THE INFRARED SPECTROMETER

APPLIED TO

THE STRUCTURE OF CARBON DISULPHIDE

by

EDWARD de LANCEY ROGERS

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The infrared absorption spectrum of carbon disulphide in the vapour state has been remeasured in the region from 2 to 15 microns. A total of six bands were measured in the region less than 15 microns. They were located at 3.38, 3.51, 4.29, 4.58, 6.52, and 11.4 microns. The measurements were made with a Perkin-Elmer spectrometer with a D.C. breaker type amplifier and Brown recorder. Cell lengths up to 100 cm were employed. The wavelengths of the observed absorption bands are given in a table, and graphs are shown of the percentage transmission over the wave drum setting of the spectrometer.

Phase shifting thyatron circuits, suitable for the accurate control of conditions of the absorbing media, are discussed.

Of interest are the measurements of the structure of the $\sqrt{3}$ band at 1535 cm$^{-1}$. The side band located at the long-wave length side of the $\sqrt{3}$ band is due to the isotopic effect produced by C$^{13}$. The bands obtained are such as to support the conclusion that carbon disulphide is a linear triatomic molecule.
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The object of the work undertaken was to study the infrared absorption spectrum of carbon disulphide in the range 2μ to 15μ, to extend observations, at present recorded by others and to investigate the effects on the spectrum of pressure and temperature changes in the absorbing medium.

The spectrum of liquid carbon disulphide has been classified in terms and combinations analogous to those that have been found to exist for carbon dioxide. The selection rules for the energy level transitions in a linear symmetric molecule are well known. It has been indicated that the molecular configuration of carbon disulphide is linear and symmetrical. Thin cells of carbon disulphide
are fairly transparent from visible region to 24 μ except for the regions of 4.6 μ and 6.6 μ. Sanderson (1) has shown that the rotational lines are equally spaced, again indicating a linear configuration of the molecules. The Raman spectrum of carbon disulphide has been widely studied and energy-level calculations based on this work have proved of great value.

Many substances have strong absorption bands in the region between 7 μ and 15 μ. However, in this region, thin layers 0.1 mm in thickness of carbon disulphide are quite transparent. As a result, carbon disulphide may be used as a solvent in the study of the absorption spectrum of compounds. Carbon tetrachloride, on the other hand, is strongly absorptive between 12 μ and 15 μ and so is not so desirable.

In succeeding sections, the theory of the infrared spectrum of polyatomic molecules is first outlined, with specific reference to the case of the molecule of type YX₂ of which carbon disulphide is a representative. First the vibrational properties of polyatomic molecules are considered, then the rotational properties followed by the symmetry properties. A general resume of the experimental installation is next outlined. This is followed by a description of two temperature controls designed to control the temperature of the absorption cell of the spectrometer.

The calibration of the spectrometer is next described and photographs of the calibration traces and curves are included. Absorption curves obtained for the six bands of carbon disulphide located at 3.38, 3.51, 4.29, 4.58, 6.52, and 11.4 microns are displayed and the results discussed.
II.

THEORY.

Correlations between molecular configurations and infrared spectra are a very potent means of qualitative analysis. Moreover, when several atoms are brought together one immediately needs to know whether such an aggregation will form a molecule. It was not until the advent of a quantum mechanical treatment, that the physicist was able to interpret the rules of valence that had been developed to supply the answer.

Heitler and London (1) showed that valence is connected with the symmetry characteristics of the wave functions of the outer electrons in each atom. These ideas arising from the theory of the formation of homopolar diatomic molecules can be extended to molecules with more than two atoms. By assuming that a stable configuration of the atomic nuclei does exist, then the space configuration of the nuclei and the force function acting upon the nuclei in the

neighbourhood of their equilibrium position may be considered.

A. VIBRATIONAL PROPERTIES OF POLYATOMIC MOLECULES

A resume of the vibrational spectra of diatomic molecules will be made as the theory can be directly applied to the polyatomic case. Let the two molecules A and B be in a position of stable equilibrium at $r = r_0$.

When the two molecules are very close then the force is very large and tends to separate them. The force vanishes at $r = r_0$ and the linearity of the curve in this region is a measure of how nearly the oscillator may be considered as simple harmonic. For larger $r$ the force reaches a maximum at the point of inflection of the potential curve and as $r$ increases towards infinity the potential approaches asymptotically a straight line whose height represents the work of dissociation of the molecule. Since infrared absorption bands are concerned with transitions from lowest energy shells to those not far distant, the most useful region for the present purpose that that where the force function is nearly linear.

The wave function is only different from zero in the immediate neighborhood of $r = r_0$. The frequency of radiation emitted and absorbed is close to the mechanical frequency. The intensity of radiation is near the classical
value obtained from electrodynamics and varying on the square of the amplitude of the change of the electric moment. This applies also to polyatomic molecules. If \( s \) is the number of atomic nuclei having an equilibrium position, then the internal degrees of freedom will be \( n = 3s - 6 \).

If \( q_1, q_2, ... q_s \) are the displacements from the equilibrium position and remembering that amplitude is small compared to distances involved:

\[
T = \frac{1}{2}(a_{11}q_1^2 + \cdots + a_{nn}q_n^2 + 2a_{12}q_1q_2 + \cdots)
\]

\[
V = \frac{1}{2}(b_{11}q_1^2 + \cdots + b_{nn}q_n^2 + 2b_{12}q_1q_2 + \cdots)
\]

By linear transformation \( q_i = \sum_{k=1}^{n} C_{ik} X_k \), this becomes,

\[
T = \frac{1}{2}(x_1^2 + x_2^2 + \cdots + x_n^2)
\]

\[
V = \frac{1}{2}(\lambda_1 x_1^2 + \lambda_2 x_2^2 + \cdots + \lambda_n x_n^2)
\]

Thus \( H = H_1 + H_2 + \cdots + H_n \)

where \( H_j = \frac{1}{2} p_j^2 + \frac{1}{2} \lambda_j x_j^2 \)

Converting to wave mechanical notation:

\[
\psi^{V_1 V_2 \cdots V_n} = \psi_{y_1}^{V_1} \psi_{y_2}^{V_2} \cdots \psi_{y_n}^{V_n}
\]

\[
\mathcal{W}^{V_1 V_2 \cdots V_n} = \mathcal{W}_{y_1}^{V_1} \mathcal{W}_{y_2}^{V_2} \cdots \mathcal{W}_{y_n}^{V_n}
\]

Here \( \psi_{y_1}^{V_1} \) is the \( V_1 \) Hermitian orthogonal function where \( y_1 = (2\pi)^{\frac{1}{2}} \hbar^{-\frac{1}{2}} \lambda_{\frac{1}{2}}^{-\frac{1}{2}} x_1 \). Then function \( \mathcal{W}_{y_1}^{V_1} = (V_1 \psi_{\frac{1}{2}}) \hbar^{\frac{3}{2}} / 2\pi \)
and \( V_i \) is an integer. The classical theory shows that the system will vibrate with a number of characteristic frequencies given by:

\[
\nu_i = \frac{\lambda_i^2}{2\pi} \text{ so } y_i = 2\pi \nu_i^2 h^2 x_i
\]

and \( W V_i = (V_i + \frac{1}{2}) h y_i \).

\[\psi^0(y) = \pi^{-1/4} e^{-y^2/2}\]

\[\psi^1(y) = \pi^{-1/2} ye^{-y^2/2}\]

\[\psi^2(y) = \pi^{-1/2} \frac{1}{2} (2y^2 - 1)e^{-y^2/2}\]

\[\psi^3(y) = \pi^{-1/2} \frac{1}{3} (2y^3 - 3y)e^{-y^2/2}\]

Let the components of \( R \), the electric moment of the system, along three perpendicular axes in the molecule be \( R_\xi \ R_\eta \ R_\zeta \). Anyone of these can be expressed:

\[R_\xi = (R_\xi)_0 \pm \sum A_k x_k\]

Where \((R_\xi)_0\) is the permanent electric moment in the direction while the coefficients \( A_k \) may be determined for any system whose Hamiltonian is known. These matrix elements are:

\[R_{V_i}^{V_n} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} R_\xi \psi_i(y_1) \psi_i'(y_2) \psi_n(y_1) \psi_n'(y_2) dy_1 dy_2\]

But the Hermitian orthogonal function vanishes unless the \( V'' \) and \( V' \) differ by one. Then

\[\int_{-\infty}^{\infty} y \psi V \psi V^{-1} dy = V^2 / 2\]
Thus the diagonal elements
\[ R_{\xi}^V \frac{V_1}{V_1} \cdots \frac{V_n}{V_n} = (R_{\xi})_0 \]
and
\[ R_{\xi}^V \frac{V_1}{V_1} \cdots \frac{V_k}{V_k} \cdots \frac{V_{k-1}}{V_{k-1}} \cdots \frac{V_n}{V_n} = A_k \frac{h^2 V_k^2}{\pi} \frac{2^3/2}{2} \sqrt{\frac{k}{k}} \]
will be the only matrix elements remaining from \( R_{\xi} \); the others will be zero.

Thus based on two approximations, namely, that the motion is small compared to the inter atomic distances and that the force fields are linear near the equilibrium position, the above expression for the electric moment gives the desired selection rules and these are seen to indicate that the frequencies of radiation emitted and absorbed are the same as obtained by classical calculations. The above selection rule will not be obeyed rigorously due to multiple changes in the quantum numbers giving rise to harmonic and overtone bands.

The intensity \( I \) is difficult to determine as the band consists of rotation lines whose width is much narrower than the degree of resolution of the spectrometer. The fine structure lines may be broadened by examining the gas under high pressure or by using so little gas that the transmission is always high. The true intensity might be ten times the apparent intensity. The intensity of absorption between two states with quantum numbers \( a \) and \( b \) has been calculated by Tolman (1).

(1) Tolman, R.C., Statistical Mechanics with Applications to Physics and Chemistry, New York, 1927.
\[ I_b^a = (8\pi^3 \nu_b N_a / 3c h g_a) (R_a^b)^2 (1 - e^{-\frac{h\nu}{kT}}) \]

Here \( g_a \) and \( g_b \) are the weights of the two states, \( N_a \) the number of molecules per c.c. in state \( a \) and \( R_a^b \) is the electric moment due to \( b \rightarrow a \). The components give

\[ (R_a^b)^2 = (R_{\xi a}^b)^2 + (R_{\eta a}^b)^2 + (R_{\zeta a}^b)^2 \]

which, when comparing several fundamental absorption bands, reduces to the form:

\[ (I_0^b)_k = (N\pi g_1 / 3c g_0) (A_k^2 + B_k^2 + C_k^2) \]

and this is similar to the classical form.

The wave mechanical treatment of the vibration spectrum of molecules accounts for the system absorbing and/or emitting radiation with a range of 'normal' frequencies which correspond to those obtained by the classical theory of small oscillations. The amplitude of the electric moment for the normal vibrations governs the intensity of the absorption of the corresponding fundamental bands.

Certain molecules have been solved by making use of models of the molecules and by making certain assumptions in order to obtain an expression for the potential energy. Geometric symmetry of the molecule was assumed in its equilibrium configuration. The potential function was also assumed to have the same symmetry as the geometric configuration. (1)

This theory can be applied to the triatomic molecules

(1) Brester, C.J., Kristallsymmetrie und Reststrahlen, 1923.
of the type $YX_2$. The substance under investigation, carbon disulphide, is a special case of this type of triatomic molecule.

In the general case of the triatomic molecule of the type $YX_2$, it can be assumed that the atoms lie at the corners of an isosceles triangle, with $Y$ at the vertex and with the potential function of the same form. $\nu_1$ is the frequency which occurs when the force field between the $X$ atoms is very much stronger than that between the $X$ atom and the $Y$ atom. As the $Y$-$X$ forces increase, the $Y$ atom becomes perturbed but the symmetry in the force field causes its motion to be along the bisector of the apex angle. In the limiting case the problem becomes similar to the vibration of a mass point elastically bound to a rigid bar. $\nu_2$ will be a normal vibration when the two $X$ atoms move in parallel directions and opposite to the $Y$ atom. The motion of the $Y$ atom relative to the centre of gravity of the $X$ atoms has an amplitude which is that of a harmonic oscillator having a frequency $\nu_2$ and a mass $\mu = {2mM}/(2m+M)$ where $m$ is mass of each $X$ atom, and $M$ is mass of the $Y$ atom.

$\nu_3$ results from the tipping of the $X$ atoms relative to the $Y$ atom. Using the approximation that the amplitudes of the motion are small compared to the distances at equilibrium, the $Y$ atom moves along a line perpendicular to the bisector line. The electric moment changes perpendicularly to the line bisecting the apex angle. The amplitude of the
displacement of the Y atom relative to the centre of gravity of the X atom is that of an oscillator of frequency $v_3$, and mass $\mu_3 = \frac{2mM}{(2m+M)^2} + \frac{2mM^2}{(2m+M)^2} \tan^2 \alpha$ where $\alpha$ is half the apex angle. This displacement is independent of the force fields but dependent on the masses of particles and the geometry.

When the 2nd and higher order theory is developed it is found that, while $v_1$ and $v_2$ deviate from the simple harmonic oscillator, they still remain symmetrical about the line bisecting the apex angle. Thus overtone bands, if any, will appear at $n_1v_1 + n_2v_2$ where $n_1$ and $n_2$ are integers and the fine structure will be similar to $v_1$ and $v_2$. However, for the harmonic $n_3v_3$, the change of electric moment will be along the bisector line for even $n_3$ and perpendicular for odd $n_3$. Owing to the presence of $n_3$, the general overtone, $n_1v_1 + n_2v_2 + n_3v_3$, will follow the same rule. This can be shown by wave mechanics.

There are two special cases; first when all the atoms are equal, and second when the three atoms lie along a straight line. The second case is of interest here as CS$_2$ is an example of this type. Here for the $v_1$ vibration, the charge of electric moment is zero and the Y atom remains stationary. The frequencies $v_2$ and $v_3$ are both active. The distance between the X atoms remains unchanged. For the linear model with only two degrees of rotational freedom, there should be four normal frequencies, because the Y atom
may move with linear motion and with isotropic motion in a plane perpendicular to the axis of the figure.

The analysis of the motion may be summarized as follows. With respect to a Cartesian set of axes with the $z$ axis along the figure axis, let the $X$ atoms, mass $m$, have coordinates $x_1 y_1 z_1$ and $x_2 y_2 z_2$ and the $Y$ atom, mass $M$, have coordinates $x_3 y_3 z_3$. The kinetic energy $T$ is thus:

$$T = \frac{1}{2}(x_1^2 + y_1^2 + z_1^2 + x_2^2 + y_2^2 + z_2^2) + \frac{1}{2}(x_3^2 + y_3^2 + z_3^2)$$

If $q$ is the change in distance between $x_1 y_1 z_1$ and $x_2 y_2 z_2$, and if $x y z$ gives the relative displacements of $Y$ relative to the centre of gravity of the $X$ atoms, then

$$T = \frac{1}{2}(\frac{m}{4})q^2 + (\frac{\mu}{2})(x^2 + y^2 + z^2)$$

with $\mu = \frac{2mM}{2m + M}$

The coefficients of the cross terms vanish and leave

$$V^0 = \pi^2 m \sqrt{2} q^2 + 2\pi \sqrt{2} \mu (x^2 + y^2) + 2\pi^2 \sqrt{3} \mu z^2.$$ 

Converted to polar coordinates these equations are:

$$T = \frac{1}{4}(m)q^2 + (\frac{\mu}{2})(r^2 + \rho^2)$$

$$V^0 = \pi^2 \sqrt{2} mq^2 + 2\pi \sqrt{2} \mu r^2 + 2\pi^2 \sqrt{3} \mu z^2$$

The general solution (1) is the wave equation

$$\psi = \psi_1 \psi_3 \psi_3 R V_2^L e^{+i\phi}$$

with \( \sigma = 2\pi \left[ \nu_1 m / 2\hbar \right]^{1/2} q \)

\[ \zeta = 2\pi \left[ \nu_3 \nu / \hbar \right]^{1/2} a \]

\[ \rho = 2\pi \left[ \nu_2 \nu / \hbar \right]^{1/2} r \]

The energy constant has the form

\[ W^0 = \hbar \nu_1 (V_1 + \frac{1}{2}) + \hbar \nu_2 (V_2 + l) + \hbar \nu_3 (V_3 + \frac{1}{2}) \]

There are \( V_2 + l \) independent wave functions for each value of \( V_2 \) and this is the weight of each state. \( V_1 \), \( V_2 \), \( V_3 \), and \( l \) are all positive integers. For each value of \( V_2 \) there are a number of values of \( l \) of which \( V_2 \) is the highest. This describes a system similar to the vibrating molecule system. Here one and one only of \( V_1 \), \( V_2 \), or \( V_3 \) changes by one and where the spectrum consists of \( \nu_1 \), \( \nu_2 \), \( \nu_3 \) where \( \nu_1 \) is zero due to symmetry considerations. By introducing small perturbations to this motion, the kinetic energy is uncharged by the potential energy becomes \( W^0 + V' \) when \( V' \) is a function of \( q \), \( z \), and \( r \). \( V' \) must be independent of \( \phi \) and must be an even function of \( \nu \) and of \( \nu \). For each \( l \) except \( l = 0 \), there are two wave functions whose dependence upon \( \nu \) is the same but which depend upon \( \phi \) as \( e^{i\phi} \) and \( e^{-i\phi} \).

The degeneracy caused by the falling together of two energy levels whenever \( l \neq 0 \) cannot be removed by taking into account any number of higher approximations with perturbing functions of the form \( V' \) but it will be removed by the magnetic field caused by the rotation of the molecule as a whole.
Two conclusions depending on the symmetry properties or the kinetic and potential functions and not on the order of approximation are: (1), for elements giving the components of the electric moment perpendicular to the axis may have values \( \neq 0 \) if \( \Delta l = 1 \), \( \Delta V_3 \) is an even integer \( \Delta V_2 \) is an odd integer. (2), The elements giving the component of the electric moment along the axis may have values differing from zero if \( \Delta l = 0 \), \( \Delta V_3 \) is odd \( \Delta V_2 \) is even. Thus if \( n_2 \) is even, the change of the electric moment is along the figure axis while if \( n_2 \) is odd, it lies perpendicular to this axis.

For collinear and symmetrical atoms, say CS\(_2\), the sum of the figure of any two observed bands (overtones fundamentals or combination bands) will not be the frequency of an active overtone. This may be indicated by considering the two active frequencies to be \( \nu^1 \) and \( \nu^2 \).

\[
\begin{align*}
\nu^1 &= n_1^1 \cdot \nu_1 \cdot n_2^1 \cdot \nu_2 \cdot n_3^1 \cdot \nu_3 \\
\nu^2 &= n_1^2 \cdot \nu_1 \cdot n_2^2 \cdot \nu_2 \cdot n_3^2 \cdot \nu_3
\end{align*}
\]

Then the sum will be

\[
\nu^1 + \nu^2 = (n_1^1 + n_1^2) \cdot \nu_1 + (n_2^1 + n_2^2) \cdot \nu_2 + (n_3^1 + n_3^2) \cdot \nu_3
\]

Here, since \( \nu^1 \) and \( \nu^2 \) are active,

\[
\begin{align*}
n_1^1 \cdot n_1^1 \quad \text{is odd} \\
n_2^2 \cdot n_3^2 \quad \text{is odd}
\end{align*}
\]

hence \( (n_1^1 + n_1^2) + (n_3^1 + n_3^2) \) is even.

Which make \( \nu^1 + \nu^2 \) inactive.
B. ROTATIONAL PROPERTIES OF POLYATOMIC MOLECULES.

Rotational energy possessed by a molecule is exhibited by a fine structure of the near infrared bands and by the existence of a far infrared absorption spectrum. As the far infrared is more difficult to explore experimentally, it is usual to examine the fine structure in the near infrared. The vibration can be treated separately from the rotation of the molecule and the results combined. There are two assumptions which must be made. The first is that the rotational forces between atoms is small compared with the vibration forces. The second is that, as before, the amplitude of vibration is small compared with interatomic distances.

Thus \[ H = H_V + H_R \]

and \[ \psi = \psi_V + \psi_R \]

where, \( \psi_R \) and \( \psi_V \) correspond to the rotational and vibrational quantum numbers respectively and when each forms an orthogonal set.

By considering two systems of orthogonal axes with both origins at the centre of gravity of the system, one fixed in the molecule and the other fixed in space the matrix elements for the electron momentum of one set of axes can be found and this again leads to the selection rules. The far infrared bands are caused by changes in the rotational quantum numbers. Only when the molecule has a
permanent dipole moment will such bands have a definite intensity. The product of the vibrational and rotational matrix elements will give the matrix element representing the near infrared bands.

The quantum mechanical solution of the problem of the symmetrical top rotator has been solved (1). The total angular momentum \( P \), the component of \( P \) along the C axis \( P_c \) and the component of \( P \) along the Z axis \( P_z \) are

\[
P^2 = J(J+1)\hbar^2/4\pi^2
\]

\[
P_c = Kh/2\pi
\]

\[
P_z = Mh/2\pi
\]

The weights of the states are:

\[
g_{JK} = 2J \cdot 1 \quad K = 0
\]

\[
g_{JK} = 2(2J \cdot 1) \quad K \neq 0
\]

By an examination of the matrix elements representing the electric moment, a determination may be made of the selection rules and intensities. Two types of bands may be produced in the near infrared vibration-rotation bands of a symmetrical top molecule. Parallel bands where the electric moment oscillates along the C axis and perpendicular bands in which the electric moment oscillates perpendicular to the C axis.

In the parallel type band the selection rules are:

\[
\Delta J = \pm 1, 0 \quad \text{and} \quad \Delta K = 0.
\]

The intensities of the lines of parallel band may be

indicated by:

\[- \text{branch } I_{J-K}^J = A \sum_{K=0}^{J-1} \left( \frac{[2](J^2-K^2)}{4J} \right) e^{-\sigma(J^2+J) - \sigma K^2} \]

\[\text{0 branch } I_J^J = A \sum_{J=0}^{J} \left( \frac{K^2(2J+1)}{2J(J+1)} \right) e^{-\sigma(J^2+J) - \sigma K^2} \]

\[\text{+ branch } I_{J-1}^{J-1} = (I_{J-1}^J)e^{2\sigma J} \]

where \( \sigma' = \frac{h^2}{8\pi^2 k T} \).

When the moment of inertia \( C=0 \) then these expressions become those for the diatomic molecule:

\[I_{J-1}^J = (A J/4) e^{-\sigma(J^2+J)}\]

and

\[I_{J-1}^{J-1} = (A J/4) e^{-\sigma'(J^2+J)}\]

The perpendicular type band has considerable fine structure and depends on the ratio of the moments of inertia. The intensity of the absorption lines of the \( K^{th} \) negative single band will be:

\[- \text{branch } I_{J-1}^{J-K} \left( J \right) = (A(J+K-1)(J+K)/(8J)) e^{-\sigma(J^2+J) - \sigma K^2} \]

\[\text{0 branch } I_{J-K}^{J} \left( J \right) = A \sum_{J=K}^{\infty} \left( \frac{(2J+1)(J+K)(J+K)/8J(J+1)}{J^2} \right) e^{-\sigma(J^2+J) - \sigma K^2} \]

\[\text{+ branch } I_{J}^{J-1} \left( J \right) = (I_{J-1}^{J-K}((J-K)/(J+K))e^{2\sigma J} \]

For cases where \( \sigma \) is small the summation may be replaced by integrals.

The more complex polyatomic molecules cannot be represented by the symmetrical top rotator but can be solved by the use of the asymmetrical top rotator. This theory has
been developed fully by H.A. Kramers and G.P. Ittmann (1) and by O. Klein (2). In all cases the allowed transitions are those for which \( \Delta J = \pm 1, 0 \). Transition probabilities can be calculated and then dependence on the change of electric moment and moment of inertia obtained. The intensity relations are also developed in these investigations.

C. SYMMETRY PROPERTIES OF POLYATOMIC MOLECULES.

The frequencies present in the infrared spectra of polyatomic molecules are dependent on the vibration and rotation of the molecules. The spectra are dependent on the quality of two or more of the atomic nuclei forming the molecule. The energy states of systems consisting of several equal particles may be separated into a number of classes. Each of these classes will have a symmetry character which is determined by the effect on the wave functions when particles of the system are interchanged. It has been shown by Heisenberg (3) that no transitions may take place between states possessing different symmetry characters. Symmetrical wave functions will thus be associated with energy states of the same class and so transitions may occur from a state of one class to a state of any other class. The difficulties arising from consideration of a system with r different classes behaving as r different systems with no intercombina-


tions is removed by application of the Pauli Exclusion Principle. The single symmetry class which exists is either totally symmetrical or totally anti-symmetrical depending upon whether the nucleus contains an even or an odd number of particles.

The energy of a polyatomic molecule can be expressed as the sum of the four energies - electronic, vibrational, rotational, spin - which are in descending order of magnitude. The total wave function of the molecule may consequently be written:

\[ \psi = (\psi_E)(\psi_V)(\psi_R)(\psi_S) \]

The limits placed on the symmetry of a molecule by the exclusion principle does not place similar limits on the symmetry of a component of this wave function. Transition probabilities will depend on the size of the factor which permits the transition. Should this be the nuclear spin, then the transition probability would be small.

D. THE MOLECULE YX2.

In applying the the above considerations to the molecule YX2 the electronic transitions need not be of concern as the electronic state remains unaltered by the transitions giving rise to infrared spectra. The vibrational, rotational and spin wave functions, however, must be considered.

Where \( V_3 \) is an even integer the wave function upon reversing the directions right and left, remains unchanged.
but, if $V_3$ is an odd integer, the wave function retains its form but undergoes a change in sign corresponding to symmetrical and antisymmetrical modes of the vibrational part of the wave function.

The symmetry character of the part of the wave function depending on rotation, when the least moment of inertia falls along the bisector of the apex angle, is that the lowest level is always symmetrical, the next two are antisymmetrical, the next two symmetrical etc. When the middle moment of inertia falls along the bisector of the apex angle, the levels are alternately symmetrical and antisymmetrical. For even $J$ the lowest and highest levels are symmetrical and for odd $J$, they are antisymmetrical.

The fine structure lines of the near infrared bands correspond to simultaneous changes in both vibrational and rotational quantum numbers. Applying the rule that transitions may occur only between levels having like symmetry characters, it follows that in a near infrared band corresponding to an even change in the vibrational quantum number $V_3$, the fine structure lines will be caused by transitions between rotational levels having the same symmetry. When $V_3$ is odd, transitions will be between rotational levels of opposite symmetry characters.

For the linear molecule, the symmetry character will be the same as above when the vibrational part is considered. The wave function is symmetrical for even values
of $V_3$ and antisymmetrical for odd values while it is independent of $V_1$.

An interchange of the two $X$ atoms can be effected and the resulting behaviour of the wave function may be calculated. When $\ell = 0$ all states with even $J$ are symmetrical, and, antisymmetrical for $J$ odd for that part of the wave function depending on $V_2$, 1, $J$ and $M$. When $L \neq 0$ there are two coincident levels, one of which is symmetrical for an interchange of nuclei and the other antisymmetrical.

The symmetry characteristics of the wave functions of the molecule of type $YX_2$ will depend on the nuclear spin wave functions which can be obtained in the same way as for homopolar diatomic molecules.\(^{(1)}\)

The fine structure of the near infrared bands of molecules of the type $YX_2$ should consist of two sets of lines. One set arises from transitions between two levels for which the vibrational and rotational wave functions are symmetrical. The wave function of the levels giving rise to the other set are antisymmetrical. Intercombination lines between the two sets will be faint due to the smallness of the spin interaction. The ratio of intensity of these two sets of lines will be $S + 1$ where $S$ is the spin quantum number. All the levels giving both sets of lines, are either symmetrical or antisymmetrical in the vibration-rotation spin parts of their wave functions.

\(^{(1)}\) Herzberg, G., Molecular Spectra and Molecular Structure, Vol.1, Diatomic Molecules, New York, 1939.
Experimental results have given much confirmatory evidence in favour of the above theory. In particular, the infrared absorption spectrum of $\text{CS}_2$, in the vapour state has been measured by Bailey and Cassie (1). By using the values obtained by Krishnamurti (2) for the chief lines in the Raman Spectrum in conjunction with their own readings in the infrared, they were able to conclude that the $\text{CS}_2$ molecule was linear and symmetrical. The doublet structure was shown to be associated with the excitation of the symmetrical mode of vibration of the rectilinear molecule which is optically inactive but capable of combining with the other modes of vibration to give bands in the infrared, where the doublet structure was first observed. Doublet structure is therefore attributable to the excitation of two types of vibration associated with slightly different amounts of energy and corresponding to two types of binding.

Bailey and Cassie (3) calculated the value of the moment of inertia and found it to be $264 \times 10^{-40}\text{gr.cm}^2$ and from it, using $\omega V = \frac{\hbar}{4\pi^2I_0c}$, the rotational line separation within a vibrational-rotational band was found to be of the order of $0.2\text{cm}^{-1}$. The molecule is, however, symmetrical and rectilinear and the fine structure should exhibit alternating intensities corresponding to the symmetrical and the antisymmetrical functions with the result that

one set should have an almost vanishing probability and
the apparent effective separation should be twice this
amount. Bailey and Cassie checked their results by ther-
mochemical data on determination of the heat of formation.

Dennison and Wright (1) also concluded that the CS$_2$
molecule was linear and symmetrical. The differences
between the observed infrared bands were shown to corre-
spond to the Raman frequencies. A very intense absorption
band was found whose envelope possessed P, Q and R bran-
ches lying at 389.4, 396.8 and 405.8 cm$^{-1}$. The doublet se-
paration obtained from these reflection grating measure-
ments was 16.4 cm$^{-1}$ which leads to $I = 172 \times 10^4$ g cm$^2$
and a distance between S atoms of 2.54 x 10$^{-8}$ cm. These
values were in accord with theory and while lower than
those obtained by Bailey and Cassie (2) are due to better
dispersion in the method of measurement.

Fermi (3) showed that the energy levels of the mole-
cule may possess perturbation terms which are of the
first order in contrast to normal theory where perturba-
tions are always second order. The first order perturba-
tions may be shown to go over into the usual second order
perturbation expression when the difference between $\nu_1$
and $2 \nu_2$ is large compared with certain of the anharmonic
constants.

(1) Dennison, D.M., and Wright, N., Physical Review,
vol.38, p.2077, 1931.
(2) Bailey, C.R., and Cassie, A.B.D., Proceedings of the
Work by Sanderson (1) on the infrared absorption of CS$_2$ in the 4.6$\mu$ band revealed that the rotational lines are equally spaced. Average values of $B$ and $B'$ were found to be 0.112 and 0.111 while the separation of the P and R branches of the band is 13.3 cm$^{-1}$. The best representation of the rotational lines is by means of the relation

$$\nu = 2184.50 + 0.224M - 0.00025M^2$$

Sanderson's measurement of the location of the centre of the band at 2184.5 cm$^{-1}$ did not agree with previous determination of 2179 cm$^{-1}$ and 2167 cm$^{-1}$ by Bailey and Cassie. Sanderson was able to resolve 27 lines in the R branch and 30 in the P branch. Due to the antisymmetrical nature of the wave function in the sulphur nuclei, alternate rotational lines are missing. Since both nuclei obey the same statistics, the missing lines in the CS$_2$ spectrum are those for which the $J$ of the lower state is odd.

Adel and Dennison (2) while working with CO$_2$, extended this work by introducing a second order energy perturbation and computing the correction term for a general linear symmetrical triatomic molecule. Modification of this formula is possible so that it is applicable to the CS$_2$ molecule.

III.

EXPERIMENTAL.

Before actual investigation of the infrared spectrum of carbon disulphide could be commenced, it was necessary to undertake several modifications of the spectrometer, to build certain additional components, to devise a method of maintaining a continuous low humidity atmosphere in which to operate the spectrometer, and, to build temperature controls so that the temperature of the absorbing medium might be held under controlled conditions for extended periods. The salient portions of this experimental arrangement will now be outlined.

A. SPECTROMETER AND ACCESSORIES.

A Perkin-Elmer spectrometer Model 12-B was used as the dispersing instrument in these investigations. The prism face is 55mm. by 75mm. and an off-axis mirror of 27cm. focal length is used as the collimator. The instrument will
not be described in detail here as a complete description is available in the instruction book accompanying the instrument. Auxiliary equipment includes a Perkin-Elmer Breaker Type D.C. Amplifier, Brown Recorder and Sola powerstat. A NaCl prism (most useful range 2.5 - 15 microns; 4000 - 666 cm⁻¹) was used.

The radiation from a source passes through a collimator, absorption cell, monochrometer and is absorbed by a thermocouple. The signals from this thermocouple are amplified by the D.C. amplifier and recorded on the Brown recorder. The source used in the spectrometer is a globar element which is an attempt to approximate black body radiation. This source is provided with a water cooled housing and has a normal operating power of 200 volt amps. For a fixed slit width the maximum radiation was found to occur in the region of 2/μ.

The thermocouple is a high vacuum compensated type of bismuth-bismuth tin elements. The thermal elements are opposed and so arranged that one measures the radiation passing through the spectrometer and the other corrects for ambient temperature. Its sensitivity is approximately 0.3 microvolts per erg per second. Although rated a being compensated to over 95%, there is evidence of slight drift. Variations of room temperature despite the very heavy thermal lagging of the spectrometer and the thermostat control of room temperature, as later described, accounted in part
for instabilities in the thermocouple output. The pressure inside the thermocouple is kept low by means of a getter of activated charcoal. The thermocouple approaches its final output in about \( 1\frac{1}{2} \) seconds after it is exposed to radiation. A reasonably smooth trace is obtained when the amplifier is not operated on too high gains.

The signal from the thermocouple is fed into a pair of breaker points operated at 80 cycles per second by a synchronous motor mounted in the amplifier. Thus the direct current signal is converted into a low voltage alternating current which is subsequently amplified by step-up transformers and three stages of R.-C coupled amplification. The resulting signal is rectified again by a second set of breaker points operated directly from the same control shaft as the first pair. Data on the amplifier are as follows:

- **Breaker frequency** - 80 cycles per second
- **Voltage amplification (approx.)** - 1000 to 300,000
- **Input resistance (d.c.)** - 30 ohms
- **Input noise level (optimum)** - \( 2 \times 10^{-9} \) volts
- **Non linearity** - less than \( \frac{1}{2} \% \)
- **Power** - 50 watts, 110v, 60 cycles.

The recorder is provided with a filter which is adjusted to cut off at about 2 cycles per second so that 60 cycle pick up and high frequency noise are kept out of the recorder. The response time of the recorder is four seconds for
full scale deflection, and, two seconds for 10 percent deflection. The sensitivity is ten millivolts for full scale deflection. Reproducibility is 0.2% or better. The Brown recorder contains a self-calibration device which automatically places a small calibration mark of approximately one quarter inch in length on the chart every 10 minutes. The Brown recorder and D.C. Amplifier are shown in Plate VI.

The wave length micrometer, which rotates a Littrow mirror inside the spectrometer, is arbitrarily calibrated from 1 to 2000. Each small division corresponds to 16.1 seconds of arc. A range of 9 degrees covers all the spectra of the LiF, KBr and NaCl prisms.

When the instrument was obtained there was no wave drive or control panel. A wave drive capable of driving the spectrometer wave micrometer at four speeds - 62, 124, 312, and 624 seconds per revolution of 100 scale divisions and a control panel to enable the operator to activate separately or simultaneously the pen, chart drive motor and wave drive motor, was designed and built by Mr. M. Mitchenen, a co-worker on this project. Moreover, an auto stop switch was provided whereby the pen, chart and wave drive would stop automatically at the completion of one revolution of the wave length micrometer on the spectrometer. The wave drive motor operates the spectrometer from longer wave lengths to shorter ones as this direction reduces the errors due to drift to about half those observed when it is run in
the opposite direction.

An automatic safety switch was added to the spectrometer so that, if the wave drive were to drive the wave length micrometer beyond the calibration, the power would be turned off. This was accomplished by mounting a micro-switch in such a position that the arm activated by the wave-length micrometer would trip the switch when the micrometer was tuned beyond its calibration. The micro switch operated a relay which in turn opened the power circuit.

The spectrometer is enclosed and a drying agent is kept in both the prism and the source compartments. As a result, the amount of water vapour absorption is reduced. It is not necessary, ordinarily, to completely remove the water vapour as the absorption bands produced by water vapour and carbon dioxide serve as internal calibration and a constant check on the resolution of the instrument.

B. INSTALLATION

The spectrometer has a tendency to drift when subject to changes in temperature. A maximum variation of three degrees is permissible. Thus the spectrometer should be located in a temperature controlled space. Moreover, the location should be as free from vibration as possible. The recorder method of measurement of the output of the thermocouple is not as critical in this respect as is a galvanometer but vibration still remains an important consideration.
The windows of the spectrometer and sample cells are of rock salt which is slightly hygroscopic. Exposure to an atmosphere of more than 60% relative humidity causes thick fog to appear on them and for higher humidities the windows and prism would dissolve. With NaCl windows, a relative humidity of 50% can be tolerated for extended periods; however, 30% is much too be preferred. Fortunately fogged windows transmit better in the infrared than in the visible and may thus be used long after they appear fogged.

As a compromise, it was decided that before the NaCl prism could be taken from its sealed container, it would be necessary to provide an atmosphere of 40% humidity or less.

Attempts to reduce the humidity of the entire Research room to 40% or less having failed, it was decided to construct a smaller chamber thus reducing the magnitude of the dehumidification task.

A double walled box of dimensions 6'x 9'x 8' was constructed with sheets of well seasoned three play with 2-inch spacing between inner and outer walls. This space was packed with rock wool and both walls lined with moisture resistant paper on the inner surfaces next to the rock wool. All joins were vapour sealed and an airlock system of double doors provided for entrance and exit. The airlock is of dimensions 1.5' x 2.5' x 8'.

A General Electric commercial refrigeration unit is
used to reduce the humidity inside the chamber. The condensing unit is powered by a \( \frac{1}{2} \) H.P., 110 volt, 60 cycle, single phase, continuous duty motor. In addition to the condensing unit, this unit consists of cooling coils with fan, back pressure valve, throttle valve and solenoid valve. A type H63A Humidity Controller made by the Minneapolis Honeywell Regulator Company was employed. This instrument has a range of 20 to 96 percent R.H. and a differential of 2 percent R.H. at 50% (slightly wider above; slightly lower below 50% setting). A Friez thermostat with a differential of 3°F. at 65°F. was used. The refrigeration unit employs Freon gas as the active thermal agent.

The main functions of these controls are as follows. The throttle valve is variable and controls the rate of fluid input to the cooler coils by means of a gas pressure bellows actuated by a thermal probe attached to the exit flow tube. If the temperature of the exit gas is low, then the bellows in the throttle valve contracts, thus diminishing the rate of flow of input fluid and vice versa. The back pressure control is situated on the condenser unit and controls the on-off operation of the pump. The control is actuated by the pressure of the returning gas. If the pressure is low, corresponding to a cold return temperature, the pump will stop and vice versa. This control can be reset for any temperature. In the case under discussion, it was set for a pressure corresponding to a temperature of 35°F.
BLOCK DIAGRAM OF CHAMBER.
The solenoid valve is an on-off control on the input fluid flow to the cooling coils. It is actuated by the humidistat. The solenoid valve cuts out the flow of input fluid thus causing the return pressure to drop actuating the back pressure control and stopping the motor of the condensing unit.

Thus, the motor of the condensing unit may be stopped (or started) in either of two ways:

1. By the action of the back pressure control alone.
2. By the solenoid valve action followed by the back pressure control.

The condensing unit was mounted outside the chamber as in Diagram I. The cooling coils and fan unit was bolted to the ceiling inside the chamber in the corner above the position marked for the temperature control in this same diagram. As the electric motor used to drive the fan of the cooling coil unit was of the induction type and so of non-variable speed, a system of adjustable louvers had to be designed so that the rate of flow of air past the cooling coils could be controlled. These louvers were designed to limit the 'air intake' of the fan. The slower the flow of air past the cooling coils the lower the temperature to which the air might be cooled and consequently the more moisture that could condense out of the air onto the coils, collect and run down the drain.

Beyond the cooling coil, mounted to it but screened
from it by metal screening to prevent heat radiation, three 660 watt cone heaters were mounted.

The primary of the relay controlling the heaters is in series with the thermostat and the contacts of a second relay whose primary is across the terminals of the condensing unit motor. Thus the heaters can be turned on or off by the action of the thermostat if the motor of the condensing unit is in operation. However, if the motor is not running, the heaters will not operate. This control was introduced to reduce fire hazard due to overheating.

If the fan were allowed to remain in operation after the condensing unit had been stopped by one of the above controls, then the moisture, that had already been condensed out of the system but had remained on the coils, would evaporate and would be reintroduced into the system. To prevent this, a relay with primary across the terminals of the motor of the condensing unit and secondary contacts in the fan circuit was installed. Hence, when the motor stops, the fan must also stop.

This arrangement permits control of humidity and temperature independently. The circuit, as installed, maintains a steady 40% relative humidity even when four persons are in the chamber. A minimum of 32% relative humidity can be attained.

The location of the apparatus inside the chamber is
indicated in Diagram I. A photograph of the experimental arrangement is shown in Plate I. On the extreme left can be seen a portion of the powerstat by which the voltage is regulated to any given value. Next to it can be seen a wattmeter arranged in the circuit to give a continuous reading of the power input to the globar. Next the control panel followed by the temperature control which will be described in detail in Part III C, of this report. On the right is seen the Perkin-Elmer Spectrometer model 12-B. Comparison with Plate III will give an indication of the thermal lagging which was applied to the spectrometer, absorption cell and leads to the D.C. amplifier. It will be seen that the spectrometer and amplifier have been partially enclosed with a shield. This acts as a thermal shield from any sudden variations in temperature due to the on-off action of the heaters. In addition, electrostatic shielding for the thermocouple and amplifier is provided as the majority of this cover is made of sheet iron separated by asbestos.

The mercury manometer to measure the pressure inside the absorption cell is seen extending to the floor in front of the spectrometer, in Plate I. The 100 cm. absorption cell is not in position in the picture but can be seen resting on top of the box which surrounds the spectrometer.

Directly above the temperature control in this same illustration will be seen the expansion coils and fan unit, and, the box containing the three 660 watt heaters. The louvre
system for controlling the air flow over the coils may be seen towards the left of this unit and the drainage pan and tube may be seen extending from the bottom of the unit.

C. TEMPERATURE CONTROL.

Before useful readings of an absorption spectrum can be taken, accurate control must be obtained of the conditions under which the absorption occurs. A one meter gas cell was obtained from the Perkin-Elmer Company. Using this cell, it was proposed to investigate changes in the absorption spectrum due to variations of the temperature and pressure of the absorbing medium.

It was therefore necessary to design and construct a temperature control which would be accurate to at least ±0.1°C. and capable of controlling the temperature of this cell for extended periods without lag or drift. The minimum range of this control should be from room temperature to 100°C. It would be preferable that the device should be compact, and, so that it might be adapted to other uses at a later date, should be capable of controlling at least 500 watts.

To meet these requirements, two phase shifting thyatron circuits were adopted. The overall dimensions of the finished control are 9½ x 11 x 16½ ins. The weight is 25 lbs. approximately. The sheet aluminium cover is so designed that it could be removed for inspection purposes without
CIRCUIT DIAGRAM

of

TEMPERATURE CONTROL

I

DIAGRAM II.

To Face Page 36.

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The diagram illustrates a circuit diagram for temperature control. It includes various components such as resistors (R1, R2, R3, R4, R5, R6, R7, R8, R9, R10, R11) and capacitors (C1, C2, C3, C4, C5), as well as other electrical elements like transformers (T1, T2) and a vacuum tube (V1, V2). The diagram is detailed, showing the connections and flow of electrical current through the circuit.
affecting the circuit or the operation of the control. Air-vents are provided in the lower sides and upper rear of the cover to provide suitable circulation of air.

In Diagram II is shown the circuit diagram (1) of temperature control I. The values of the components of the circuit are shown in Table I:

<table>
<thead>
<tr>
<th>TABLE I.</th>
<th>Table of Components of Temperature Control I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁ = 50 ohms</td>
<td>R₁₀ = 2000 Watt, 110 v. heater coil.</td>
</tr>
<tr>
<td>R₂ = 50 ohms</td>
<td>R₁₁ = 20 ohms, 6 amp. variable resistor.</td>
</tr>
<tr>
<td>R₃ = 0-100 ohms (variable)</td>
<td>C₁ = 0.25 μf</td>
</tr>
<tr>
<td>R₄ = 50,000 ohms</td>
<td>C₂ = 0.25 μf</td>
</tr>
<tr>
<td>R₅ = 30-100 ohms (fixed)</td>
<td>C₃ = 8 μf</td>
</tr>
<tr>
<td>R₆ = 10,000 ohms</td>
<td>C₄ = 0.007 μf (300 v.)</td>
</tr>
<tr>
<td>R₇ = 250,000 ohms</td>
<td>C₅ = 0.1 μf.</td>
</tr>
<tr>
<td>R₈ = 10⁶ ohms</td>
<td></td>
</tr>
<tr>
<td>L = Hammond #372, 700 H. Choke.</td>
<td></td>
</tr>
<tr>
<td>V₁ = 6J7G tube.</td>
<td></td>
</tr>
<tr>
<td>V₂ = FG57 thyatron tube.</td>
<td></td>
</tr>
<tr>
<td>B = 270 volts with tap at 90 volt.</td>
<td></td>
</tr>
<tr>
<td>E₁, E₂ = 115 volt, 60 cycle.</td>
<td></td>
</tr>
<tr>
<td>Filament Transformer, Hammond 167B for 6J7G.</td>
<td></td>
</tr>
<tr>
<td>Filament Transformer, Hammond #1123, 5V., 50 V.A. for FG57.</td>
<td></td>
</tr>
<tr>
<td>T₁ = 115v, 60 cycle to 5 volt centre tapped.</td>
<td></td>
</tr>
<tr>
<td>T₂ = Audio transformer, Hammond #312, 50-200 ohm input to 1000 ohms.</td>
<td></td>
</tr>
</tbody>
</table>
A general view of the control is shown in Plates II and V, while Plate IV shows the internal wiring.

Both \( E_1 \) and \( E_2 \) are from the same 115 volt, 60 cycle supply to ensure that no phase shift is introduced from extraneous sources. A polarized plug was used on the mains cable and this circuit fused for 10 amperes.

Every effort was made to reduce stray fields which would effect the phase shifting properties of the device. As will be seen from Plates IV and V, the alternating current bridge and amplifier stage is completely separated and shielded from the thyatron circuit. Shielded cable was used wherever there was a possibility of stray fields and great care was taken to ensure that the shielding was connected securely to the chassis, which was in turn grounded. The resistors used were either non-inductively wound as were \( R_1, R_2, R_3, R_6 \), or so placed in the circuit as to be free from pick up from stray fields.

The optimum rate of change of terminal voltage with temperature for an A.C. bridge circuit such as the one here described can be easily shown to exist when all four arms of the bridge are of equal value. The circuits described in this paper were both designed so that this maximum sensitivity could be attained. \( R_1 \), and \( R_2 \) and \( R_3 \) were non-inductively wound by hand from B. and S. #28 guage "Advance" wire \((\alpha = 0.00002 \text{ per degree Centigrade, resistance = } 1.81 \text{ ohms per foot})\). Due to this low temperature coefficient of
resistance of "Advance" wire, these resistors may be considered to be invariant under the small temperature changes of the control chassis.

$R_3$ is provided with both coarse and fine control and a "check" switch which inserts or removes a resistance of approximately 1.5 ohms (the value is not critical) into the $R_3$ branch of the bridge, to facilitate the adjustment of the sensitivity of the bridge. The $R_3$ branch is also provided with a five position switch by which the value of $R_3$ may be varied in steps of 20 ohms up to 100 ohms. This arrangement was devised in order that the instrument might be readily adapted to a number of resistance thermometers, $R_6$, of different resistances between 20 and 100 ohms. In any case, $R_6$ should be non-inductively wound from B. and S. #28 gauge or thicker resistance wire. A wire with a temperature coefficient of resistance per degree centigrade of at least 0.003 should be used.

$R_7$, $R_8$, and $R_9$ are standard low wattage resistors. $R_{11}$ is a standard slide wire laboratory resistor outside the unit itself. $R_{10}$ is the heater which is wound around the absorption cell. Heater and cell are then encased in asbestos and felt lagging.

The transformer $T_2$, was chosen so that it matched the impedance of the bridge (approximately 50 ohms) to the impedance of the 6J7G tube. An inexpensive audio transformer such as the one listed in Table I is very satisfactory for
PANEL OF TEMPERATURE CONTROL.
The value of the condenser, \( C_4 \), was so chosen that it is in resonance with the inductance \( L \) at 60 cycle. For this reason, any tube that is capable of high amplification may be used in place of the 6J7G with few changes in the circuit. A larger value of \( L \) would be most acceptable but if used, a corresponding value for \( C_4 \) would be necessary.

The adjustment of this circuit is direct and rapid. The greatest sensitivity of the thyratron occurs when it passes current for one quarter cycle. Hence \( R_{11} \) is adjusted so that the tube can pass a maximum current equal to approximately twice that required to maintain constant temperature. The control of \( R_4, R_5 \) is then moved so that the greatest continuous variation of anode current with change in \( R_3 \) is obtained. This change in \( R_3 \) is effected by using the 'check' switch. If \( R_4 \) is too small, on-off operation results; if \( R_4 \) is too large, the sensitivity of the control is greatly reduced. After these adjustments, the dial settings of \( R_3 \) may be calibrated directly in terms of temperature.

A diagram of the control panel of the temperature control is shown in Diagram III. Switch A controls the 110 volt 60 cycle alternating current to the entire unit. When placed in the "on" position, the transformers supplying filament current to the FG57 and to the 6J7G as well as transformer \( T_1 \) are energized. Switch B is in the plate circuit
CIRCUIT DIAGRAM
of TEMPERATURE CONTROL

DIAGRAM IV.
of the FG57. The thyratron requires a heating period of five minutes. After the lapse of this period of time with switch A in the "on" position, the unit may be put in operation by placing switch B in the "on" position. Failure to wait this period may result, if not incomplete destruction, at least in serious damage to the emissivity of the filament of the thyratron. D is the control for R4, R5. When turned counter-clockwise, R4 is decreased. F is the 'check' switch and introduces 1.5 ohms into the R3 branch of the bridge when in the "on" position. G is the coarse control and E the fine control of the value of the resistance in the R3 branch. C is the 5-position switch introducing 20, 40, 60, 80, or 100 ohms into R3. Obviously the resistors controlled by C, E, G and that shorted by F, must all be in series. The meter while graduated from 0 to 50, reads 5 amperes full scale. It is in the plate circuit of the thyratron.

The operational rise in temperature of the control in the most critical region, that of the bridge, was found not to exceed 10° C. As the three arms of the bridge are of "Advance" wire, this change in temperature produces negligible drift in the control.

In Diagram IV is shown the circuit diagram of the second temperature control. The values of the components of the circuit are listed in Table II:
- 41 -

**T-A-B-L-E II**

Table of Components

of

Temperature Control II.

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>50 ohms</td>
</tr>
<tr>
<td>R₂</td>
<td>50 ohms</td>
</tr>
<tr>
<td>R₃</td>
<td>50 ohms</td>
</tr>
<tr>
<td>R₄</td>
<td>50 ohms</td>
</tr>
<tr>
<td>R₅</td>
<td>10 meg ohms</td>
</tr>
<tr>
<td>R₆</td>
<td>1500 ohms</td>
</tr>
<tr>
<td>R₇</td>
<td>1 meg ohm</td>
</tr>
<tr>
<td>R₈</td>
<td>250,000 ohms</td>
</tr>
<tr>
<td>R₉</td>
<td>2000 watt, 110v. heater coil</td>
</tr>
<tr>
<td>V₁</td>
<td>6J7G tube</td>
</tr>
<tr>
<td>V₂</td>
<td>FG105 thyratron tube</td>
</tr>
<tr>
<td>C₁</td>
<td>8 μf</td>
</tr>
<tr>
<td>C₂</td>
<td>0.1 μf</td>
</tr>
<tr>
<td>C₃</td>
<td>0.003 μf</td>
</tr>
<tr>
<td>B</td>
<td>270 volts with tap at 90 volts</td>
</tr>
</tbody>
</table>

E₁, E₂ = 115 volt, 60 cycle.

Filament Transformer, Hammond 167B for 6J7G.

Filament Transformer, Hammond #1123, 5v., 50 V.A. for FG105.

T₁ = 115v, 60 cycle to 5 volt, centre tapped transformer.

T₂ = Audio transformer, Hammond #312, 50-200 ohms input to 100 ohms.

The construction is essentially the same as in the temperature control first described. R₁, R₂ and R₃ are wound non-inductively from "Advance" wire while R₄ is non-inductively wound from "Hytēmco", a resistance wire of high temperature coefficient of resistance as well as high resistivity. In this control, a permanent phase shift of 90 degrees is obtained between the plate voltage and grid voltage of the
thyratron by means of condenser $C_3$. Temperature control results from the increment or decrement to this phase shift obtained when the bridge becomes unbalanced. If the temperature of the body to be controlled is too high, then the resistance of $R_4$ is too large and the phase angle between plate voltage and grid voltage of the thyratron is increased so that the thyratron is firing for less time per cycle than it was before. If the temperature should fall, the $R_4$ is too small and the thyratron fires for a longer time per cycle than before. The sensitivity of the control can be readily adjusted by varying the setting of the potentiometer $R_5$. In this circuit an FG105 thyratron was used, thus permitting up to 5 amperes in the heater circuit.

Temperature control in a range from room temperature to 140°C. with an accuracy of at least ±0.05°C. has been attained. With further adjustment, it is probable that the accuracy will be increased to ±0.01°C. The unit is completely portable and its operation direct. The maximum current is limited by the current carrying capacity of the thyratron in the present circuits but by means of a suitable system of shunts, control of up to 5 kilowatts should be possible without appreciable decrease in sensitivity.

D. ALIGNMENT OF SPECTROMETER.

Great caution must be exercised throughout the adjustment procedure not to fog or damage the rock salt
DIAGRAM V A. Energy Distribution vs Wavelength.

DIAGRAM V B. Energy vs Slit Width at 2.5 \( \mu \).

DIAGRAM V A and B.
prism or windows. They should not be touched with the fingers or breathed upon, and rubber gloves should be worn in handling them.

The order in which the different parts are set up is such that most of the parts need to be adjusted once only and their adjustment is not affected by subsequent changes. A low-power microscope mounted vertically with a 45 degree prism attached to the bottom, a mercury arc of high intensity and a cardboard box to replace the monochromator cover are of aid in the alignment.

The general alignment of the system should be first checked to ensure that the light is falling approximately on the centres of the various optical parts. The centers of the source, slits and mirrors are all at the same height, 2\(\frac{1}{4}\) inches, above the base of the spectrometer.

The detailed alignment procedure of the spectrometer will not be given here as it is set forth completely and in great detail in the "Instruction Manual for Infrared Spectrometer, Model 12-B" which accompanies the instrument.

The energy distribution with wave length, using a sodium chloride prism, has the general appearance as indicated in Diagram V-A. The peak of the curve occurs in the region of 2.5\(\mu\). The band at approximately 3\(\mu\) is due to carbon dioxide and water vapour. That at 4\(\mu\) is due to carbon dioxide while the band at 6\(\mu\) is due to water vapour. The band at 15\(\mu\) is due to carbon dioxide. The variation
of the energy as a function of slit width at the peak of the energy curve is shown in Diagram V-B. It should be a straight line passing through the origin. The fact that it does not pass through zero could be rectified by a change in the index on the slit micrometer of the indicated amount. Otherwise a correction factor may be added to each setting of the micrometer. The curve at the bottom end however indicates the slits do not close simultaneously. The curve shown is the optimum obtained after many resettings of the slits.

The resolution obtained with the spectrometer depends on the wave length and slit width used. The width of the band of nearly monochromatic light which is isolated by the instrument can be calculated. The traces showing the variation in resolution with wave length is shown in the "Instruction Manual". The band width used is the half intensity width, which is equal to the separation of two barely resolvable lines. This matter is considered in some detail by R.B. Barnes, R.S. McDonald and Van Z. Williams in their article.(1)

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IV.

RESULTS

The calibration procedure and the resultant calibration curves are first discussed. This is followed by those results pertaining to carbon disulphide which have been obtained to date.

A. CALIBRATION.

The arbitrary numbers of the wave length drum were calibrated into wave numbers by observing the settings corresponding to known lines and absorption bands. The absorption bands of water vapour and carbon dioxide gas occurring as atmosphere constituents were used for calibration of the longer wave lengths. In addition the absorption spectrum of ammonia gas was used. In this manner a fairly large number of calibration points distributed throughout
<table>
<thead>
<tr>
<th>Drum Setting</th>
<th>Wave Number in cm(^{-1})</th>
<th>Drum Setting</th>
<th>Wave Number in cm(^{-1})</th>
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<tbody>
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<td>517</td>
<td>667.0</td>
<td>1184</td>
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<tr>
<td>589</td>
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<td>Drum Setting</td>
<td>Wave Number in cm$^{-1}$</td>
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<tr>
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<td>1685</td>
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<td></td>
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</table>
the spectrum was obtained.

Plates VII, VIII, IX, and X are photographs of actual traces obtained from the recorder in the regions and under the conditions indicated. Identification of the bands was made from the work of Oetgen, Chao-Lan Kao and Randall. (1) The frequency in cm$^{-1}$ of each band identified is indicated below the trace, while the figures above the trace indicate the wave drive readings.

Together the spectra of these three substances - carbon dioxide, water vapour and ammonia - provide over 100 points in the region between 2.5$\mu$ and 15$\mu$ from which the calibration curve may be obtained. In Table III is displayed the wave length drive drum setting and the corresponding values of the wave numbers in cm$^{-1}$ which were obtained from the recorder traces, and which were used as calibration points for the spectrometer.

Plates XI, XII, and XIII are photographs of the calibration curves which were plotted from the above readings for the regions 700 - 1300 cm$^{-1}$, 1260 - 2000 cm$^{-1}$ and 1800 - 3900 cm$^{-1}$ respectively. Each of the original calibration curves is plotted on a sheet of graph paper of approximately 20 x 30 inches. These originals are used for identification of wave numbers from wave drive drum settings.

B. RESULTS.

The number of fundamental vibrations for a molecule of \( n \) atoms is \( 3n - 6 \). For carbon disulphide there would be 3 such fundamental bands, \( \nu_1, \nu_2, \) and \( \nu_3 \). In addition to these there are many combination and harmonic bands. The observed spectrum does not show such a large number of absorption bands. This reduction in the number is due to the fact that a number of the bands are located beyond the range of the instrument and that the symmetry properties reduce the number of vibrations which would be active in the infrared absorption.

A total of six bands were found in the region less than 15 microns. They were located at 3.38, 3.51, 4.29, 4.58, 6.52, 11.4\( \mu \). Cell lengths of 100 cm to 10 cm were employed depending on the degree of absorption necessary to display the band to best advantage. All measurements were made using a sodium chloride prism and were made at 20°C.

The graphs of percentage transmission vs wave length drum setting were obtained from the recorder traces for these six bands. To obtain these graphs, the distance was measured between two fiducial lines placed on the recorder trace by means of the switch "Microvolt Test" in the amplifier. This distance was then divided into a number of subdivisions. The base line was drawn between the two ends of the trace corresponding to periods when the aluminized
shutter was closed and consequently when there was no signal on the thermocouple. The vertical distances between the base line and the trace were then measured corresponding to each of the subdivisions. This procedure was carried out for each of the traces obtained, first with a known path length of carbon disulphide and then with the same cell evacuated. The readings obtained for the carbon disulphide were divided by those obtained from the trace of the vacuum and the quotient multiplied, by one hundred to give the percent transmission. The wave length drum setting corresponding to each of the fiducial lines and hence to each of the subdivisions was known, hence, the graphs of percentage transmission vs wave length drum setting could be plotted. Photographs of these are shown in Plates XIV to XVIII.

The difference band $\nu_3 - \nu_1$ is shown in Plate XIV. The absorption minimum corresponding to the missing Q branch occurs at 928 wave length drum setting which, by reference to Plate XI, corresponds to 877 cm$^{-1}$. The P branch, on the right, is well defined while the R branch is a little broader. The band is of medium intensity as can be seen from the cell length and pressure values given.

The structure of the $\nu_3$ band is shown in Plate XV. It is a strong band occurring at 6.52$\mu$ (1535 cm$^{-1}$) for the vapour of carbon disulphide. The graph was obtained as an average of six independent sets of readings, each with a cell length of 10 cm. and an extremely small pressure. The
P and R branches are well defined on the right and left of wave length drum setting 1486.7. A definite side band can be seen on the long wave length side of the band. The existence of this side band is strongly dependent on the conditions in the absorbing medium. If the pressure is too high, there is a general broadening of the band. If the pressure is too low the side band disappears and the P and R branches remain.

The combination band $\nu_1 + \nu_3$ is shown in Plate XVI. This graph was the result of averaging four independent sets of readings, each taken under the same conditions. The band occurs at 4.58 microns (2185 cm$^{-1}$), and is fairly weak.

Plate XVII shows the combination band $\nu_3 + 2 \nu_2$. The band is very weak. It occurs at 4.29 microns (2332 cm$^{-1}$).

The combination bands $\nu_3 + 2 \nu_1$ and $\nu_1 + \nu_3 + 2 \nu_2$ are shown in Plate XVIII. These bands occur at 3.51 and 3.38 microns (2838 and 2959 cm$^{-1}$) respectively. The resolution of the instrument when using a rock salt prism is too low to allow the structure of the bands in this region of the spectrum to be observed. A lithium fluoride prism would provide the necessary resolution.

In Table IV are shown the observed and calculated values based on the indicated values of the fundamental vibrations $\nu_1$, $\nu_2$, and $\nu_3$. The calculated values of the wave number when using the value of 1535 cm$^{-1}$ for $\nu_3$ are seen to agree much more closely with the observed values.
than those when $\nu_3 = 1523\text{cm}^{-1}$ is used. The results of other observers are likewise brought more closely into agreement, by use of this value for $\nu_3$.

TABLE IV.

Absorption Bands of Carbon Disulphide Vapour.

<table>
<thead>
<tr>
<th>Term</th>
<th>Wave Number</th>
<th>Wave Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Observed cm$^{-1}$</td>
<td>Calculated cm$^{-1}$</td>
</tr>
<tr>
<td>$\nu_1$</td>
<td>655(1)</td>
<td>655</td>
</tr>
<tr>
<td>$\nu_2$</td>
<td>397</td>
<td>397</td>
</tr>
<tr>
<td>$\nu_3$</td>
<td>1535 ± 2</td>
<td>1523</td>
</tr>
<tr>
<td>$\nu_3 - \nu_1$</td>
<td>877 ± 1</td>
<td>868</td>
</tr>
<tr>
<td>$\nu_1 + \nu_3$</td>
<td>2185 ± 5</td>
<td>2178</td>
</tr>
<tr>
<td>$\nu_3 + 2\nu_2$</td>
<td>2332 ± 5</td>
<td>2317</td>
</tr>
<tr>
<td>$\nu_3 + 2\nu_1$</td>
<td>2833 ± 6</td>
<td>2833</td>
</tr>
<tr>
<td>$\nu_1 + \nu_3 + 2\nu_2$</td>
<td>2959 ± 6</td>
<td>2972</td>
</tr>
</tbody>
</table>

The probable errors stated in Table IV were obtained in the following manner. An accuracy of plus or minus half of one division was assumed in the wave drive drum setting on the instrument. Then, by using the three calibration charts, photographs of which are shown in Plates XI, XII, and XIII, the corresponding probable errors were obtained for the various regions of the spectrum.

For bands of wave length less than 5$\mu$ the error in the experimental values cannot be less than 5cm$^{-1}$. As a
consequence, from Table IV it will be seen that the case for the use of $\nu_3 = 1535 \text{ cm}^{-1}$ is further strengthened as by its use the agreement between observed and calculated values becomes closer.

When the absorbing medium employed is in the liquid state, it is to be expected that some changes in the spectrum will occur due to the closeness and association of the molecules in the liquid state. Moreover all these bands occur at longer wave length in the liquid than in the vapour.

The band $\nu_1$, which arises from the transition, $(1\circ\circ\circ \longleftrightarrow 0\circ\circ\circ)$ from the ground state was not observed in vapour, but it has been observed by other workers in the liquid. This is in accord with the theory, since, the proximity of the neighbouring molecules in the liquid or solid might exert sufficient force on the molecule to produce a certain degree of asymmetry thus permitting the transition. The side band observed in the structure of $\nu_3$ (Plate XV) on the long wave length side is due to the isotope effect of $^{13}\text{C}^{32}\text{S}_2$. 
V

CONCLUSION.

The infrared absorption spectrum of carbon disulphide in the vapour state has been remeasured in the region from 2 to 15 microns. A total of six bands were measured, and were found to be located at 3.38, 3.51, 4.29, 4.58, 6.52, and 11.4 microns. While the ultimate object, that of the investigation of the anomalous bands of the carbon disulphide molecule under different conditions of association, has not been fully realized to date, work on this will continue with a thorough investigation of the changes in the absorption spectrum due to changes in the temperature and pressure of the absorbing medium.

The $V_3$ term has been confirmed and its structure investigated. A measure of the absorption of carbon disulphide vapour at a stated temperature and pressure has been attained. The bands obtained are such as to support the conclusion that carbon disulphide is a linear triatomic
molecule. The side branch shown on the long-wave length side of the fundamental band at 6.52 is due to the isotopic effect produced by Cl\textsuperscript{13}.

Although the exact spectrum of any compound cannot be found without measurements, a great deal of its quantitative form can be predicted from a knowledge of the relation between infrared spectra and molecular structure. When the differences between the absorption frequencies of the different components are great enough, identification can often be made directly, especially when the sample is known to contain relatively few possible structures. As the infrared absorption spectrum of a compound is the sum of all the possible vibrations of its parts, this spectrum is a unique property of the compound which gives rise to it. There is one to one correspondence between spectrum and compound. Correlation between the molecular configurations and the infrared spectra may be used for accurate analysis both in the research laboratory and in industry.
VIEW OF INTERIOR OF CHAMBER
TEMPERATURE CONTROL
(SIDE VIEW)

PLATE II
CONTROL PANEL, TEMPERATURE CONTROL AND SPECTROMETER.
TEMPERATURE CONTROL
(Showing Internal Wiring)

PLATE IV
TEMPERATURE CONTROL
(Rear View)

PLATE V
D.C. BREAKER AMPLIFIER AND BROWN RECORDER.
CALIBRATION CHART
For PE INFRA-RED SPECTROMETER Model 128 Serial #213
With No. 1 Prism in the Region T = 660 cm⁻¹ to ν = 720 cm⁻¹
(i.e. λ = 14.7 to 15 μm) Calibration from the 14.5 μm CO₂ Absorption Band Performed March 12, 1948 Identification from R.S.I. 13,515, 1942 Slit Width 0.1mm Temp 70°F Globar Power 200 Watts, Maximum Gain 10 Humidity 35% Wave Drive Speed 5 1/12" per rev. Cell Length 40 cm Pressure 150 mm Hg. Figures below curve are frequencies in cm⁻¹. Figures above curve are wave drive readings.

PLATE VII
**PLATE VIII**

**CALIBRATION CHART**

For P.E. Infrared Spectrometer Model 1206 Serial No. 2

With NaCl Prism in the Region 7500 cm\(^{-1}\) to 6000 cm\(^{-1}\)

Calibration in 13 cm\(^{-1}\) Calibration from the 1046 NH\(_2\) Band

Performed March 10, 1958. Identification from

R.S.I. 13,575, 1942. Slit width 0.15 mm. Temp 70° F.

Gained Power 15 watts. Gain 40. Humidity 22%.

Wave Drive Speed 5 cm per Rev. Cell Length 10 cm.

Pressure 100 mm Hg.

**FIGURES BELOW ARE FREQUENCIES IN CM\(^{-1}\)**

**FIGURES ABOVE WAVE ARE UNIVERSE IDENTITIES.**
CALIBRATION CHART
For P.E. Infra-Red Spectrophotometer Model 12B Serial No. 5333
with NaCl Prism, in the region 7 μm to 12 μm
I.e. λ = 0.5 μm
Calibration from the 6.4 μm H₂O Absorption Band
Performed February 24, 1976
ID: 1,315, 1976
Sale width 0.050 mm
Temperature 70°F
Sample purity 900 watts
Maximum gain 10
Humidity 60%
Minimum wavenumber 300 μm
Speed 10" per rev.

Plates IX

Below curve are frequencies in cm⁻¹;
Red line above curve are wavenumber readings.
CALIBRATION CHART

For PE INFRA Red Spectrometer Model 128 Serial # 213

With NaCl prism in the range 2,500 cm⁻¹ to 3,800 cm⁻¹

(c.e. M = 2.5 to 3.3 M Calibration from the 3.3 M NaCl)

Band 3; Performed March 13, 1948 Identification From

R.S.T.: 1,988 ft. SLIT WIDTH: 0.009 mm TEMP: 70°F

GLOBAR Power 200 WATTS Maximum Gain 10 Humidity 35%

Minimum Wave Drive Speed: 14.7 cm per line 160 cm per second

Coil Length 40 cm Pressure at Critical

N₂ Cell Length 150 cm Pressure 300 cm

Figures above are wave drive readings
CALIBRATION CURVE

FOR P.E. INFRARED SPECTROMETER
   MODEL 128

Calibration taken with an NaCl prism from the N2 absorption bands in the region from 900 to 1200 sec⁻¹ (15µm to 10µm)

as tabulated in R.I. 15, p. 18, 1942.

May 12, 1942
THE DIFFERENCE BAND $\nu_3 - \nu_1$

Temperature: 20°C
Pressure: 30 cm
Cell Length: 100 cm

Transmission vs. Wavelength
STRUCTURE OF THE $\nu_3$ BAND

Temperature: 20°C
Pressure: <1 mm.
Cell Length: 10 cm.
\[ \nu_1 + \nu_5 \]

Temperature: 20°C
Pressure: 20 cm
Cell Length: 100 cm

---

PLATE XVI
THE COMBINATION BAND

$\nu_3 + 2\nu_2$

Temperature: 20°C
Pressure: 50 cm
Cell Length: 10 cm
The combination bands
$
u_3 + 2\nu_1$ and $\nu_1 + \nu_2 + \nu_3$

Temperature: 20°C
Pressure: 20 cm
Cell length: 100 cm

Wavelength Drum
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