of subheads. The subheads themselves would be shaded in the direction suggested by the change of the large moments of inertia, while the shading of the gross structure would refer to the change in the small moment of inertia. Inspection of the sulphur dioxide bands (both of the 3000 and the 2000 A systems) indicates the presence of subheads, which are frequently very narrow and for which the direction of shading cannot usually be specified with certainty. The gross structure is, however, definitely shaded towards the red. Thus it would appear that the small

moment of inertia is increased by the excitation. This is most probably explained as a diminution in the $\widehat{OSO}$ angle, in accordance with the calculations of Jonescu.

On the short wave-length side of the 2300–1850 A bands there is a region of transparency. Below 1600 A we come to the next electronic system. This consists of three rather weak diffuse bands, whose approximate wavelengths are 1573, 1558, and 1529 A. It is difficult to know whether to class these bands with those at longer wave-lengths as having their upper states represented by anti-bonding orbitals, or to group them with the bands at still shorter wave-lengths, which are of a Rydberg type. The former interpretation is considered to be the most likely one. It should also be mentioned that in the region 2700–2400 A, there seems to be evidence of a separate electronic transition. If this is so, then it would appear that sulphur dioxide has at least four electronic transitions above 1500 A.

The bands in sulphur dioxide, which might be regarded as resonance bands approaching the ionization potential, occur below 1350 A. They have a complicated appearance and comparatively little can be done with the component bands of the individual electronic states. This complexity may possibly result from strong resonance between OSO* and O*SO, which is likely to disturb some of the higher excited states. In spite of this, it is fairly easy to pick out the regions of absorption corresponding to separate electronic transitions. For instance, the bands between 1350 and 1308 A obviously correspond to a different electronic transition from those between 1280 and 1240 A, both on account of their appearance, and of the well-defined break in the absorption. The comparatively narrow frequency spread of the electronic states indicates that an electron of not very large bonding, or anti-bonding power is being removed. Between 1215 and 1140 A there is a wide region of transparency, after which there appears a set of weaker bands. It is almost certain that these bands are the successive Rydberg members of a series starting with the absorption in the 1350–1215 A region, especially as still weaker bands corresponding to the higher members of such a set appear at shorter wave-lengths. A rough Rydberg extrapolation indicates that the ionization of the molecule will occur at $12 \cdot 05 \pm 0 \cdot 05$ V. This is supported by the fact that the regions of absorption of the bands of sulphur dioxide occur a little to the long wave-length side of the corresponding ones in water.† (Absorption also assumed to arise from transitions between orbitals, which are closely atomic (non-bonding) in character.) The extrapolation of the Rydberg series in water leads to an

† Similarities can be traced between the AB series in water, and the observed bands in sulphur dioxide.

ionization potential of 12·56 V (Price 1936a). A value of 12·05 V for the ionization potential of sulphur dioxide is therefore in agreement with its spectrum. The electron impact value of $13·1 \pm 0·3$ V (Smyth and Mueller 1933) seems a little high. There is no doubt that this ionization potential corresponds to the removal of an electron which has little bonding power, and which is roughly a $2p_0$ electron. The predicted value for such an electron is 14·7 V (Mulliken 1934). Part of the discrepancy is to be attributed to the $\overset{-+-}{OSO}$ polarity (dipole moment 1·6 D), the accumulation of negative charge in the oxygen atoms reducing the ionization potentials of the electrons localized on them. Part of it, however, is probably a result of the electron retaining a certain amount of the anti-bonding power, which it would possess in a very marked degree, if the molecule were linear (Mulliken 1935c). The electron configuration of molecules having sixteen outer electrons (e.g. CO_2, CS_2 and N_2O in their normal states) consists in a set of firmly bound closed shells, giving a chemically saturated structure like that of N_2. Additional electrons introduced into such a structure, in an attempt to get the configuration of NO_2 (one more) or SO_2, Cl_2O, O_3 (two more), would have to go into anti-bonding orbitals, as in the somewhat similar diatomic cases of NO and O_2. However, as Mulliken has pointed out, the triatomic molecules given above avoid this by assuming a triangular form, and in this way acquire a different set of orbitals. In the triangular configuration, it seems that the additional electrons have relatively little anti-bonding power, since, at least for SO_2, the diminution in the ionization potential is not very much greater than that which might be expected from charge transfer effects alone.

THE ABSORPTION SPECTRUM OF CARBON DISULPHIDE

The absorption spectrum of carbon disulphide, though it differs in many of its fundamental characteristics from that of sulphur dioxide, has nevertheless several important features in common with it. These are particularly prominent for the bands lying at wave-lengths greater than 1800 A. The first moderately intense electronic absorption of carbon disulphide occurs at 3600–2900 A, see fig. 3c, Plate 4. It appears strongly only when pressures greater than several centimetres are used, the path length being ~1 m. This is much weaker than the corresponding system in sulphur dioxide (probably by a factor of 50). Mulliken (1935c) has tentatively assigned this system to a certain forbidden transition, stating that it becomes allowed because of the possibility of the molecule assuming a

triangular form in the excited state. The selection rules for the symmetry $D_{\infty d}$ are then replaced by those of C_{2v}, and the transition becomes possible as in the case of sulphur dioxide. The appearance of the spectrum is more complicated than that of sulphur dioxide, and its analysis has not yet been satisfactorily accomplished.

A much more intense system occurs at shorter wave-lengths, see fig. 3 *a*, Plate 4. In the region 2200–1800 A there is a considerable degree of regularity apparent among the bands. Inspection of the small photograph (Fig. 3 *d*) indicates the presence of a many membered vibrational progression, which rapidly widens with increase in pressure. (These photographs were taken on a small exploratory spectrograph, and serve mainly to give a bird's eye view of the spectrum, and to show its variation with pressure.) It can be seen from the high dispersion picture that each band is really built up from many components, the band at 2080 A, for example, shows several heads. Their narrowness is in part accounted for by the very large moment of inertia of carbon disulphide. Of all the possible explanations for the multiplicity of these bands, we consider that the best is that they are due to a rotational structure, which arises as a result of the molecule becoming very slightly bent in the upper state, and thus acquiring one relatively low moment of inertia. It may be mentioned here that the separation of the heads is about 40 cm.$^{-1}$ and that the structure as a whole appears to be shaded towards the red. This is compatible with the hypothesis that the molecule is bent through an angle of two or three degrees as a result of the excitation. A similar explanation will be given later to account for the structure of the band at 1600 A.

The advance of the 2200–1850 A progression towards longer wave-lengths with increase in pressure is at first quite rapid, and it reaches 2150 A with pressures of 0·5 mm. and a 1 m. path length. To extend the absorption further requires much higher pressures. At 40 cm. the bands can be followed as far as 2300 A, and the system shows signs of continuing still further. As in the case of sulphur dioxide, it was found that when the centres of gravity of the bands are taken, the gross structure forms a fairly good progression with only slight variations in the frequency separations of consecutive members. Their frequencies are given in Table II, the 45,950 cm.$^{-1}$ band is indicated as the first member by temperature variation experiments. It is even more certain in this case, than in that of sulphur dioxide, that we are dealing with a single electronic upper state, and with a vibrational progression involving only one type of vibration. The frequency difference is found to be about 410 cm.$^{-1}$ (varying between 390 and 430 cm.$^{-1}$). This is undoubtedly to be assigned to the symmetrical valence

frequency ν_1, which has a value of 656·5 cm.$^{-1}$ in the ground state. The reasons for this assignment are as follows: the appearance of the spectrum indicates that, as a result of the excitation, there has been a change in the vibration frequency; this is almost certainly a diminution. From the fact that the bands appear at such low pressures, it is certain that the electronic transition is an allowed one. The selection rules then permit only the totally symmetrical vibration frequencies to appear in absorption from the vibrationless ground state. As the only totally symmetrical frequency in carbon disulphide is ν_1, both the diminution in the frequency, and the selection rules point to this assignment for our 410 cm.$^{-1}$ separation. The absence of periodic fluctuations in the intensity of the bands is probably to be connected with the fact that neither of the other two vibrations of the molecule has the correct symmetry for causing such a perturbation. Some sixteen bands are included in the progression, which extends over a range of more than 10,000 cm.$^{-1}$. This range is considerably greater than that of the near ultra-violet system, which at pressures of several centimetres covers only 6000–7000 cm.$^{-1}$. Great increase in pressure will extend the latter system by about 1000 cm.$^{-1}$, but this is, of course, largely a result of transitions from the vibrating ground states. The same arguments apply here as were put forward for sulphur dioxide, to suggest that the "3000 A" bands correspond to a greater anti-bonding effect and to lower vibrating frequencies than the "2000 A" bands. Since all authors who have attempted to analyse the near ultra-violet system have found evidence of a frequency of about 250 cm.$^{-1}$, it seems possible that this corresponds to ν_1 in the excited state (Wilson 1929; Watson and Parker 1931 a, b; Jenkins 1929). However, from the complicated appearance of the spectrum, it is certain that more than one upper state frequency is strongly excited, and therefore no definite statement can be made until a complete analysis of the spectrum is forthcoming. It should be pointed out that if the molecule is bent in this excited state, as appears likely from electronic selection rules (Mulliken 1935 c), and also from the probable appearance of more than one upper state frequency, then the angle through which it is bent is fairly large ($\sim 10°$), as the narrowness of the bands indicates a high moment of inertia. However, this argument would not hold if the change in electric moment were along the SCS axis. The wide rotational structure of the 2000 A, 1600 A and possibly other systems indicates that the change in electric moment involved in these transitions is perpendicular to the SCS axis.

Proceeding to shorter wave-lengths, it is most noticeable that the strong band at 1815 A differs in type from the preceding ones. Since it is obviously unaccompanied by any vibrational structure, it must be assigned to a

transition between non-bonding atomic orbitals (possibly $3p \rightarrow 4s$). Though somewhat diffuse, it resolves itself at low pressures into two components ($\lambda 1818 \cdot 1$ and $1811 \cdot 7$ A). A similar band occurs at 1600 A where the non-bonding type is even more striking.

TABLE II. FREQUENCIES IN THE 410 CM.$^{-1}$ PROGRESSION OF
THE 2300–1800 A SYSTEM IN CS_2

I	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$	I	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
00	45,950	—	6	49,290	410
0	46,370	420	7	49,710	430
0	46,790	420	7	50,110 M	400 ⎫ 385
1	47,200	410	8	50,480	370 ⎭
1	47,610	410	9	50,900	420
2	48,020 M	410	10	51,280	380 ⎫ 410
3	48,440 M	420	8	51,720	440 ⎭
5	48,870	430	7	42,140	420

$M \equiv$ mean values.

TABLE III. FREQUENCIES IN THE 830 CM.$^{-1}$ PROGRESSION OF
THE 1750–1650 A SYSTEM IN CS_2

I	ν cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
3	56,490	—
10 (2)	57,320	830
10 D	58,170	850
8 DD	59,000	830
2 DD	59,820	820
1 DD	60,640	820
0 DD	61,420	780

To the short wave-length side of the band at 1800 A appear three weak bands, see fig. 3a, Plate 4. These form a progression with a frequency separation ~ 830 cm.$^{-1}$. With considerable increases in pressure more members appear, and it was found possible to measure seven in all, on very high pressure plates. As it seems probable that the vibration frequency to which this separation corresponds has been diminished by the excitation, it might conceivably be the ν_3 type, which has a value of 1524 cm.$^{-1}$ in the ground state. The objection to this interpretation is that this particular vibration is not a totally symmetrical one. However, it is conceivable that it might be allowed to appear because of dissymetry caused by the excitation SCS to SCS*. This will be explained later, when a similar vibration associated with the band at 1600 A is discussed. The possibility that the

bands may be due to CS formed by photodissociation, or even to small traces of COS impurity, cannot be entirely ruled out.

The strong band which occurs at 1600 A is probably the most interesting in the whole spectrum. Since only very weak bands occur in the range ± 2000 cm.$^{-1}$ on either side of this band, it must obviously be assigned to the excitation of a non-bonding electron. That this electron is extremely non-bonding (i.e. the transition approximates to one between atomic orbitals) is shown by the faintness of the accompanying vibration bands on the short wave-length side. The band towards longer wave-lengths arises as a transition from a vibrating ground state, and its intensity is therefore governed by the appropriate Boltzmann factor. The wave number separation of the centres of gravity of this band and the main one is 650 cm.$^{-1}$, which corresponds to a transition from the ν_1 (656·5 cm.$^{-1}$) vibration from the ground state. A transition from the lower frequency ν_2 (396·8 cm.$^{-1}$) is not observed, as it is forbidden by selection rules. A band $2\nu_2$ might be expected, but apparently the Boltzmann factor prevents its appearing. To the short wave-length side of the main band, and separated from it by 660 cm.$^{-1}$, there occurs another weak band. This separation must undoubtedly correspond to a vibration of the ν_1 in the upper states; an assignment which is in agreement both with the vibrational selection rules, and with the fact that the electronic excitation is that of a non-bonding electron (ν_1 changes only from 660 to 650 cm.$^{-1}$, i.e. 10 cm.$^{-1}$, as a result of an electron jump of nearly 8 electron volts, or 63,000 cm.$^{-1}$). A still weaker band appears at 1577 A, separated from the main band by about 1670 cm.$^{-1}$. This probably corresponds to the frequency ν_3, 1523 cm.$^{-1}$ in the ground state. While ordinarily it would be a forbidden transition, it seems to appear as a result of the dissymmetry induced in the molecule by the excitation (SCS to SCS*). This makes the symmetries of ν_1 and ν_3 equivalent as for example in SCO, where the analogous vibrations appear both in Raman spectra and the infra-red.

One of the puzzling features of the bands of this group is their well-resolved structure. They are composed of a number of very narrow heads (some of which are doublets $\Delta\nu \sim 21$ cm.$^{-1}$) whose frequencies can be determined accurately to two or three wave numbers. There are two possible explanations for this structure: firstly it might be caused by transitions from initial vibrating states which retained their original type of vibrational quanta in the excited state. The slight modification in the value of the frequencies in the upper state will cause a displacement of the bands relative to the corresponding ones arising from a vibrationless ground state. Such transitions should be relatively weak, and cannot account for the

fact that both the band at 1595 and that at 1577 A have two equally intense heads as their main components. Further, if the explanation is so simple, the two strongest members of the 1612 and 1595 A bands should be separated by exactly 656·5 cm.$^{-1}$, whereas no two components have been found with exactly this difference. Our frequency of 650 cm.$^{-1}$ was found by averaging over each band. The second, and probably the correct, explanation is that the structure is rotational in origin. If the molecule becomes very slightly bent in the upper state it can, in this way, acquire a sufficiently low moment of inertia to give a wide rotational spacing. The observed separations are ~ 70 cm.$^{-1}$, such as would occur if the carbon disulphide molecule deviated from its linear configuration by a degree or two, and so approximated to a symmetrical top rotator. The fact that the structure appears shaded towards the red would also support this theory. As others might desire to analyse further the bands in the 1600 A region, a table of frequencies correct to 2 or 3 cm.$^{-1}$ is given in Table IV.

TABLE IV. FREQUENCIES IN THE SYSTEM 1612–1550 A IN
CARBON DISULPHIDE

1612 A band		1595 A band		1877 A band		1553 A band	
I	ν cm.$^{-1}$	I	ν cm.$^{-1}$	I	ν cm.$^{-1}$	I	ν cm.$^{-1}$
00	61,865	0	62,250	0	63,204	0	64,324
1	61,960	3	62,626	0	63,284	2⎫	64,398
1	62,017	8	62,702	2	63,360	2⎭	64,416
3	62,080	10⎫	62,754	2	63,430	0	64,452
		10⎭	62,774	00	63,448		
		3	62,814	0	63,512		
				0	63,350		

Between 1535 and 1450 A there occurs a complicated set of bands crowded together without any obvious regularities. It is felt certain that no conceivable vibrational pattern will explain the character of this set. If the carbon disulphide molecule is very slightly bent in the excited state by a fraction of a degree, then part of the structure observed may well be rotational. On the other hand, resonance between the equivalent states S*CS and SCS* may be responsible for the complexity. The dimensions of the excited orbital seem to be of the right order for producing this effect. Below 1450 A the bands are less complicated, and obviously correspond to a large number of different electronic transitions, with little or no accompanying vibrational structure. Since, with the possible exception of a few bands in the neighbourhood of 1250 A, the multiplicity of heads characteristic of the 1600 and 2000 A systems is not a feature of the shorter

wave-length bands, it is most probable that the molecule is linear in these highly excited states, as it is in the ion. The bands are fairly strong, and well separated at long wave-lengths, but become weaker and crowd closer together towards shorter wave-lengths, after the manner of bands going to an ionization potential. They converge to a limit around 1230 A, or ~ 10 V. As the electron impact value of the ionization potential of carbon disulphide is $10 \cdot 4 \pm 0 \cdot 2$ V (Smyth and Blewett 1934), the above interpretation of the bands is highly probable. Starting from the short wave-length limit of the bands, it was found possible to pick out the members of the following Rydberg series:

$$\nu_0^n = 81,734 - R/(n + 0 \cdot 55)^2 \quad (n = 3, 4, 5, \text{etc.}). \tag{1}$$

Bands were found to fit in the formula from $n = 3$ to $n = 14$. Their frequencies are given in Table V. In spite of the complexity of the bands near the limit it is felt that there can be little doubt as to the reality of this series. The limit corresponds to $10 \cdot 083$ V, and the possible error in its determination is considered to be less than $0 \cdot 005$ V. It corresponds to the removal of a $3p\pi_S$ (or $(\pi - \pi, \pi_g)$) electron from the $^1\Sigma_g^+$ state of carbon disulphide (Mulliken 1935c). This leaves the molecular ion in a $^2\Pi_g$ state. The doublet separation in the analogous case of CO_2^+ is 161 cm.$^{-1}$. By a consideration of the relative values of the spin-orbit coupling coefficients of O, O$^+$ and S, S$^+$ and using the above value for carbon dioxide, it is possible to predict that the doublet separation for the $^2\Pi_g$ state of CS_2^+ should be about 400 cm.$^{-1}$. A search among the shorter wave-length bands revealed many differences of ~ 440 cm.$^{-1}$. Thus it appears that the doublet separation of the ion shows up in the highly excited states of the molecule, in the same way as it does for the alkyl halides (Price 1936b). In fact, each member of series (1) was found to possess a companion situated ~ 440 cm.$^{-1}$ on its long wave-length side. These latter bands are fairly well represented by the following formula:

$$\nu_0^n = 81,298 - R/(n + 0 \cdot 55)^2 \quad (n = 3, 4, 5, \text{etc.}). \tag{2}$$

It is not possible to be quite as certain of all the terms of this series as it is of those of series (1), because there is considerable overlapping at its limit. The associated ionization potential is $10 \cdot 027$ V. The difference between the two limits (i.e. 436 cm.$^{-1}$) is about the value which might be expected for the doublet separation of the $^2\Pi_g$ state of CS_2^+. The series (1) and (2) do not account for all the bands in the region 1550–1230 A. Other series must be present though they are difficult to establish. It should be stressed that all the bands in this region appear to correspond to vibrationless electronic

transitions, in agreement with the non-binding character of the electron removed. The predicted ionization potential for a completely non-bonding $3p_S$ electron is 10·8 V (Mulliken 1935 d). The discrepancies with the observed values are possibly to be attributed in part to $\overset{-+-}{SCS}$ polarity, though this effect cannot be great as sulphur is actually below carbon on the electronegativity scale of the elements (Pauling 1932; Mulliken 1934). Most of the discrepancy must therefore arise from the fact that $(\pi - \pi, \pi_g)$ is slightly S←→S anti-bonding. The slight increases of the ν_1 and ν_3 vibrations associated with the 1600 A band relative to their values in the ground state supports this.

TABLE V. TABLE SHOWING THE OBSERVED AND CALCULATED FREQUENCIES
FOR THE SERIES (1) AND (2) IN CARBON DISULPHIDE, TOGETHER WITH
THE WAVE NUMBER SEPARATION OF THE CORRESPONDING MEMBERS

	Series (1)		Series (2)		
n	ν obs.	ν calc.	ν obs.	ν calc.	(1)–(2)
3	73,050	73,026	72,570	72,590	480
4	76,400	76,433	75,974	75,997	426
5	78,170	78,171	77,732	77,335	438
6	79,180	79,176	Obscured	78,740	—
7	79,810	79,809	79,370	79,393	440
8	80,236	80,230	(79,810)	79,797	426
9	80,515	80,531	80,087	80,095	428
10	80,743	80,748	80,307	80,312	436
11	80,911	80,911	80,475	80,475	436
12	81,036	81,037	80,590	80,601	446
13	81,136	81,137	(80,710)	80,700	426
14	81,218	81,215	80,778	80,780	438
∞	—	81,734	—	81,298	436

( ) means used in series (1), i.e. probably two overlapping bands. The accuracy of the measurements varies according to the nature of the band measured. For some of the sharper bands it is as great as 5 cm.$^{-1}$.

Below 1200 A various sets of diffuse bands appear, each consisting of a fairly wide vibrational pattern. They are almost certainly due to the excitation of a π_u electron from the double bond. Judging from the wave-length at which they first appear (1200 A), they probably go to an ionization potential in the neighbourhood of 13·5 V (i.e. ~3·5 V more than for the non-bonding electron). This is compatible with the values assigned to the analogous electrons in carbon dioxide (Mulliken 1935 c), and suggests that the CS_2^+ emission bands are to be expected in the region 3500 A. The diffuseness of the bands below 1200 A is probably due to pre-ionization. The excited π_u electron communicates its energy (~10·5 V) to the π_g

electron (e.g. by collision) and so ejects it. Absorption bands situated just above the minimum ionization potential of a molecule frequently show this phenomenon. Oxygen is a striking example, here direct photoionization of a $v\pi$ electron is very improbable (Price and Collins 1935), but the Hopfield bands ($w\pi$ electron excited), which lie just above the ionization potential of this electron (i.e. ~1000 A) show considerable diffuseness, which is almost certainly due to pre-ionization.

Before concluding it is perhaps worth while making some remarks in connexion with the electronic nature of the 3000 and 2000 A absorption regions of sulphur dioxide and carbon disulphide. Roughly speaking, it may be said that near ultra-violet absorption spectra correspond to transitions to anti-bonding orbitals associated with the electronic configuration of the ground state, or with configurations which differ but little from it. Far ultra-violet absorption spectra, on the other hand, are of a Rydberg type, and correspond to electronic jumps involving change in the principal quantum number. As the number of excited states associated with a given molecular configuration increases with the complexity of the bonds, it is natural that near ultra-violet absorption spectra should be most prolific for those molecules in which there is the greatest degree of unsaturation. Electrons in single bonds (e.g. C—C, C—H) do not give rise to any absorption in the near ultra-violet. They seem only to absorb in their first strong resonance (Rydberg) bands which lie in the vacuum region. Double bonds, on the other hand, possess two types of absorption. In addition to the absorption of the strong resonance bands, there is a much weaker absorption between 2000 and 2500 A (e.g. work by Carr and collaborators (1936) on ethylene and its derivatives). This has been attributed to the excited state $[x+x]^{-1}[x-x, b_{2g}]^1B_{1u}$. (Mulliken 1935a), i.e. the transition of the outer bonding electron to the lowest anti-bonding orbital of the double bond. A similar explanation has been put forward by Sklar (1937) to account for the various near ultra-violet absorption regions of benzene. The far ultra-violet absorption of benzene observed by Price and Wood (1935) corresponds to the photo-ionization of the π_h electrons of this molecule, the spectra being in excellent agreement with what is expected of these electrons.†
The near ultra-violet absorption spectrum of benzene is shifted to the red relative to that of ethylene, because it corresponds to the excitation of a π_h electron from the more weakly bonding group. If an electron starting from a non-bonding orbital jumps into an anti-bonding orbital, then one

† The electrons from the "four" group should be very little bonding, and correspond to the lowest ionization potential, those of the "two" group should be more bonding, and go to the higher ionization potential.

would expect the absorption to appear still further to the red, since the electron jumps from a higher initial state. This is apparently what happens in the first ketonic absorption which occurs around 3000 A (for formaldehyde the upper state of this band is most probably $(2py)_O^{-1}[z_{CH_2}-z_O]$ (Mulliken 1935 *b*)). Now there is considerable apparent similarity between the absorption spectra of ketones and that of carbon disulphide and sulphur dioxide. This is no doubt to be related to the fact that in these molecules we have lone pairs adjoining double bonds. Thus it might be expected that the near ultra-violet bands of the latter molecules would correspond to the excitation of a non-bonding electron from the S or O atom respectively, to some anti-bonding orbital of the double bond. In addition to the similarity of the 3000 A systems, it seems that the 2000 A band in ketones bears considerable relation to the bands in carbon disulphide and sulphur dioxide, occurring in this particular region. There is much evidence to show that the bands in acetone, acetaldehyde and formaldehyde, which lie in the range 2000–1700 A, are different in nature from the Rydberg bands at shorter wave-lengths. They do not fit into the Rydberg formulae which express the latter bands and, further, in the case of acetone and acetaldehyde their appearance is quite different. It is possible that they may be ascribed to a transition $2p \rightarrow (x_C - x_O)$. Thus, if the corresponding bands in carbon disulphide and sulphur dioxide are similar in origin, it seems likely that this fact will help in the final identification of their excited states. It must be stressed, however, that although relations can be traced between $\rangle C = O$ and $O = C = O$, or $\rangle C = S$ and $S = C = S$, and in both cases it is justifiable to speak of $C = O$ and $C = S$ double bonds, the electronic structure of these bonds is very different (Mulliken 1935 *c*). It is the difference in the electronic nature of the bonding orbitals (i.e. their closed shell configuration) which accounts for the so-called resonance energy of the CO bond in CO_2 relative to that in ketones (Pauling and Sherman 1933). The non-bonding electrons are apparently not much affected by the resonance. Also it should be pointed out that similarities between near ultra-violet spectra can only be drawn when the ionization potentials of the molecules compared do not differ greatly. For instance, the bands in CO_2 which are probably analogous to the 3000 A bands of CS_2, occur below 1700 A (Leifson 1926; Mulliken 1935 *c*). This is due to the fact that the ionization potential of CO_2 is nearly 4 V greater than that of CS_2.

Summary

The absorption spectra of sulphur dioxide and carbon disulphide have been investigated by means of a vacuum spectrograph down to 1000 A. For both molecules the systems of bands can be divided into two classes: (1) those which exhibit wide vibrational structure, (2) those which exhibit little or no vibrational structure. The former class probably correspond to transitions to anti-bonding molecular orbitals, while the latter are due to the transitions of comparatively non-bonding electrons to excited orbitals, which are mainly atomic in character. In the case of sulphur dioxide, the extrapolation of the bands of class (2) to their limit gives a value of $12 \cdot 05 \pm 0 \cdot 05$ V for the ionization potential of the molecule. A similar procedure for carbon disulphide yields the much more accurate values $10 \cdot 083$ and $10 \cdot 027$ V for ionization to the two components of the doublet state $^2\Pi_g$ of CS_2^+ ($\Delta\nu = 436$ cm.$^{-1}$). The experimental evidence indicates that while carbon disulphide is slightly bent in the earlier stages of the excitation, it finally returns to a linear configuration in CS_2^+. A vibrational analysis of the bands of class (1) is also given, and some general features of the electronic spectra of polyatomic molecules are discussed.

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A suggestion for unifying quantum theory and relativity

By M. Born

Introduction

There seems to be a general conviction that the difficulties of our present theory of ultimate particles and nuclear phenomena (the infinite values of the self energy, the zero energy and other quantities) are connected with the problem of merging quantum theory and relativity into a consistent unit. Eddington's book, "Relativity of the Proton and the Electron", is an expression of this tendency; but his attempt to link the properties of the smallest particles to those of the whole universe contradicts strongly my physical intuition. Therefore I have considered the question whether there may exist other possibilities of unifying quantum theory and the principle of general invariance, which seems to me the essential thing, as gravitation by its order of magnitude is a molar effect and applies only to masses in bulk, not to the ultimate particles. I present here an idea which seems to be attractive by its simplicity and may lead to a satisfactory theory.

1. Reciprocity

The motion of a free particle in quantum theory is represented by a plane wave

$$A \exp\left[\frac{i}{h} p_k x^k\right],$$