

## BAND SPECTRUM OF CARBON-DISULPHIDE, PART II.

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### 1. GENERAL SURVEY

In part I of this series, Ramasastry and K. R. Rao (1947)\* reported the results of their investigations on the absorption spectrum of carbon-disulphide in the 2000A. region. The bands were ascribed to an allowed electronic transition and the long main progression of intense bands first reported by Price and Simpson (1938) involving the totally symmetrical vibration of the upper state having a frequency of  $410 \text{ cm.}^{-1}$  was confirmed. From a second similar progression, newly observed, the energy of the bending or the deformation vibration of the excited electronic state was estimated to be about  $235 \text{ cm.}^{-1}$ , on the basis of Herzberg and Teller's selection rules for an allowed transition between two electronic states in both of which the molecule is linear. The intensities of the bands within each progression and between the two progressions, considered in relation to the Franck-Condon principle, indicate that the bond distance is considerably increased due to the electronic excitation while the bond angle has not altered sensibly from  $180^\circ$ .

In this part, it is proposed to give the details of an investigation on the near ultraviolet absorption of  $\text{CS}_2$  vapour in the region 3800A.-2900A. Wilson (1929) published a comprehensive catalogue of the wavelength data of about 670 absorption peaks in this region. The work of Wilson (1929), Jenkins (1929), and Watson and Parker (1931) was, however, done when not much was known even about the ground electronic state of the molecule. A fairly complete knowledge of this state is available at the present day. The molecule is linear in the ground state, the two non-degenerate vibrations, one of which is totally symmetrical and the other anti-symmetrical, are known to have energies of about  $\nu_1'' = 656.5 \text{ cm.}^{-1}$  (in liquid) and  $\nu_3'' = 1523 \text{ cm.}^{-1}$  (in gas) and the third which is the doubly degenerate bending vibration has the frequency  $\nu_2'' = 396.7 \text{ cm.}^{-1}$  (in gas). Later, Liebermann (1941) analysed the rotational structure of six bands in this region. He mentioned that Herzberg also attempted an analysis of the bands (unpublished work). Mulliken (1935, 1937, 1941, 1942) in a series of articles developed the view that the upper state of the near ultraviolet band system of  $\text{CS}_2$  is probably  ${}^1\Pi_g$  if the molecule remained linear; the forbidden electronic transition between this and the  ${}^1\Sigma_g^+$  ground electronic level being, however, made allowed by vibronic selection rules (due to the excitation of non-totally symmetrical vibrations). The observed low intensity of absorption in this region compared to that in the  $\lambda$  2000 region points to such a possibility. More recently, supported by the work of Liebermann (1941), Mulliken (1941) confidently asserts that the molecule is bent in the equilibrium configuration of the upper electronic state in which case the  ${}^1\Pi_g$  (of the linear molecule) level would split into  ${}^1A_2$  and  ${}^1B_2$  electronic states (appropriate for a bent molecule). This would make

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\* See this for earlier references.

extensive series in  $\nu_1'$  and  $\nu_2'$  possible which can probably explain the perplexingly large number of the bands observed.

## 2. APPROACH TO THE PROBLEM

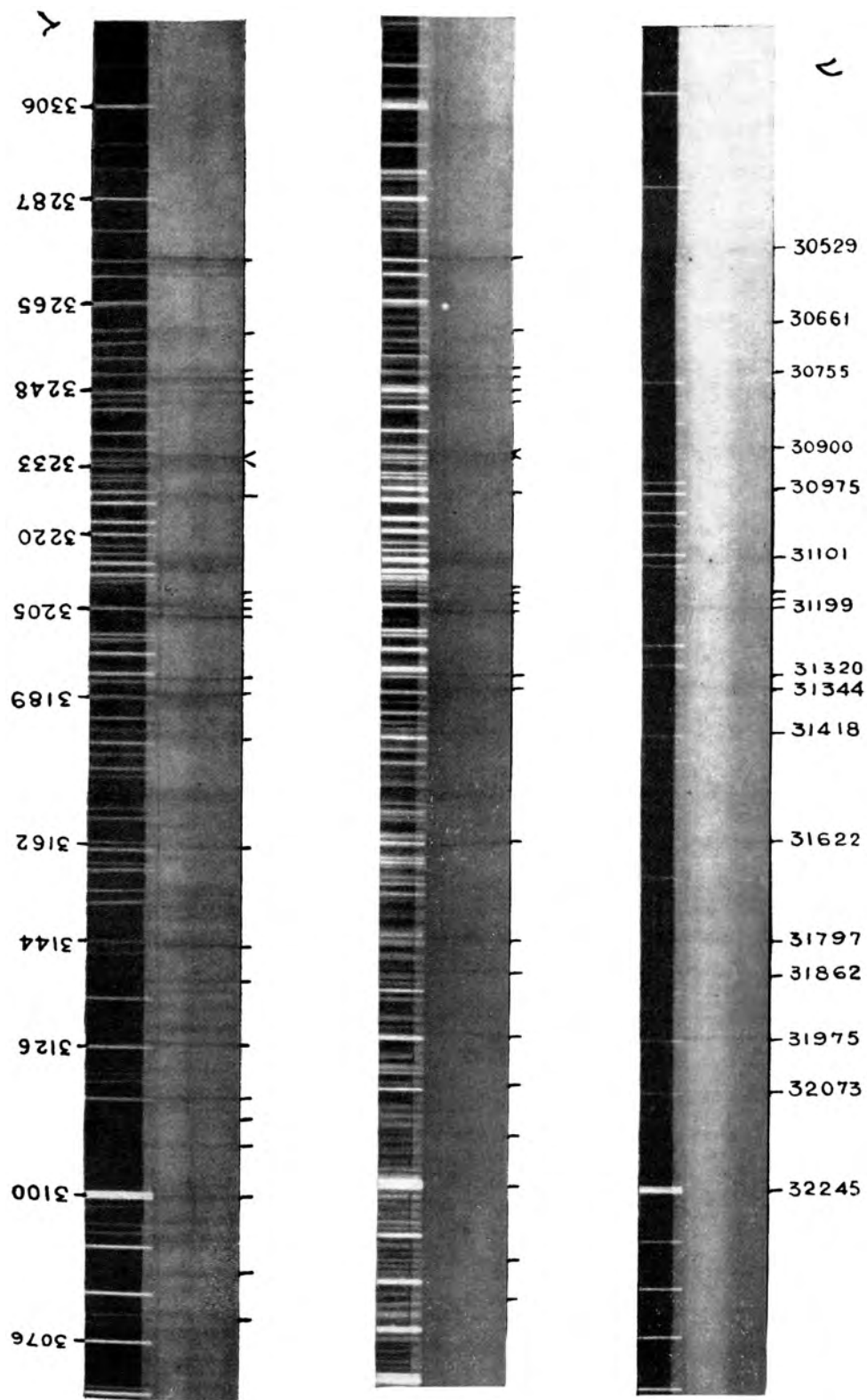
As a part of the general programme of work in the spectroscopy laboratory of the Andhra University, the author considered it desirable to investigate the 3300A. system of CS<sub>2</sub> molecule in the light of the excellent work on the XY<sub>2</sub> type triatomic molecules initiated by Mulliken at the Ryerson Physical Laboratory (on the 30,000 lines/inch 30 ft., 5½ in. ruled surface Chicago grating) and in view of the recent developments in the interpretation of the vibrational structure of the near ultraviolet spectra of polyatomic molecules, particularly benzene and its derivatives. As the number of absorption bands of CS<sub>2</sub> recorded by Wilson between 3800A. and 2900A. is very large, it is considered necessary to find out in the first instance to what conditions of the absorbing gas do the various measurements correspond. As it is well known that the absorption bands grow more intense and broader with increase in the number of molecules of the gas encountered in the absorbing path and the temperature of the gas, and also because it is known from the work of Jenkins (1929), Kush and Loomis (1939), and Liebermann (1941) that the structure of each band extends in certain cases to as much as 17 to 20 wave-number units, it is expected that a study in the proposed direction should make it possible to associate some of the bands measured by Wilson with the rotational detail of the more prominent ones. If this is done, there may be only a comparatively smaller number of bands that are to be accounted by vibrations. The most intense portion of a band can also be accurately located for use in the vibrational analysis. This has necessitated a close study of the development of the bands right from the condition when they made their first appearance to that when they are obliterated by continuous absorption due to the intensification, broadening and consequent overlapping by neighbouring bands.

Also, as has been pointed out by Wilson (1929) qualitatively and Mulliken (1941) from theoretical considerations, the apparent complexity of the spectrum may be due to the presence of more than one overlapping system. In such a case, it can be argued that because the positions and intensities of all such systems will not in general be exactly equal, it might be possible to isolate at least the intense bands belonging to the most intense of these systems by reducing the number of molecules in the absorbing path to such an extent that bands of the other less intense systems, if any, become either extremely weak or do not appear. If the expected simplification of the spectrum occurs, it would also be easier to attempt a vibrational analysis of the bands. In planning these experiments, the author had in mind the absorption spectra of the near ultraviolet band systems of substituted benzenes.

## 3. EXPERIMENTAL

So it is sought to reduce the number of molecules in the absorbing gas until the number of bands recorded is the minimum. Such a condition is shown in Plate V(a) from which about a dozen prominent bands alone could be measured. The absorbing column is 2.5 cm. long and the side tube containing the CS<sub>2</sub> liquid is kept surrounded by ice + salt mixture at -15°C. The experimental set-up is similar to that employed in the earlier investigation on CS<sub>2</sub>. Plate V(b) represents the spectrum taken with a 3-cm. all-quartz absorption cell at a temperature of 27°C., pressure is not known. The condition just marks a slight intensification of the absorption over that in Plate V(a).

Ilford Special rapid plates were used to photograph the bands. Exposure time ranged from two minutes on the Hilger Medium Quartz to one hour on the Hilger Quartz Littrow with the source of continuum a 12-volt 25-watt tungsten filament lamp with a special sucked-in thin pyrex window, supplied by the General Electric Company.



## 4. ANALYSIS

In this section, some regularities observed in the absorption spectrum of  $\text{CS}_2$  vapour, in the region  $\lambda$  3450– $\lambda$  2900 will be presented. Though they have not led to a complete vibrational analysis of the entire band spectrum from  $\lambda$  3800 to  $\lambda$  2900, it is considered that the regularities noticed are of significance and may as well form the starting point for the analysis.

To begin with, bands observed in Plate V(a) alone are considered. No two prominent bands differed by any of the ground state vibrational frequencies of  $\nu_1'' = 656$ ,  $\nu_2'' = 397$  and  $\nu_3'' = 1523$   $\text{cm}^{-1}$ . However,  $31199 - 30529 = 670$ ,  $31183 - 30529 = 654$  and  $31975 - 31318 = 657$  were noted, of which the last one only is consistent with the relative intensities of the two bands concerned. The picture did not also reveal any unmistakable progressions.

A search has also been made among these bands for an interval of about 270  $\text{cm}^{-1}$ , long and prominent progressions of which were noticed by the earlier investigators in the long wavelength region between 3750A. and 3425A. This was also not successful. The author's findings on these long wavelength progressions are reserved for publication in a subsequent communication. Suffice it here to say that these 270  $\text{cm}^{-1}$  progressions started in the 3700A. region and tend to progress towards shorter wavelengths. The interpretation of 270  $\text{cm}^{-1}$  as an upper state vibrational frequency necessitates the location of the origin of the band system at the long wavelength end of the spectrum. The absence of this interval in the  $\lambda$  3300–2900 region shows that there are two different band systems involved, one in the long wavelength region and the other in the short wavelength region. It should be noted in this connection that in Plate V(a) there are no bands recorded on the red side of  $\lambda$  3274.6,  $\nu$  30529 and only a few isolated bands developed at moderately higher absorption paths. Between 3450A. and 3350A. the region of maximum overlap between the two band systems, one can expect some bands of the short wavelength system which arise from the vibrating ground state of the molecule. It has thus become possible to some extent to isolate the bands belonging to the short wavelength system which is found to be more intense than the long wavelength system. Experimentally it appears justified to consider most of the bands in the reproductions, Plate V, as belonging to a single system.

From the absorption pictures obtained at moderately higher pressures and longer path lengths, particularly the Medium Quartz spectrogram shown in Plate VI, it has become possible to find a few progressions of bands involving an interval of about 450  $\text{cm}^{-1}$ . These are indicated below.

*Progressions*

30529		30755		30901		31166
	446		444		443	
30975		31199		31344		31621
	448		451		453	
31423		31650		31797		32072
	459				448	
31882				32245		32530
	453				458	
32335				32703		32975
	454				453	
32789				32156		
	458				461	
33247				32617		
					457	
				32074		

30661	31318	31975	31940
31101	31767	32413	32382
31549	32215	32869	32833
31997			
32450			
32099			
32451			
32904			
33352			

Most of the intense bands in the region 3300A.-2950A. could be included in the above progressions. It should be mentioned here that Wilson (1929) also observed the differences  $31344 - 30900 = 444$ ,  $31198 - 30755 = 443$  and  $31182 - 30738 = 444$ .

The irregularities in the above-mentioned  $450 \text{ cm.}^{-1}$  progressions are within the errors of measurement, as even in the most favourable cases the different measurements differed by about two wave numbers. This is due to the nature of the bands. Where sharp heads are found these are measured, while in most other cases the centres are measured. Jenkins (1929) pointed out that most of the bands are of simple *P-R* branch type and it is the positions of the intensity minima rather than the maxima that are to be used in forming the progressions; the former correspond to the so-called missing lines while the positions of the latter are liable to fluctuations with changes in the absorbing path of the gas. The location of the minima is no doubt possible in the case of certain bands even under the comparatively lower dispersion employed in the present investigation. As it could not, however, be done in the case of most other bands, the above-mentioned method of measurement is adopted. If higher dispersion is employed in this region of the absorption spectrum, it could be expected to systematise the intervals in the above progressions and indicate sudden jumps, if any. In forming the above progressions the qualitative appearance of the individual bands is kept in mind to be of guidance in the interpretation of the vibrational structure. The reality of the progressions cannot be doubted and an average value of  $450 \text{ cm.}^{-1}$  is adopted as the characteristic interval of these progressions.

From its magnitude this  $450 \text{ cm.}^{-1}$  has to be considered as a vibrational frequency of the *upper* electronic state. There are two possibilities for its interpretation: (1) as the C-S bending vibration  $\nu_2'$  (ground state value  $397 \text{ cm.}^{-1}$ ); (2) as the C-S stretching valence vibration  $\nu_1'$  (ground state value  $656 \text{ cm.}^{-1}$ ). The first of these accepts an increase in the vibrational frequency due to the excitation of the electron. The observed violet degradation of some of the bands also indicates that the moment of inertia has decreased in the upper state. If the molecule retained its linearity, this would mean a decrease in the internuclear distance presumably due to an increase in the bond energies which would result in an increase of the vibrational frequencies. However, in the case of the polyatomic molecules the vibrational frequencies generally decrease with the electronic excitation, though the possibility of increase cannot be altogether ruled out. For a molecule linear in both the electronic states, Herzberg and Teller's selection rules do not permit the appearance of  $\nu_2$  progressions which require the corresponding quantum number to change progressively by 0, 1, 2, 3, etc. The same arguments of the appearance of lengthy progressions advanced by Mulliken (1941) against the interpretation of  $270 \text{ cm.}^{-1}$  (observed

among the long wavelength bands) as due to  $2\nu_2'$  of a linear molecule are also applicable here. Moreover, the molecular orbital considerations of Mulliken led him to consider that there should be a decrease in the vibrational frequencies due to the excitation of the electron. At the same time the decrease should not be considerable as only one electron has jumped while eight bonding electrons remain.

This brings us to the other possibility of regarding the  $450 \text{ cm.}^{-1}$  frequency as representing the totally symmetrical C-S bond stretching (breathing) valence vibration of the upper state. There is the expected fall in frequency from 656 to 450 as the molecule goes from the ground to the excited electronic state. The selection rules are not against its appearance. In such an event, the decrease of at least one of the moments of inertia required to explain the observed violet degradation of the bands is probably due to a slight bending of the molecule in the upper state.

In what follows, a discussion will be presented regarding the various possibilities of the upper state. As for the ground state, the molecule carbon-disulphide is homologous to carbon-dioxide. Both have zero dipole moments. The infra-red and Raman activity of the fundamental vibrations indicates that  $\text{CS}_2$  like  $\text{CO}_2$  is linear and symmetrical and has the symmetry  $D_{\infty h}$ . The lowest vibronic state,  $(000)^+$ , which is totally symmetrical can be represented by  ${}^1\Sigma_g^+$  following the nomenclature recommended by Mulliken from an analogy of the diatomic molecules.

*Case i.*—Linear symmetrical upper state; allowed electronic transition; inter-nuclear distance not altered. One may expect strong 0-0 band associated with a number of weaker bands due to 1-1 transitions of both the totally symmetrical and non-totally symmetrical vibrations. The appearance should *somewhat* correspond to the  $\Delta v = 0$  sequence of a normally developed band system of a diatomic molecule. Bands with  $\Delta v_1 = 1, 2, 3$ , etc. will be weak while those with  $\Delta v_1 = -1, -2, -3$ , etc. will be weaker. Weak transitions with  $\Delta v = 2, 4$ , etc. and weaker (due to the effect of Boltzman factors in absorption work) transitions with  $\Delta v = -2, -4$ , etc., of the non-totally symmetrical vibrations ( $\nu_2$  and  $\nu_3$ ) can also be expected. All these will be displaced from the 0-0 band by values equal to the appropriate multiples of the corresponding vibrational frequencies. Associated with each of the bands which arise from change in the quantum number of either of the non-totally symmetrical vibrations there can be present bands due to the 1-1 transitions of the totally symmetrical vibration, giving the appearance somewhat akin to the  $\Delta v = 1, 2, 3, -1, -2, -3$ , etc. sequences of the diatomic case.

Such features are, however, very rarely met with in the absorption spectra of polyatomic molecules, but when observed are to be ascribed to the excitation of an electron from one non-bonding orbital to another or between two equally bonding orbitals. Then it follows that the vibrational frequencies in the two electronic states differ only slightly and such a transition can generally be expected in the vacuum ultraviolet.

In the near ultraviolet absorption spectrum of  $\text{CS}_2$ , the band at  $\lambda 3204.3, \nu 31199$  conforms to the above description. It is a clearly violet degraded band with a sharp *P*-head. Three or four weaker but equally sharp bands developed on its long wavelength side at longer effective paths, their intensity decreasing with their distance from the main band.

31198.3 (16.5) 31181.8 (16.3) 31165.5 (15.2) 31150.3 (17.3) 31133.

The mean interval between these bands is about  $16 \text{ cm.}^{-1}$ . If, as stated above, these form the so-called  $\Delta v_1 = 0$  sequence, one has to explain their positions as due to a decrease by  $16 \text{ cm.}^{-1}$  of the frequency of the totally symmetrical breathing vibration from its value of  $656 \text{ cm.}^{-1}$  in the ground state as the molecule gets into the upper electronic level.  $\nu_1'$  will then have a value of about  $656 - 16 = 640 \text{ cm.}^{-1}$ . But this interval does not recur among the other bands. In this case the expected picture of the band system is extremely simple and cannot explain the large number of bands actually present.

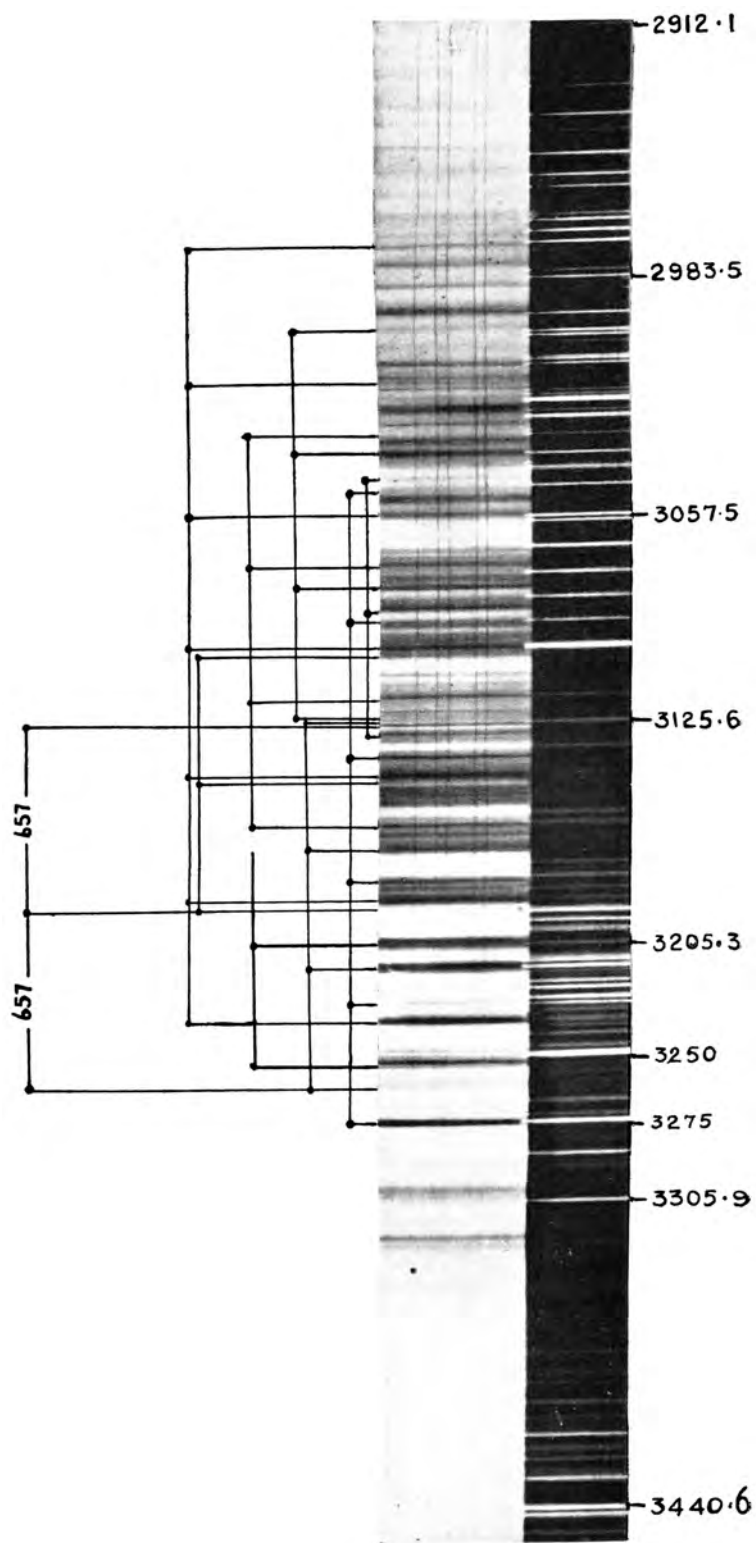
The possibility of regarding this  $16 \text{ cm.}^{-1}$  as  $\Delta \nu_2$  will be considered in the next section.

*Case ii.*—The molecule is linear symmetrical in its upper state and the electronic transition is an allowed one. Also the internuclear distances in the two electronic states differ only moderately (slightly less or slightly more for the stationary positions of the nuclei). In this case the 0-0 is generally very strong though not the strongest. But the excitation of the totally symmetrical vibration of the upper state by a few quanta (1, 2, 3, 4, etc.) can make the internuclear distance at the end positions of the oscillation approximately the same as in the vibrationless ground state—a condition according to the Franck-Condon principle most suitable for the electronic transition; the electron jump takes place and the molecule finds itself in a vibrating upper state. The corresponding band will be the strongest.

The expected prominent features of such an electronic transition would be the presence of long progressions of single frequency, the most intense of which will be  $(\nu 00)'-(000)''$ . Next in order of intensity will be the progressions  $(\nu 20)'-(000)''$ . The intensities of the progressions arising from the vibrationless ground state decrease in the order  $(\nu 00)'-(000)''$ ,  $(\nu 20)'-(000)''$ ,  $(\nu 40)'-(000)''$ , . . . and  $(\nu 02)'-(000)''$ ,  $(\nu 04)'-(000)''$ , . . . and other  $\nu_2 \nu_3$  combinations  $(\nu 22)'-(000)''$ , etc. All the above represent allowed vibronic transitions for a molecule linear in both the electronic states and the electronic transition a permitted one. However, the F-C principle favours only the first of these while it is against the others in which either  $\Delta \nu_2$  or  $\Delta \nu_3$  or both are greater than zero. There are a further set of progressions allowed by the vibronic selection rules and favoured by the F-C principle. These are  $(\nu 00)'-(\nu 00)''$ ,  $(\nu 10)'-(\nu 10)''$ ,  $(\nu 20)'-(\nu 20)''$ , . . .  $(\nu 01)'-(\nu 01)''$ ,  $(\nu 02)'-(\nu 02)''$ , . . . , and  $(\nu 11)'-(\nu 11)''$ , etc., all of which involve  $\Delta \nu_2 = \Delta \nu_3 = 0$  and  $\Delta \nu_1$  any value. But the Boltzmann factors are against these as they arise from vibrating lower state. The F-C principle is against one set and the Boltzmann factors against the other, the  $(\nu 00)'-(000)''$  is the only one which is favoured by both. An attempt has been made to fit in the observed bands of  $\text{CS}_2$  into the above scheme of analysis but it proved futile. For instance, taking 30529 band as the first member, the intense bands do not form into regular progressions. (Compare the appearance of the 2000A. system.) From the description of the bands in the region  $\nu 31139-\nu 31133$  given under case (i), they may as well be due to  $\Delta \nu_2 = \Delta \nu_3 = 0$ . If they represent the 0-0, 1-1, 2-2, etc. transitions involving the deformation vibration, we have  $\nu_2''-\nu_2' = 16 \text{ cm.}^{-1}$  or  $\nu_2' = 381 \text{ cm.}^{-1}$ . The appearance of as many as four members on the red side with such intensity can be more easily explained from the point of view of both Boltzmann and statistical weight factors when the transitions involve the bending vibration which has the smallest frequency of the ground state  $\nu_2'' = 397 \text{ cm.}^{-1}$  rather than  $\nu_1'' = 656 \text{ cm.}^{-1}$  which was considered in case (i). A search for intervals of  $2\nu_2' = 762 \text{ cm.}^{-1}$  proved futile. Though the two prominent bands, 30529 and 30900-30909, differed by  $371-380 \text{ cm.}^{-1}$ , this frequency value of  $380 \text{ cm.}^{-1}$  for the upper state deformation vibration could not explain the other intense bands in a consistent way.

*Case iii.*—Linear symmetrical upper state, allowed electronic transition, the internuclear distances change considerably. The expected features will be almost the same as in case (ii), the 0-0 band will, however, be very weak because of F-C principle. Nevertheless it should be possible to locate the 0-0 band at higher pressures and/or longer path lengths of the absorbing gas (reference Metropolis's analysis of the near U.V. absorption bands of  $\text{SO}_2$  and also the  $\text{CS}_2$  bands in the 2000A. region). The  $\lambda 3300$  absorption of  $\text{CS}_2$  is very remote from such a structure.

*Case iv.*—Linear upper state, electronic transition a forbidden one, moderate change in the internuclear distances. This leads to interesting possibilities. From the observed low intensity of absorption of these bands compared to the  $\lambda 2000$  system, Mulliken put forward the view that the electronic transition is probably a forbidden one and may be represented by  ${}^1\Pi_g-{}^1\Sigma_g^+$  if the molecule is linear in the





excited electronic state also; the  $g-g$  selection rule disallows the electronic transition. However, absorption bands can appear due to vibronic selection rules. For instance, the well-known near U.V. absorption spectrum of benzene has been ascribed to a forbidden electronic transition and interpreted on the basis of the selection rules appropriate to vibronic levels. Similarly in the case of  $\text{CS}_2$ , even though the transition  ${}^1\Pi_g - {}^1\Sigma_g^+$  is not allowed by purely electronic selection rules, the excitation of vibrations of suitable symmetry either in the lower or in the upper electronic states can give rise to vibronic states of such character as to make the transition between them allowed. For instance, the excitation of the anti-symmetrical vibration  $\nu_3$  by one or any odd number of quanta in the totally symmetrical ground electronic state,  ${}^1\Sigma_g^+$  would alter its gerade character into ungerade. Thus the transition  $(000)' - (001)''$  is allowed by the vibronic selection rules. The band  $(001)' - (000)''$  can also appear for similar reasons. Also  $(000)' {}^{ev}1\Pi_g - (010)'' {}^{ev}1\Pi_u$  and  $(010)' {}^{ev}1\Pi_u - (000)'' {}^{ev}1\Sigma_g^+$  represent allowed transitions. The various vibronic states associated with the two electronic levels  ${}^1\Sigma_g^+$  and  ${}^1\Pi_g$  and the vibronic allowed transitions with their polarisation characters are given by Mulliken (1941). In trying to apply these considerations to the  $\text{CS}_2$  spectrum, one is tempted to interpret  $31199 - 30529 = 670$  as  $397 (\nu_2') + 273 (\nu_2'')$  (sum of the deformation frequencies of the lower and upper states). This is all the more encouraging because long progressions characterised with an interval of this ( $270 \text{ cm.}^{-1}$ ) magnitude were observed by the previous investigators among the long wavelength bands and Liebermann (1941), also Mulliken (1941), were inclined to ascribe  $270 \text{ cm.}^{-1}$  to the bending frequency  $\nu_2''$  of the upper state. Starting with these two bands as  $(010)' - (000)''$  and  $(000)' - (010)''$  as first members, one should find progressions of the totally symmetrical vibration  $\nu_1'$  of the upper state. This feature, however, is not present in the spectrum in a convincing manner. It may be mentioned here that these two bands 31199 and 30529 are members of two separate progressions, each involving the same interval of about  $450 \text{ cm.}^{-1}$  and 30529 is also the first member of one of these, but 31199 comes out only as the second member in the other progression. Also as Boltzmann factors come into play in these absorption studies the  $(v00)' - (010)''$  progression should be of lower intensity, member for member, than the  $(v10)' - (000)''$  progression. But no conclusive statements could be made at present as to the relative intensities of these two progressions.

*Case v.*—The molecule is bent in the excited electronic state. This case has been discussed at great length by Mulliken (1941) from the theoretical standpoint. In the first place, it would easily explain the violet degradation of the bands without the necessity of postulating an increase of bond energies due to the excitation of electron. As was shown by Liebermann (1941), the observed rotational structure of some of the bands in the long wavelength region consisting of simple  $P-R$  branches is not inconsistent with a bent upper state even if the degree of bending were to be as large as to reduce the  $SCS$  angle from  $180^\circ$  to  $125^\circ$ .

Molecular orbital considerations of Mulliken (1941) led him to consider that the upper electronic state of the near ultraviolet bands of  $\text{CS}_2$  has the symmetry properties of  ${}^1\Pi_g$  if the molecule is linear. But if the molecule is bent, as is most likely to be the case, the superposition of two electronic states of types  $A_2$  and  $B_2$  with their symmetry characters appropriate to the  $C_{2v}$  point group of the bent molecule gives the symmetry characteristics of the  ${}^1\Pi_g$  state. In other words, the  ${}^1\Pi_g$  state appropriate to the linear molecule will split into the two electronic states  ${}^1A_2$  and  ${}^1B_2$ . Mulliken has thrown further light on these states that the  $\text{CS}_2$  molecule should have greater bending at equilibrium and a lower energy minimum for the  ${}^1B_2$  than for the  ${}^1A_2$ . On this basis, he attributes most of the long wavelength bands to the transition  ${}^1B_2 - {}^1\Sigma_g^+$ ; the considerable bending in the  ${}^1B_2$  state makes possible the appearance of extensive progressions of the  $\nu_2'$  bending vibration of the upper state. This

expected structure has made it possible to assign a value of about  $270 \text{ cm.}^{-1}$  for  $\nu_2'$  of the  ${}^1B_2$  state.

It will now be attempted to fit the short wavelength bands observed in the present work into the expected vibrational scheme of the  ${}^1A_2-{}^1\Sigma_g^+$  transition. Firstly, the location of this system as a whole is consistent with the higher energy of  ${}^1A_2$  with respect to  ${}^1B_2$ . The molecule may not be considerably bent in this state and so one may not expect very long progressions of the  $\nu_2'$  vibration such as those noticed in the  ${}^1B_2-{}^1\Sigma_g^+$  transition which gives the long wavelength bands. The absence of prominent progressions of  $\nu_2'$  vibration (those of  $450 \text{ cm.}^{-1}$  were interpreted earlier as due to the  $\nu_1'$  frequency) is probably due to the smallness of bending in the  ${}^1A_2$  state. In trying to get the allowed vibronic transitions, Mulliken (1941) made use of the gyrovibronic quantum number  $K$ , which is the quantum number for rotation about the axis of least moment of inertia in the molecule. For the case of interest to us at present, the spacing of the gyrovibronic levels varying as  $CK^2$  becomes very large because of the constant  $C$  which would be very large because of the smallness of bending.

It is enough if the relative positions of the first members of the various  $450 \text{ cm.}^{-1}$  progressions are interpreted in terms of the vibrations because the other members in each progression are already explained as due to  $\Delta v_1 = 0, 1, 2, 3, \dots$

$\lambda 3274.6, \nu 30529$  is a clearly violet degraded band having a sharp red edge. The weaker, broad and diffuse absorption appearing at  $30535$  probably represents the  $R$ -branch; the band on the whole appears to be one of parallel type (having  $P$ - $R$  branches only and the  $Q$ -branch missing). Being a very strong band occurring on the red end of the spectrum, it should very likely involve only very small energies in both the upper and lower electronic states. On the basis of the selection rules of Mulliken (1941), this may be designated as  $(00^10)' {}^1A_2 - (01^10)'' {}^1\Pi_u$ , a parallel band involving  $397 \text{ cm.}^{-1}$  energy in the lower state and only the gyrovibronic quantum  $CK^2$  (with  $K = 1$ ) in the upper state. (The single and double primes outside the brackets refer to the upper and lower electronic states as usual, the numeral on the central quantum number gives the quantum number for angular momentum along the axis of the least moment of inertia, corresponding to the  $l$  value for the linear molecule and the  $k$  value for the bent molecule.)

The next intense band,  $\lambda 3250.5, \nu 30755$ , somewhat weaker than  $30529$ , also looks like one of parallel type. Displaced by  $226 \text{ cm.}^{-1}$  it can perhaps be interpreted as involving one quantum of the  $\nu_2'$  vibration, the transition being  $(01^10)' {}^1A_2 - (01^10)'' {}^1\Pi_u$ . It may be significant to note that this  $226 \text{ cm.}^{-1}$  is roughly half the  $450 \text{ cm.}^{-1}$  interval observed in the prominent progressions. Under these conditions there are two possibilities of interpretation: (a)  $450 \text{ cm.}^{-1}$  represents two quanta of the  $\nu_2'$  vibration or (b) it represents a single quantum of the  $\nu_1'$  vibration, the magnitude of  $2\nu_2'$  approximately equalling  $\nu_1'$  being merely accidental. The former was not tenable for reasons stated earlier. In the latter event, one should expect the Fermi resonance and a wide separation of the levels by mutual repulsion.

Probably  $\nu 30900$  and  $\nu 30975$  arise due to such a splitting. It should, however, be pointed out that  $30900$  is much stronger than  $30975$  and there is a sudden fall in intensity at  $30975$  in the progression starting with  $30529$  of which  $30975$  is the second member.  $30975$  can be represented as  $(10^10)' {}^1A_2 - (01^10)'' {}^1\Pi_u$  and  $30900$  as  $(12^10)' {}^1A_2 - (01^10)'' {}^1\Pi_u$ . Fermi resonance, if present here, has reduced the intensity of one member while it has displaced the position of the other.

The imposing appearance of  $\lambda 3204.3, \nu 31199$  has already been mentioned. It is the second member of the  $450 \text{ cm.}^{-1}$  progression starting with  $\nu 30755$  band and can thus be designated as  $(11^10)' {}^1A_2 - (01^10)'' {}^1\Pi_u$ , i.e. the location of  $31199$  band at a distance of  $670 \text{ cm.}^{-1}$  from  $30529$  can be interpreted as due to the excitation of  $\nu_1' + \nu_2'$  ( $450 + 226$ ).

The band 3126.6,  $\nu$  31975 has got an interesting variation in appearance as the effective absorbing path length is altered. It is one of those few main bands which appear in Plate V(a), at a very low effective absorbing path length of the vapour. It shows no direction of degradation. Being line-like, it has got a more prominent appearance than other more intense bands. At slightly longer paths it shows a definite degradation towards the violet but does not broaden appreciably, while most of the other bands which appear along with it in the first picture (Plate V(a)) develop into broad absorption regions or patches. The author is tempted to consider it as having a strong  $Q$ -branch and classify it as  $(0\bar{0}1)' {}^1A_2 - (0\bar{0}0) {}^1\Sigma_g^+$  arising from the vibrationless ground state and involving one gyrovibronic quantum  $CK^2$  ( $K = 1$ ) superposed on one quantum of the anti-symmetric vibration  $\nu_3'$  of the upper state. If this interpretation is correct, the displacement of 31975 from 30529 by  $1447 \text{ cm.}^{-1}$  can be used to estimate the value of  $\nu_3'$  as  $1447 - 397 = 1050 \text{ cm.}^{-1}$ . This makes possible the interpretation of 31318 and 30661 displaced to the red respectively by 657 and  $2 \times 657$  from 31975 as arising from vibrating ground state vibrating in the  $\nu_1$  mode and having the same upper level as 31975.

A perusal at the table of selection rules given by Mulliken (1941) indicates that transitions to one and the same upper level are possible from both the 397 ( $\nu_2$ ) and 1523 ( $\nu_3$ ) levels of the lower state. As most of the bands in the above progressions are found to arise from the 397 level, one can expect bands, at higher progression paths and temperatures, displaced from the above bands by  $1523 - 397 = 1126 \text{ cm.}^{-1}$  towards the longer wavelengths. Such bands were in fact observed in the expected positions and with the expected lower intensity. These and other bands arising from the various vibrational levels of the ground electronic state will be dealt with later.

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### SUMMARY

The near ultraviolet absorption bands of  $\text{CS}_2$  in the region 3800A. to 2900A. have been photographed under various conditions of pressure and path length. Experimental evidence has been presented to indicate that there are two band systems present, the more intense of which is the short wavelength one in the region 3300A.-2900A. Long progressions were observed in this region with an interval of  $450 \text{ cm.}^{-1}$  which is interpreted as representing the totally symmetrical valence vibration ( $\nu_1'$ ) of the upper state. All the various possibilities for the geometrical configuration of the upper state were considered and attempts were made to fit in the observed regularities with the expected band spectrum appearances for the different upper states. Most probably the electronic transition is between the linear ground state and a slightly bent upper state. On the basis of the selection rules put forward by Mulliken (1941) for such a transition, the bending vibration  $\nu_2'$  and the anti-symmetrical vibration  $\nu_3'$  of the upper state could be assigned the frequencies of  $226 \text{ cm.}^{-1}$  and  $1050 \text{ cm.}^{-1}$  respectively. The accidental equality of  $\nu_1' = 450$  and  $2\nu_2' = 452$  has led to a considerable displacement of the  $2\nu_2'$  level due to a kind of Fermi resonance. A value of  $657 \text{ cm.}^{-1}$  for the  $\nu_1'$  vibration of the lower state has been confirmed from the ultraviolet absorption spectrum.

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