THE INFRARED ABSORPTION SPECTRUM

OF CARBON DISULPHIDE

by

THOMAS HARVEY EDWARDS

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ABSTRACT

This paper deals with the problem of setting up an infrared spectrometer and recorder under suitable conditions, and in applying the instrument to the absorption spectrum of CS_2 in the vapor phase.

Six absorption bands, corresponding to the fundamental vibration ν_3 at 1535 cm^{-1}, the difference band $\nu_3 - \nu_1$, at 877 cm^{-1}, and the four combination bands $\nu_1 + \nu_3$ at 2185 cm^{-1}, $\nu_3 + 2\nu_2$ at 2332 cm^{-1}, $\nu_3 + 2\nu_1$ at 2838 cm^{-1}, and $\nu_1 + \nu_3 + 2\nu_2$ at 2959 cm^{-1} have been examined.

Using this value for ν_3, a better agreement between the force constant of the C S bond, calculated from ν_3, with that calculated from ν_1, is obtained.

The work is to be continued.

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ACKNOWLEDGMENT

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I   INTRODUCTION

It has been our goal to set up the Perkin-
Elmer infrared spectrometer and associated instruments
under suitable conditions of temperature, humidity, and vi-
brational control; to calibrate them, and apply them to the
absorption spectrum of CS_2 in the vapor phase.

The infrared absorption spectrum of CS_2 has
been measured by several observers,(refs. 1,4,10), both in
the liquid and vapor phases. It is significant that these
observers do not agree on the frequencies in cm.$^{-1}$ at which
certain bands appear. Further, the observed values differ
occasionally from the theoretical values. We desire to
check those frequencies which fall in the region over which
our instrument is calibrated. The third normal frequency
is the most important of these, since calculation of force
constants and calculations of the frequencies of combina-
tion bands depend on it.

According to Herzberg, (ref. 8), CS_2 has
certain bands in its absorption spectrum which, assuming
that the CS_2 molecule is linear, should not be present.
Since these bands appear most strongly in the liquid, if at
all in the vapor phase, it is believed that the degree of
association of the molecules is responsible for the presence
of these bands. Their presence represents a breakdown of

selection rules. In addition, bands involving ν_3 occur at longer wavelengths in the liquid state.

It was hoped that the study of the absorption spectrum under independent variation of pressure and temperature would provide fruitful data for further theoretical study of the CS_2 molecule and of the intermolecular forces involved in chemical association.

The general theory of molecular spectra and molecular structure is well presented in Herzberg's two volumes, (refs. 7,8), and Wu, (ref. 15), presents a good treatise on vibrational spectra with special reference to the linear symmetrical YX_2 molecule, to which type we believe CS_2 belongs.

The spectra of molecules appear in three more or less distinct regions of the spectrum; the ultra-violet or visible, the near infrared, and the far infrared. In order to account for these three types of band spectra and their fine structure, it is postulated that the internal energy of a molecule is essentially of three kinds,- namely - electronic, vibrational, and rotational, each of which is quantized. The order of magnitude of these energies is about 5 ev., .1 ev., and .oo5 ev. respectively; hence the frequencies associated with them are in the regions 40,000 cm^{-1}, 800 cm^{-1}, and 40 cm^{-1}.

The structure of the electronic bands indicates that vibrational and rotational transitions may accompany

vibrational transitions which occur within a given electronic level, usually the ground level. It is with these vibration rotation bands that we shall be concerned.

On the basis of these three energy types, the energy levels of a molecule can therefore be represented as in FIGURE I. The widely spaced levels are electronic and to each of these corresponds a set of vibrational levels. Finally, each vibrational level has a set of rotational levels associated with it. The diagram is not to scale.

In general, transitions do not occur for which there is no change in the electric dipole moment. However, weak lines do occur where the quadropole moment or magnetic dipole moment change.

With this introduction then we will now examine some of the most useful parts of the theory of vibrational spectra, some of which was discussed in the seminars held by the group working on molecular structure.

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FIGURE I
MOLECULAR
ENERGY LEVELS.

ELECTRONIC LEVELS   VIBRATIONAL LEVELS   ROTATIONAL SUB-LEVELS

$h\nu_e$

$\downarrow h\nu_v$

$h\nu_r$
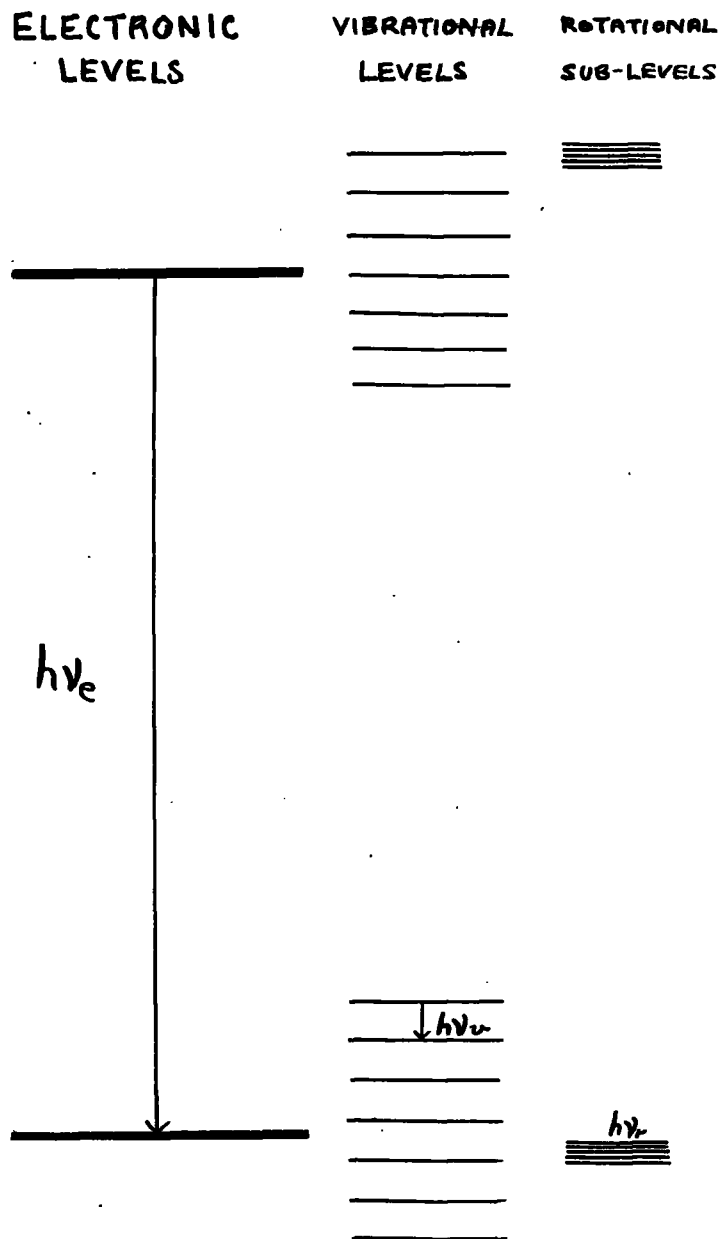
II THEORY

An essential step in the study of the spectra of a polyatomic molecule is the mechanical problem of vibrational modes.

A molecule consisting of n atoms has, in general, 3n-6 degrees of freedom, but since there is one degree of free internal rotation in linear molecules, they have 3n-5 vibrational degrees of freedom. Representing this number by s then, we may choose coordinates $q_1, \ldots q_s$, giving the displacements of the atoms from their positions of equilibrium. The potential energy V can now be expanded in a Taylor series of the form -

$$V = V_o + \sum_i \left(\frac{\partial V}{\partial q_i}\right)_o q_i + \frac{1}{2!} \sum_{ij} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o q_i q_j + \frac{1}{3!} \sum_{ijk} \cdots + \cdots \qquad (1)$$

where the zero subscripts refer to values taken at the equilibrium positions. Choosing $V_o = 0$, and seeing that $\left(\frac{\partial V}{\partial q_i}\right)_o = 0$ we have therefore -

$$V = \frac{1}{2} \sum_{ij} b_{ij} q_i q_j + \frac{1}{6} \sum_{ijk} b_{ijk} q_i q_j q_k + \cdots \qquad (2)$$

For small vibrations, terms beyond the quadratic may be neglected and we have -

$$V = \frac{1}{2} \sum_{ij} b_{ij} q_i q_j \quad \text{WHERE} \quad b_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) \qquad (3)$$

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Similarly the kinetic energy may be written -

$$T = \frac{1}{2} \sum_{ij} a_{ij} \dot{q}_i \dot{q}_j \qquad (4)$$

where the a's are functions of the masses of the atoms.
The corresponding Lagrangian equations of motion are -

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_k}\right) - \frac{\partial L}{\partial q_k} = 0 \qquad (5)$$

or for these T and V

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_k}\right) - \frac{\partial V}{\partial q_k} = 0 \qquad (6)$$

where k = 1,2,...s

Evaluation of these equations yields s equations of the form

$$\sum_j \left(a_{jk} \ddot{q}_k + b_{jk} q_k\right) = 0 \qquad (7)$$

which have general solutions of the form

$$q_k = A_k \sin\left(\sqrt{\lambda}\, t + \alpha\right) \qquad (8)$$

an equation of wave motion with amplitude A_k, phase constant α, and frequency given by $4\pi^2 \nu^2 = \lambda$ (9)

Substitution of (8) in (7) yields s linear homogeneous simultaneous equations

$$\sum_j \left(b_{jk} - a_{jk} \lambda\right) A_k = 0 \qquad (10)$$

which have non-trivial solutions for the A_k if the secular determinant of the sth degree is zero;

i.e. (11)

$$\left| b_{ij} - a_{ij} \lambda \right| = 0$$

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This equation yields s values for λ in terms of the a's and k's.

As shown by Whittaker,(ref. 14), it is always possible to make a linear transformation of coordinates; viz.-

$$q_\kappa = \sum_{\lambda=1}^{\kappa} c_{\kappa\lambda} \, Q_\lambda \tag{12}$$

such that all cross-product terms are eliminated in the expressions for the potential and kinetic energy (3) and (4). These may now be written -

$$V = \frac{1}{2} \sum_\lambda \lambda \, Q_\lambda^2 \tag{13}$$

and

$$T = \frac{1}{2} \sum_\lambda \dot{Q}_\lambda^2 \tag{14}$$

This procedure is called normal coordinate transformation, and yields the following Lagrangian equation of motion -

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{Q}_\lambda}\right) + \frac{\partial V}{\partial Q_\lambda} = 0 \tag{15}$$

Since T and V contain no cross terms, and the a's are unity, equation (7) becomes -

$$\ddot{Q}_\lambda + \lambda \, Q_\lambda = 0 \tag{16}$$

with solutions $\quad Q_\lambda = B_\lambda \sin\left(\sqrt{\lambda_\lambda} \, t + \beta\right) \tag{17}$

The λ_λ here are the same as before and further, the B_r's are related to the A_k's through equation (12), so that

$$A_\kappa = \sum_{\lambda=1}^{\kappa} c_{\kappa\lambda} \, B_\lambda \tag{18}$$

Hence the c's can be determined to enable us to transform from the q_k to the normal coordinates Q_r.

Substitution of (17) in (12) yields

$$q_k = \sum_{\lambda=1}^{\rho} c_{k\lambda}\, B_\lambda \sin\left(\sqrt{\lambda_\lambda}\, t + \beta_\lambda\right) \qquad (19)$$

for k = 1,2,...s

For certain vibrations all the B_r except one, say $B_{r'}$ are zero; then

$$q_k(\lambda') = c_{k\lambda'}\, B_{\lambda'} \sin\left(\sqrt{\lambda_{\lambda'}}\, t + \beta_{\lambda'}\right) \qquad (20)$$

with k = 1,...s

which indicates that the nucleus undergoes simple harmonic motion of frequency $\nu_{\lambda'}$ related to $\lambda_{\lambda'}$, as shown before by

$$4\pi^2 \nu_{\lambda'}^2 = \lambda \quad \text{with all vibrations in the same phase.}$$

Such a vibration, where the nuclei vibrate with the same frequency and are in phase, is called a normal vibration of the molecule. In general there are s normal modes of vibration given by $\nu = \dfrac{\sqrt{\lambda}}{2\pi}$ where the λ's are the s solutions of the secular determinant. Knowing the a_{ij} and b_{ij} we can evaluate the normal vibration frequencies of the molecule. If two normal molecular vibrations have the same frequency, and hence energy, they are degenerate. Such degeneracy is usually due to molecular symmetry.

In general, any complex motion of the nuclei can be treated as equivalent to the superposition of the s, separate, relatively simple, normal vibrations of the molecule. This is called a Lissajous motion.

We wish to connect vibrational energy with these normal vibrations. The wave equation of the motion of the nuclei is

$$-\sum_i \frac{\hbar^2}{2m_i} \nabla^2 \psi + (E - V)\psi = 0 \qquad (21)$$

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where Ψ is the nuclear wave function and m_i is the mass of the ith nucleus. In terms of the displacement coordinates q_k (21) becomes -

$$\frac{\hbar^2}{2} \sum_{k=1}^{a} \frac{1}{m_k} \frac{\partial^2 \Psi}{\partial q_k^2} + (E - V)\Psi = 0 \qquad (22)$$

Transforming to normal coordinates we have -

$$\frac{\hbar^2}{2} \sum_{\lambda=1}^{a} \frac{\partial^2 \Psi}{\partial \varphi_\lambda^2} + \left(E - \frac{1}{2} \sum_{\lambda=1}^{a} \lambda_\lambda \varphi_\lambda^2\right)\Psi = 0 \qquad (23)$$

Expressing $\Psi = \Psi_1 (\varphi_1) \Psi_2 \varphi_2 \cdots \Psi_a (\varphi_a)$ we can separate equation (23) into s independent equations of the form

$$\frac{\hbar^2}{2} \frac{\partial^2 \Psi_j}{\partial \varphi_j^2} + \left(E_j - \frac{1}{2} \lambda_j \varphi_j^2\right)\Psi_j = 0 \qquad (24)$$

each being associated with one of the normal coordinates. These equations are of the same form as those of the harmonic oscillator for which the eigenvalues are known to be

$$E_j = \left(v_j + \frac{1}{2}\right) h c \nu_j \qquad (25)$$

where E_j is the vibrational energy

v_j is the vibrational quantum number

and ν_j is the frequency in wave numbers of the jth normal vibration.

Assuming no interaction, the energies are additive; and hence

$$E_\nu = \sum_{j=1}^{a} E_j = \sum_{j=1}^{a} \left(v_j + \frac{1}{2}\right) h c \nu_j \qquad (26)$$

where the selection rule is $\Delta v_j = \pm 1$, since the motions are assumed harmonic.

It is instructive to see just how selection rules are calculated. It is known from quantum mechanics that the

probability of a transition between two states m and n, whose wave functions are ψ_m and ψ_n, which is accompanied by absorption or emission of dipole radiation, is determined by the matrix element P_{mn}, where

$$P_{mn} = \int \psi_m^* \mu \, \psi_n \, d\tau \tag{27}$$

where μ is the dipole moment.

In general all P_{mn} for which the integral vanishes, represent forbidden transitions.

A simple harmonic oscillator has a potential of the form $V = \alpha x^2$, where x is the displacement and α is a positive constant. The Schroedinger equation is then -

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - \alpha x^2)\psi = 0 \tag{28}$$

for which the solutions are the eigenfunctions ψ_n containing the Hermite Polynomials and are given by

$$\begin{aligned}
\psi_n &= e^{-\frac{\xi^2}{2}} H_n(\xi) \\
&= (-1)^n e^{\frac{\xi^2}{2}} \left(\frac{d}{d\xi}\right)^n e^{-\xi^2} \\
&= (-1)^n e^{\frac{\xi^2}{2}} D_n \, e^{-\xi^2}
\end{aligned} \tag{29}$$

where $\quad \xi = x \dfrac{\sqrt{2m\alpha}}{\hbar}$

and the ψ_n are orthonormal; i.e. $\int \psi_m^* \psi_n \, d\tau = \delta_n^m$ (30)

For oscillations along the x axis

$$P_{mn} = \int \psi_m^* \mu_x \psi_n \, dx \tag{31}$$

substitution yields

$$P_{mn} = (-1)^{mn} \int e^{\frac{\xi^2}{2}} D_m \, e^{-\xi^2} K x \, e^{\frac{\xi^2}{2}} D_n \, e^{-\xi^2} \, dx$$

since

$$\mu_x \propto x$$

therefore

$$P_{mn} = \text{const} \int e^{\frac{5^2}{2}} D_m \, e^{-5^2} \, \zeta \, e^{\frac{5^2}{2}} D_n \, e^{-5^2} \, d\zeta$$

Integrate once by parts $= \text{const} \int e^{-5^2} d[D_m \, e^{-5^2} \cdot D_n \, e^{-5^2}] \, d\zeta$

$$= \text{const} \int e^{5^2} [D_{m+1} \, e^{-5^2} D_n \, e^{-5^2} + D_{n+1} \, e^{-5^2} D_m \, e^{-5^2}] \, d\zeta$$

but the $\mathcal{Y}$'s are orthogonal by (30) such that

$$\int e^{5^2} D_k \, e^{-5^2} D_j \, e^{-5^2} d\zeta = 0$$

unless k = j.

Therefore in the above equation either $n+1 = m$

$$m+1 = n$$

or

therefore the selection rule is $\Delta v = \pm 1$ (32)

We note here that anharmonicity requires the inclusion
of terms of higher degree in the potential and kinetic energy
expressions. Inclusion of the cubic term gives $\Delta v = \pm 2, \pm 4$.
and inclusion of the quartic term gives $\Delta v = \pm 3, \pm 5$.
as additional selection rule possibilities. This is accom-
plished through an alteration in the eigenfunctions.

Usually we desire to know what the motions are which
are associated with the normal frequencies. We proceed by
writing out the expressions for the kinetic and potential
energies in terms of the displacements of the nuclei from
their equilibrium positions. Solving the secular determin-
ant and carrying out the subsequent calculations we deter-
mine the coefficients c_{kr} by which the displacement coordi-
nates q_k transform to the normal coordinates Q_r. By per-
forming the inverse transformation we find that the coeffi-

cients c' of $\quad Q_\lambda = \sum_K c'_{K\lambda} g_K \quad$ (33)

can be evaluated, thus determining the forms of the dis-
placements.

For the linear symmetrical YX_2 molecule there are act-
ually four normal vibrations and the determinant will be of
the fourth order, although two of the solutions are identi-
cal due to degeneracy. Direct solutions of normal coordin-
ate problems are difficult to obtain due to the size of the
determinants involved. Fortunately the application of group
theory makes it possible to use the symmetry properties of
molecules, to effect the separation of both T and V into
terms involving no cross-terms between coordinates involved
in one part with those in any other. These coordinates are
called symmetry coordinates. The coordinates involved in
each part have the same symmetry characteristics, which are
different from those in other parts. Consequently the secu-
lar equation is immediately factored into a number of equa-
tions of lower degree, each involving only one set of sepa-
rated coordinates with the same symmetry. Fortunately, for
linear symmetric molecules such as CS_2, each normal vibra-
tion belongs to a different class. In this case there are
only three constants to be evaluated and there are three
normal frequencies from which to do it.

Herzberg, (ref. 8, pages 153-154), performs this cal-
culation and arrives at $\quad 4\pi^2 \nu_1^2 = \dfrac{a_{11} + a_{12}}{m_x}$ (34)

$$4\pi^2 \nu_2^2 = \frac{2(m_y + 2m_x)}{m_x m_y} \frac{a_{33}}{\ell^2} \quad (35)$$

$$4\pi^2 \nu_3^2 = \frac{m_y + 2m_x}{m_x m_y}(a_{11} - a_{12}) \quad (36)$$

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In equations (34), (35), and (36), a_{11} is the force constant of the X-Y bond; a_{12} is the interaction constant of the two bonds; and a_{33} is the force constant for the binding of the molecule. We note that the degenerate vibration ν_2 depends only on a_{33}, whereas the non-degenerate vibrations ν_1 and ν_3 depend on a_{11} and a_{12}.

The normal vibrations of the linear YX_2 molecule are shown in FIGURE II.

ν_1 corresponds to a motion in which the S atoms oscillate symmetrically with respect to the C atom. Since the equilibrium and dynamic configurations are both symmetric the dipole moment is always zero and hence ν_1 is infrared inactive.

ν_2 consists of a motion of the C atom against the S atoms in a line perpendicular to the axis of symmetry of the molecule. The motion is doubly degenerate since there are two directions, perpendicular to this axis, along which the forces are identical. ν_2 is infrared active with a fine structure of uniformly spaced lines and with a strong zero (Q) branch.

ν_3 is an oscillation of the C atom with respect to the S atoms, along the symmetry axis. This vibration possesses a changing electric moment and is strongly infrared active. The fine structure associated with this band consists of P and R branches but no Q branch. In ν_1 the carbon atom does not move, whereas in ν_2 and ν_3 the separation of the sulphur atoms is fixed.

As was mentioned before, ν_2 is degenerate, and hence we can take a linear combination of ν_{2a} and ν_{2b} and obtain

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FIGURE II

NORMAL VIBRATIONS OF
A LINEAR SYMMETRICAL
YX_2 MOLECULE
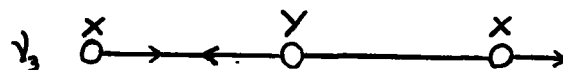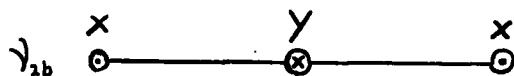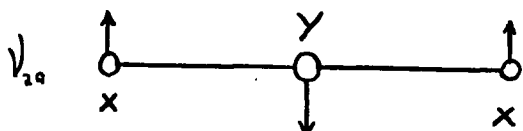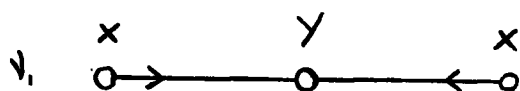
another motion of the same frequency, but where not all atoms move in phase or in straight lines. For instance, $\nu_{2a} + \nu_{2b}$ where ν_{2b} is 90°out of phase causes each nucleus to rotate in a circle about the axis. This is called nutation and results in a constant angular momentum about the axis. We specify this angular momentum by the quantum number 1.

As a result of this new concept we redefine normal vibrations to be those for which all atoms have the same frequency and the Cartesian coordinate components of their displacements perform simple harmonic motion.

It is important to note that both classical electrodynamics and the quantum theory require that the frequencies of the emitted or absorbed radiation be the same as the frequency of the mechanical vibrations.

There are several approximate methods for determining the normal frequencies, including the method of central forces, the method of extreme fields, and the valence force method. The last mentioned method works well for linear YX_2 molecules. The basic idea of the valence force treatment is that displacements of atoms along the direction of their bond brings restoring forces much greater than those due to changes in angles between valence bonds. On pages 19 and 20 Wu arrives at the expressions

$$\lambda_1 = \frac{k_1}{m_x} \tag{37}$$

$$\lambda_2 = 2 k_\delta \left(\frac{1}{m_x} + \frac{2}{m_y} \right) \tag{38}$$

$$\lambda_3 = k_1 \left(\frac{1}{m_x} + \frac{2}{m_y} \right) \tag{39}$$

which may be shown to be identical with our previous expressions (34), (35), and (36), where $a_{11} = k_1$; $a_{12} = 0$; and $\dfrac{a_{33}}{1^2} = k_\delta$. Herzberg gives for CS_2

$$k_1 = 8.1 \times 10^5 \text{ dynes / cm from } \nu_1$$

$$k_1 = 6.9 \times 10^5 \text{ dynes / cm from } \nu_3$$

$$k_\delta = .234 \times 10^5 \text{ dynes / cm from } \nu_2$$

the quality of the agreement between k_1 from ν_1 and ν_3 indicates the quality of the valence force field approximation. The previously accepted value of ν_3 was 1523 cm^{-1}. The value which we measured was 1535 cm^{-1}. Recalculating k_1 from ν_3 as we measured it, by equation (39), one obtains the value $k_1 = 7.1 \times 10^5$ dynes / cm. This indicates an even closer approximation than was previously found.

On the basis of this valence force field Mecke devised a notation for classifying normal vibrations. He employs the symbol ν for valence (stretching) vibrations, and δ for deformation (bending) vibrations. For a linear molecule which has (3n-5) normal vibrations, there are (n-1) valence vibrations, and (2n-4) deformation vibrations. Further, when the dipole moment changes, it may change in directions parallel or perpendicular to the symmetry axis, hence an additional classification is possible. Parallel changes are labelled π, perpendicular changes are labelled σ, (for the German "parallel" and "senkrecht" respectively).

In this notation, for a linear YX_2 molecule one sees that

ν_1 is a $\nu(\sigma)$ vibration

ν_2 is a $\delta(\sigma)$ vibration

ν_3 is a $\nu(\pi)$ vibration.

In addition, when a molecule possesses a centre of symmetry, vibrations which do not alter any symmetry property of the molecule with respect to inversion at the centre of symmetry, are labelled g, (for the German gerade - even). Vibrations which are anti-symmetric are labelled u, (for the German ungerade).

On this basis we can formulate a rule of mutual exclusion for molecules with a centre of symmetry. Since we get a changing dipole moment only for transitions g↔u - - i.e. between states of opposite symmetry and since for the Raman effect transitions occur only between states of the same symmetry g↔g or u↔u. We say therefore that transitions which are allowed in the infrared are forbidden in the Raman spectrum and vice-versa.

In the linear symmetric YX_2 molecule the dipole moment is zero for ν_1, at all times; hence it is not infrared active but is Raman active. ν_2 and ν_3 involve changing dipole moments however, and hence appear in the infrared though not in the Raman spectrum.

In addition to the normal vibrations, overtone combination and difference bands may occur, where the selection rules will depend on the molecular symmetry. Recalling equation (26)

$$E_v = \sum_j (v_j + \tfrac{1}{2}) h c \nu_j$$

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we find that these may be represented approximately by

$$V = n_1 V_1 + n_2 V_2 + n_3 V_3 \qquad (40)$$

where the n's may have integral values $+$ or $-$ so long as
is a positive number. If only one n is not zero then we have
an overtone band; if all the n's are positive we have a com-
bination band; and if some n is negative we have a difference
band. The fourth quantum number l, which indicates the ang-
ular momentum associated with the degenerate V_2 must be given
to completely specify the state. The four numbers n_1, n_2,
l, and n_3 completely specify the state, written in that order-
for example - 1, 2, 2, 0 means $n_1 = 1$; $n_2 = 2$; $l = 2$; $n_3 = 0$.
The possible values of l are restricted so that l can only
have values n_2, n_2-2, n_2-4, etc.

If a molecule has a centre of symmetry then totally sym-
metric vibrations have no overtones at all. For CS_2 this
means neither V_1 nor any overtone of V_1 will appear in the
infrared.

Dennison (ref. 5) has shown that

1. transitions involving perpendicular change in dipole mo-
   ment (V_2) may occur if and only if (a) n_2 is odd,

   (b) n_3 is even,

   (c) $\Delta l = \pm 1$,

   where n_1 may have any value.

2. transitions involving a parallel change in dipole moment
   (V_3) may occur if and only if (a) n_2 is even,

   (b) n_3 is odd,

   (c) $\Delta l = 0$,

   where n_1 may have any value.

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These conclusions depend on the symmetry properties of the kinetic and potential functions and not on the approximations employed. As before, writing $\nu = n_1\nu_1 + n_2\nu_2 + n_3\nu_3$ for the rough location of an overtone band where the n's are positive or negative integers, so long as ν is positive, then only such bands occur for which $n_2 + n_3$ is odd. From 1. and 2. above we see that if n_2 is even, the change in electric moment is parallel, and if n_2 is odd, the change is perpendicular.

For three colinear symmetrical atoms the sum of the frequencies to two observed bands (overtones, combination bands, or fundamentals) will not be active. For if ν' and ν'' are two active frequencies, the new n_2's and n_3's will both be odd, and hence their sum cannot be odd, as required for radiation.

One way of recognizing which frequencies are to be associated with observed vibrational bands is by their observed rotational structure. For linear molecules the rotational energy is given by

$$E_\lambda = \frac{\hbar^2}{2I} J(J+1) \qquad (41)$$

where J is the rotational quantum number and I is the common value of the two non-zero components of the moment of inertia. The vibrational energy for a given normal vibration may be written

$$E_v = \left(v + \frac{d}{2}\right) hc\nu \qquad (42)$$

where d is the degeneracy of the vibration. d =1 for a linear oscillator, but for ν_2 of CS_2, d=2. As an approximation, the vibrational and rotational energies are additive, hence

we write $E_{\nu\lambda} = \left(\nu + \frac{\alpha}{2}\right)hc\nu + \frac{\hbar^2}{2I} J(J+1)$ (43)

For the simple case of $\Delta v = \pm 1$ as a selection rule, we treat
the two types of vibration, parallel and perpendicular, sep-
arately. Parallel bands may be shown to have a selection
rule $\Delta J = \pm 1$. For $\Delta J = -1$ we get the negative or P branch of ro-
tational fine structure, and for $\Delta J = +1$ we get the positive or
R branch. The Q branch is missing.

Perpendicular bands may be shown to have transitions in-
volving $\Delta J = 0$ in addition to $\Delta J = \pm 1$. $\Delta J = 0$ is allowed when-
ever nutation occurs; therefore we obtain, in addition to the
P and R branches, a strong Q branch. It is the presence of
this Q branch at the centre of a perpendicular vibration band
which distinguishes it from parallel bands, exhibited by fun-
damental frequencies of a linear polyatomic molecule.

Since we have identified ν_2 as a perpendicular band, and
ν_3 as a parallel band, the two will be distinguishable from
their structural shapes. The separation of the rotational
fine structure lines should be $\frac{\hbar}{2Ic}$, and is too fine for
our instrument to resolve. As a matter of fact, nuclear spin
effects this value. Symmetrical linear molecules exhibit al-
ternating intensities in lines. In this case the spins of the
two X nuclei determine the relative intensities. Since the
spin of the sulphur atoms is zero, one series will be absent
and the separation becomes $\frac{\hbar}{4Ic}$. We are unable to detect it.

Three more effects are of interest in determining the
positions of vibrational bands. The first of these is acci-

dental resonance, noticed by Fermi in 1931; the second is an isotope effect; and the third is molecular association. Fermi-resonance occurs when two vibrational levels belonging to different vibrations (or combinations) have nearly equal energy. Such resonance occurs only for levels of the same symmetry. Fermi-resonance of V_i with $2V_j$ is large and is accomplished through cubic combinations of the early terms in the expression for the potential, equation (3), whereas resonance between V_i and $3V_j$ or higher overtones is accomplished through quartic combinations.

. When two levels are accidentally degenerate they repel each other, giving an increased separation between them. The two states share their wave-functions and two new functions are formed giving bands at displaced frequencies. Both bands now behave like fundamentals and their intensities are more nearly equal. In the case of CS_2, V_1 and $2V_2$ are resonant but the resonance is loose and has little effect.

The isotope effect is the change in normal (and other) vibrations due to isotopic changes. Replacement of an atom or atoms in a molecule by isotopes leaves the potential field unchanged, as is expected, but the change in mass alters the frequencies of the normal vibrations and may lower the symmetry in the molecule. In the case of CS_2 replacement of only one sulphur atom destroys the symmetry, and V_1 may appear in the infrared. Wu (ref. 15) treats the problem for the linear symmetrical YX_2 molecule on pages 41 and 42.

In general for CS_2 the percentage of molecules of other isotopes than $C^{12}S_2^{32}$ is small and hence the bands due to these isotopes are weak. The side-band to ν_3 is attributed to an isotopic shift.

The most noticeable effect of molecular association is the decrease in frequency of vibrations observed in the liquid state of certain molecules from the values in the un-associated vapour state. In ν_3 of CS_2 this amounts to about 25 cm^{-1}. The work is to be continued examining the effect of pressure and temperature on this shift.

- - - -

III EXPERIMENTAL WORK

The experimental work may be divided into five parts:

(A) Construction of a suitable room and control of humidity, temperature, and vibration therein.

(B) Construction of auxiliary equipment to control conditions of temperature and pressure of our samples in the one-meter gas cell.

(C) Experimental arrangement of the instruments and their control.

(D) Calibration of the spectrometer.

(E) Absorption spectrum of CS_2.

(This work is to be carried on throughout the summer by myself and next term by others. Now that the apparatus is properly adjusted and calibrated, results will be forthcoming more rapidly).

(A) For optimum performance of this fine apparatus it is necessary that the instruments be located where there is

1. low relative humidity - to minimize hygroscopic action which damages NaCl and KBr parts in humid locations.

2. constant temperature - to prevent excessive drift in the instrument.

3. steady position - to minimize vibrations which superpose "noise" on the readings.

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In order to satisfy these conditions, a room measuring 9' x 8' x 6' was constructed, thermally lagged, and equipped with air-lock doors. The problem of steady position was eliminated by locating the room on the basement floor in Room 109.

The question of humidity control required considerable experimental work; for the humidity in University laboratories approsimates 75% for five summer months and 50% for five months in winter. Early attempts to dry air with trays of $CaCl_2$ and circulating fans showed a negligible effect in an ordinarily closed but unsealed room. The manufacturers of the spectrometer suggested that most satisfactory installations were set up in a sealed room with humidity control. It was decided to follow this advice; but still no commercial firm in Vancouver had had experience on such units. The Canadian General Electric finally agreed to undertake the installation, and the sealed room was constructed to specifications by the University carpenters. The final room has now been operating satisfactorily for five months, after considerable experimentation and alterations.

The experimental arrangement of our air-conditioning unit is as follows: (see photo I) - the refrigeration coil and fan enclosed in a cabinet measuring 2' x 2' x 2' was mounted in the south east corner of Room 109 with the condensing unit placed outside the room in order to reduce vibrations. The compressor motor is a G.E. $\frac{1}{2}$H.P. 110V 60cycle unit, model 6M365D, and the cooling agent is Freon 12 (di-

PHOTO I HUMIDITY CONTROL APPARATUS

chlorodifluoromethane). This apparatus is not normally used as a dehumidifier. In order to make it such it was necessary to add and modify several parts.

Since a constant temperature is required in the room, an extension measuring approximately 1' x 1' x 2'6" in the form of an air tunnel, was affixed to the coil mounting, through which the air passes after being cooled by the coil. In the end section of this tunnel are located three 600 watt cone-heaters to reheat the air before it returns to the room. In the centre zone, three fine mesh wire screens are located to prevent radiant heat from reaching the coil. This was found necessary as the final section of the coil rose $6\,^{\circ}C$ under this radiation. After the screens were put in the rise was less than $2\,^{\circ}C$.

Since the rate at which air passes over the coil affects the time taken to reach the ultimate humidity obtainable, a throttle was constructed to control the flow of air. Finally, the drainage system was changed in order to facilitate the removal of water from the room, once it is collected by the coil. A "drip pan" with steep, carefully waxed sides was substituted for the shallow one supplied with the cooling unit.

Control of humidity and temperature by this air-conditioning unit is effected by the following system of controls: a wall thermostat is used to control the cone-heaters and hence the room temperature, in the customary manner. The humidity controls are standard with this coil, and operate as follows:

1. the throttle valve, a variable control at the coil, which controls the rate of flow of the fluid input to the coil's evaporator.

2. the back-pressure control, on the condenser unit, which stops the pump when the return pressure of the refrigerant is too low.

3. the solenoid valve, on the fluid input line, a positive on-off fluid switch, operated by the humidistat, which corresponds in the control of humidity to a thermostat.

When the humidistat measures a room humidity lower than it is set for, it actuates the solenoid valve, stopping the flow of liquid refrigerant to the coils. Consequently, the return pressure drops rapidly and the back-pressure control stops the condenser pump.

Either the motor switch or the back-pressure control can stop the pump. The back-pressure can be actuated by the humidistat when the humidity of the room is below setting, or by the temperature, and consequently the pressure, of the returning refrigerant being too low. If the latter case occurs often, a greater mass rate of flow of air may be passed over the coil to give better performance.
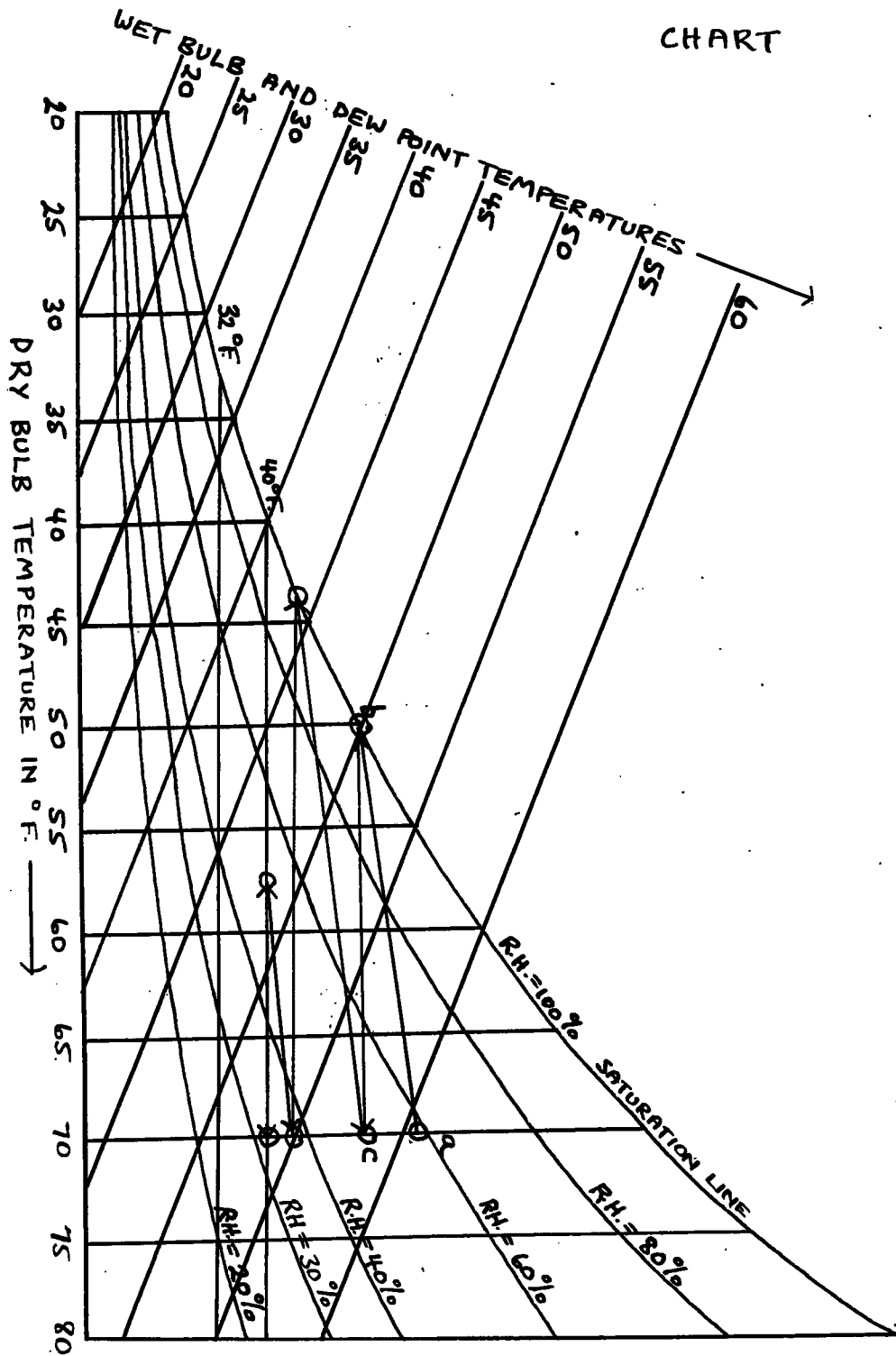
As a safety feature of the operation, we have two relays which are actuated when the pump motor is off. One of these relays turns off the cone-heaters and prevents their overheating the room or the cooling coils. The other relay stops the fan and prevents the warm, dry air from passing over the coil, picking up moisture and redistributing it about the room.

The theory of dehumidifying coils is well treated by
Brown and Marco (ref. 3); and the method of G. L. Tuve (ref.
13), which is briefly outlined below, provides a simple, di-
rect method of calculating the final humidity obtained from
a refrigeration coil system. This it does by means of a non-
logarithmic psychrometric chart such as G. E. puts out. This
method is possible since Tuve has shown, by mathematical an-
alysis and by tests, that the behaviour of a wet coil is sub-
stantially the same as that of the same coil when dry, but
with its surface at the dew-point temperature of the entering
air.

FIGURE III represents a portion of a non-logarithmic
psychrometric chart. The point "a" represents a set of poss-
ible starting point conditions, namely- a constant room dry-
bulb temperature of 70°F and initial R.H. of 60%. The line
"ab" represents a possible line of cooling and dehumidifying
on passage of air over the coil. Its slope depends upon the
ratio of latent heat removed to total heat removed in the pro-
cess. The line "bc" represents subsequent reheating to 70°F,
with a final drop in humidity at this temperature. Over a
period of several such cycles the room reaches a minimum hu-
midity, depending solely upon the dry-bulb temperature of the
room, and the dew-point temperature maintained by the coil.
At the present throttle setting these temperatures are 70°F
and 40°F respectively (measured), and hence the minimum ob-
tainable humidity is 35.5%. This calculation is confirmed
by values given in the Handbook of Physics and Chemistry.

FIGURE III

PSYCHROMETRIC

CHART

WET BULB AND DEW POINT TEMPERATURES

DRY BULB TEMPERATURE IN °F.

R.H.=100% SATURATION LINE

R.H.=80%

R.H.=60%

R.H.=40%

R.H.=30%

R.H.=20%

32°F

40°F

This value is well below the humidity required; under normal conditions the air-conditioning unit easily maintains a R.H. of 40% ± 1%, and a temperature of 70°F ± 1°F, even when several persons are in the room.

(B) The auxiliary equipment consists of two temperature controls for the gas absorption cell. One of these is a thyratron type temperature control, and the other is a self-balancing bridge type temperature control.

In general, observers of the absorption of CS_2 in the vapour phase have made little effort to control the temperature and pressure of their samples during analysis. For example, Plyler and Humphreys (ref. 10) merely placed a small quantity of liquid CS_2 in the cell and allowed it to stand for two hours to reach conditions of equilibrium. Since they were interested primarily in the appearance or failure to appear of certain bands, it was necessary for them to know the exact temperature and pressure of the gaseous CS_2. On the other hand, the variation in intensity of absorption of the bands is one of the things which we hope to observe. As a result, we have built these temperature controls. The self-balancing wheatstone bridge type temperature control is shown in photo II and FIGURE IV.

The general principle*of the self-balancing bridge type thermo-regulator (refs. 11 and 12) is as follows: the heating coil itself is made to be one arm of the bridge circuit, with the bridge-current in this arm serving as the heating current.
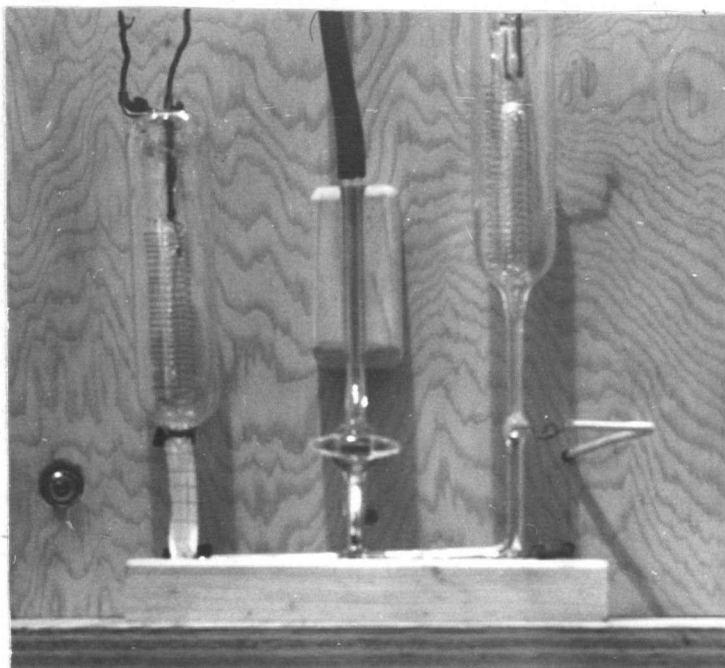
PHOTO II   FRONT VIEW OF

TEMPERATURE CONTROL

FIGURE IV
TEMPERATURE CONTROL CIRCUIT
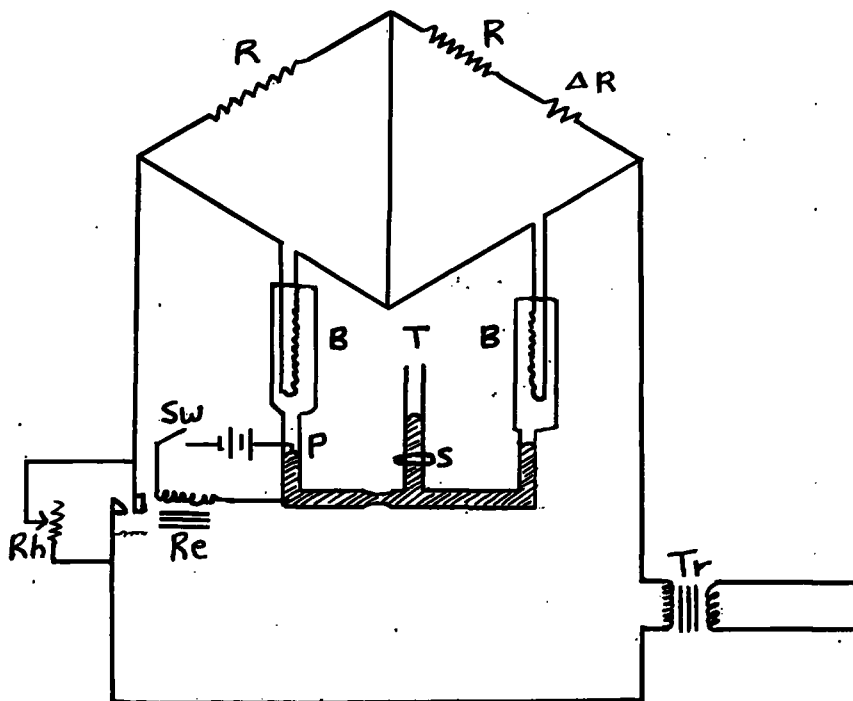
R - RESISTANCE

Rh - RHEOSTAT

Re - RELAY

AR - ADDITIONAL RESISTANCE

S - STOP COCK

Sw - SWITCH

B - BULBS

P - CONTACT POINT

C - CONSTRICTION

Tr - TRANSFORMER

T - TUBE

This branch is made of nickel with a high temperature coefficient of resistance, and the other branches are made of substances with low coefficients. The temperature is regulated by keeping the resistance of the heating element constant, and the control acts on a change in resistance of .5%.

This type of regulator has three important advantages:

1. its operation is comparatively simple.

2. there is no temperature lag between regulator and heating elements.

3. it takes up no useful space. This is important in our work since the clearances between the gas absorption cell and spectrometer are small and the coil cannot obviously be placed inside the cell, where it would be in the optical path.

The University glass-blower, Wm. Pye, did an excellent job of the glass work, using Strong's diagram as a model. The essential features of this device are the following:

(a) the two bulbs are of equal volume.

(b) they contain identical heating coils, 60 mil. nichrome wire of resistance 15 ohms.

(c) the tube is constricted at C in order to prevent rapid oscillation of the mercury, which causes unnecessary "chatter" in the relay operation.

The electric connections in FIGURE IV are obvious and the operational procedure is simple. The bulbs are air-filled at about 1 A.P. and the fixed resistance R (advance) is adjusted through T, by addition or removal of mercury

so that the surface of the left hand column of mercury is just at the contact P.

We now have equilibrium conditions. If the temperature of the feeler resistance becomes too high or too low, the heating in the two bulbs is unequal, and the resulting change in pressure in the bulbs opens or closes the mercury contact. This in turn operates a relay actuating the heating and bridge current. In effect, the right hand bulb is a measure of voltage of the heating element, and since the ratio of the fixed resistance R to that of the left hand bulb is constant, this bulb is a measure of the heating current. Essentially we are balancing the two.

In order that the temperature of the cell may be controlled by the means mentioned, we have wrapped our one meter cell with a heating coil. It has been insulated with a layer of asbestos followed by a layer of felt. The resistance thermometer is located as shown in FIGURE V.

The system devised to supply CS_2 to the cell at a definite pressure, and the method of measuring the pressure is shown in FIGURE V and photo III. The pressure is to be controlled by means of an open connection to the filling-system which is kept at a fixed temperature (lower than that of the cell) in the bath, the temperature chosen so that the vapour pressure at that temperature is the desired pressure in the cell.

As this part of the apparatus has not been needed for the work performed to this date, its usefulness cannot yet be assessed.

FIGURE V

CS$_2$ GENERATOR
AND CONTROLS

H — HEATERS
S — STOP COCKS
C — CONDENSER
T — THERMOSTAT
W.B. — WATER BATH
T.T. — THISTLE TUBE
R.T. — RESISTANCE THERMOMETER
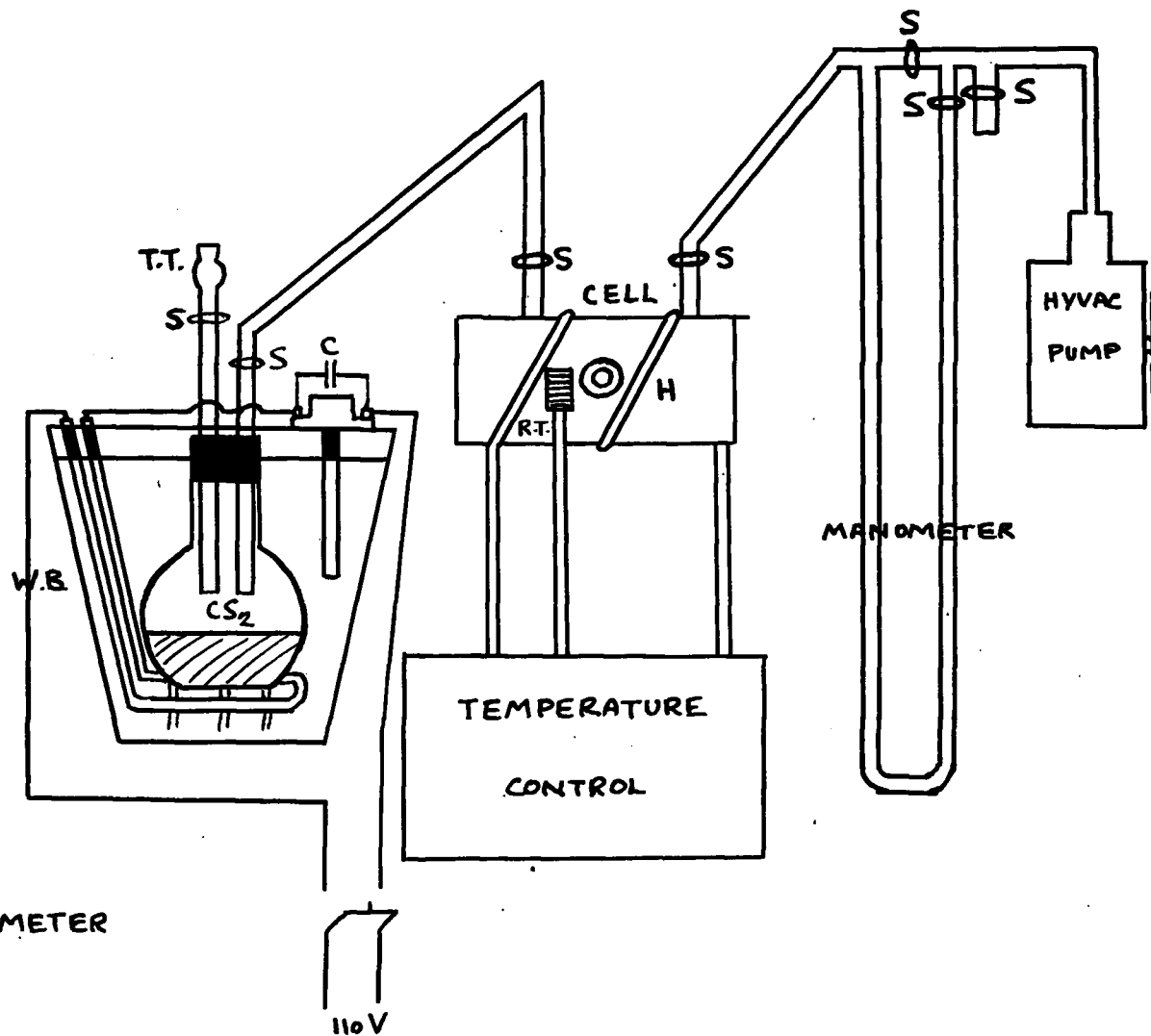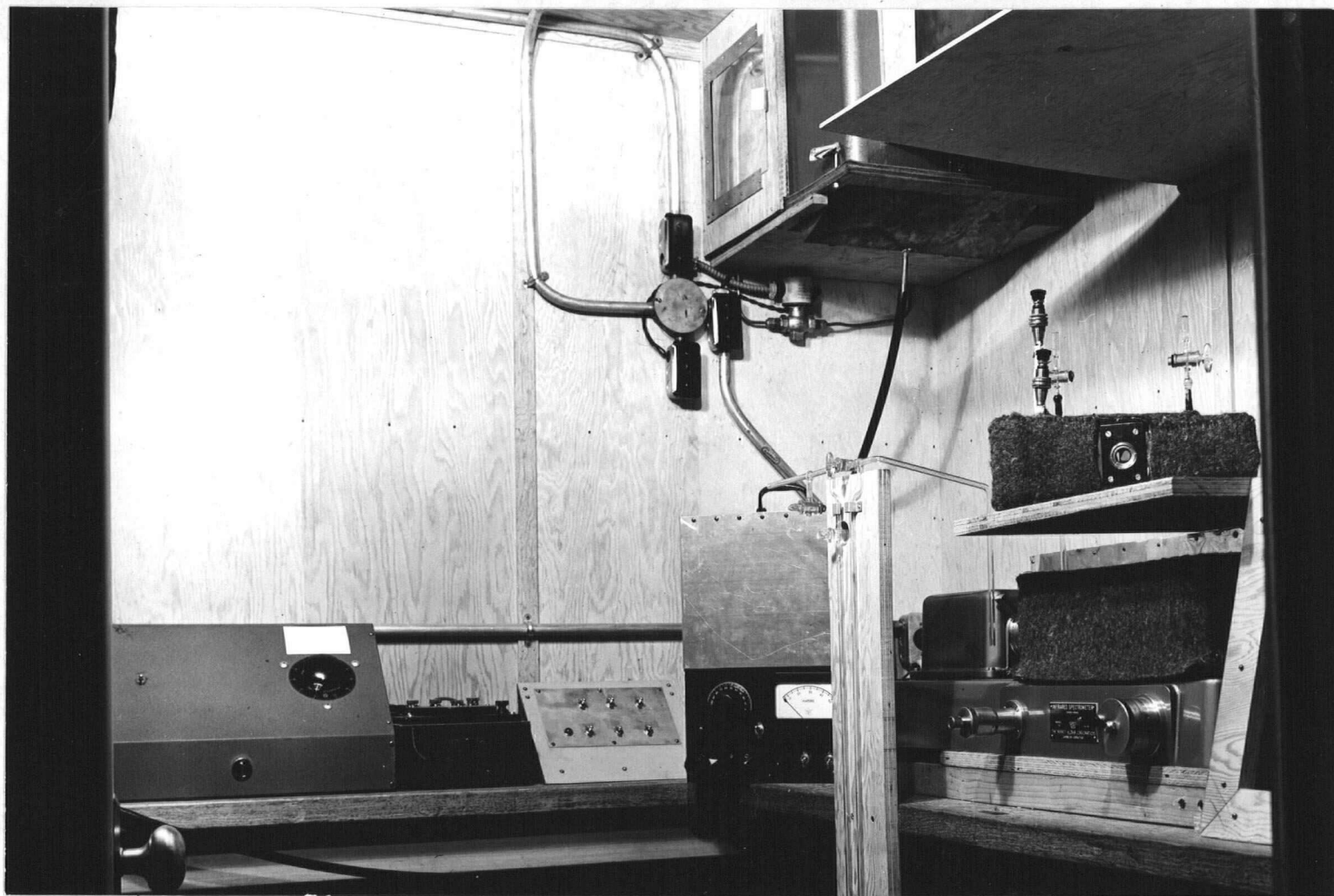
PHOTO III APPARATUS WITH SHIELDING

(C) Experimental arrangement of the apparatus: our equipment consists of the following units -

1. Perkin-Elmer (P-E) model B infrared spectrometer.

2. one-meter gas absorption cell, 10 cm. gas absorption cell, and liquid cells of assorted thicknesses.

3. P-E model 53 (G.M.) 75 cycle D.C. breaker amplifier.

4. Brown electronic recorder.

5. P-E model 54 power supply.

6. Supreme electric powerstat.

7. Control panel of our own design.

8. Synchronous wave-drive apparatus of our own making.

9. Weston model 310 wattmeter to measure power used by the globar.

It is customary to use the P-E cabinet, control panel, and P-E synchronous wave-drive units with this spectrometer. A saving of approximately $800 was effected by elimination of these parts. Redistribution of the components eliminated the necessity of a special cabinet. A modified control panel of our own making was found satisfactory, and a constant speed A.C. motor combined with available gears gives us four speeds for the wave-drive sweeps of the spectrum. These speeds are- 1' 02"; 2' 04"; 5' 12"; 10' 24" per revolution of the wave length drive shaft, which represents 1000 divisions on the wave-drive micrometer.

FIGURE VI gives a block diagram of the apparatus, and FIGURE VII shows a plan view of the room and equipment. The line voltage of approximately 110 V is supplied through the

FIGURE VI

BLOCK DIAGRAM

OF APPARATUS
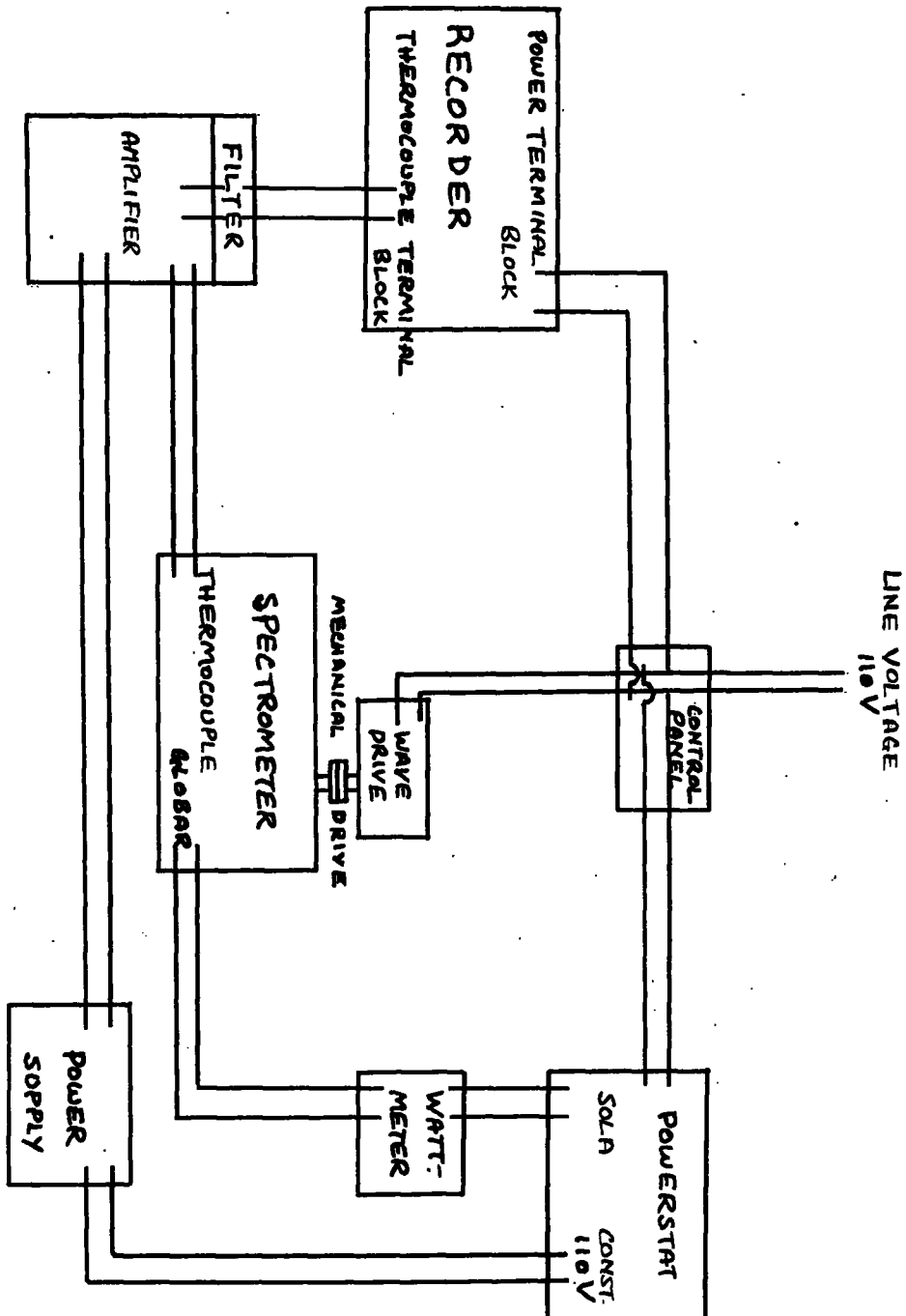
FIGURE VII
PLAN VIEW OF
EQUIPMENT

SOLA TRANSFORMER

WATT METER

CONTROL PANEL

TEMPERATURE CONTROL

CS₂ GENERATOR

SPECTROMETER

MOTOR

AMPLIFIER

SHIELD

AIR LOCK

RECORDER

DOORS
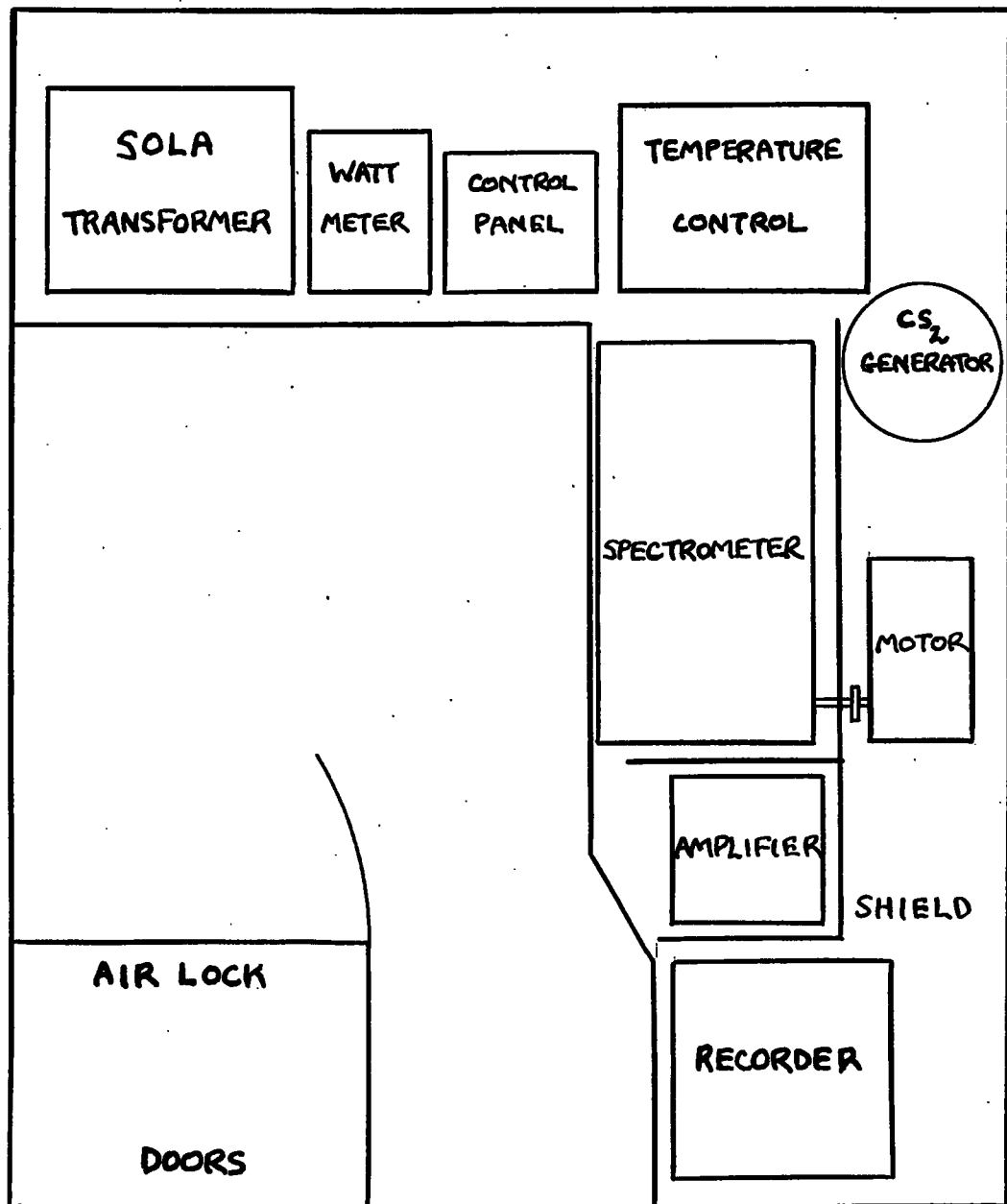
power switch on the control panel, to the powerstat and to the recorder mechanisms. The powerstat supplies a constant 110 V input to the amplifier's power supply and a variable voltage for the globar, our "black-body" type source of radiation. The wattmeter is used to control the power used by the globar in order that its radiation curve may be duplicated. The power supply sends a high-voltage D.C. input to the amplifier, and in addition supplies 80 volts A.C. for the circuit breaker. The amplifier converts minute D.C. input voltages from the thermocouple to A.C. by means of a motor-driven circuit breaker, amplifies this small A.C. voltage, rectifies it by means of a second synchronous circuit breaker, and passes it through a filter to the recorder pen mechanism.

FIGURE VIII is the circuit diagram of the control panel and affected parts of the instruments; the operation of the controls is clear- before any part of the apparatus can be operated the power switch P must be turned "on". It is easily seen that, even if the master switch M is "off", closing of the switch marked "Pen" joins terminals A and B in the power terminal block of the recorder, which actuates the pen. In a similar manner, closing of switches Ch (chart), or W.D. (wave-drive motor), operates these parts respectively.

In normal operation of the instrument, during the process of scanning the spectrum, the chart and pen are required only when the wave-drive motor is "on". Consequently, a master switch M is provided to operate these three parts sim-

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FIGURE VIII

CIRCUIT DIAGRAM

OF CONTROL PANEL
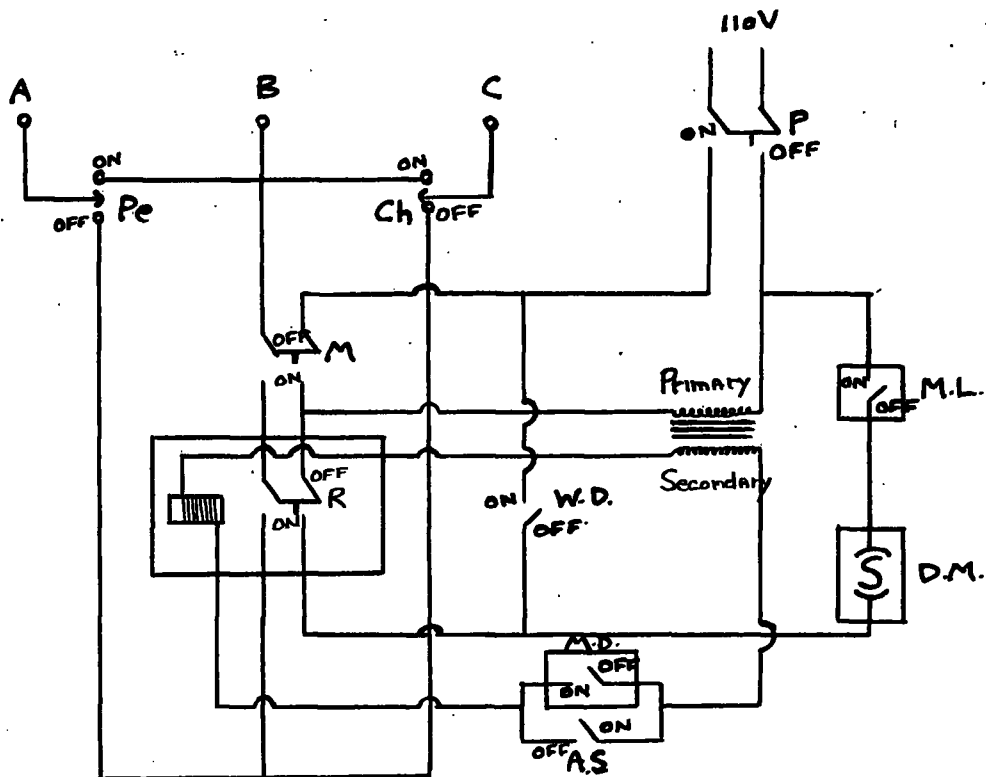
M - MASTER SWITCH
R - RELAY SWITCH
WD - WAVE DRIVE MOTOR SWITCH
Pe - PEN SWITCH
Ch - CHART SWITCH
P - POWER SWITCH
MD - MICRO-DRIVE SAFETY SWITCH
ML - MICRO-LITTROW SAFETY SWITCH
AS - AUTO STOP SWITCH
DM - DRIVE MOTOR

ultaneously. When M is closed, the relay is actuated, closing switch R, provided that M.D. is closed, as it will normally be. As a result, the three circuits are now completed.

In the normal course of operations R is closed, M.L is closed, M.D. is closed, and A.S. is open. The last three are safety switches. The purpose of the Micro-Littrow switch M.L. is to make certain that under no circumstances will the motor force the Littrow mirror past its maximum safe position. The drive-micro switch is provided to stop the spectrum sweep after each completed rotation of the wave-length drive arm, which corresponds to 1000 divisions. It opens the relay switch R, equivalent to opening the master switch, and thereby stops the motor, pen, and chart simultaneously. This makes it possible to adjust the slit width, gain, etc., as may be expedient in regions of different wave-length. Closing of the auto-stop switch A.S. for sufficient time to allow the micro-drive switch to clear, recompletes the circuit, and the next cycle of scanning is under way.

Instruction booklets provided with the apparatus show clearly how the spectrometer should be assembled, special care being given to the $NaCl$ and KBr parts involved. Photo IV shows parts of the apparatus, the spectrometer, cell, amplifier, and recorder, before final shields and insulation were in place. Photo III shows the present arrangement with shielding and insulation. The only precaution necessary to insure proper operation is to keep the power supply well away from the amplifier and recorder. This was achieved by situ-
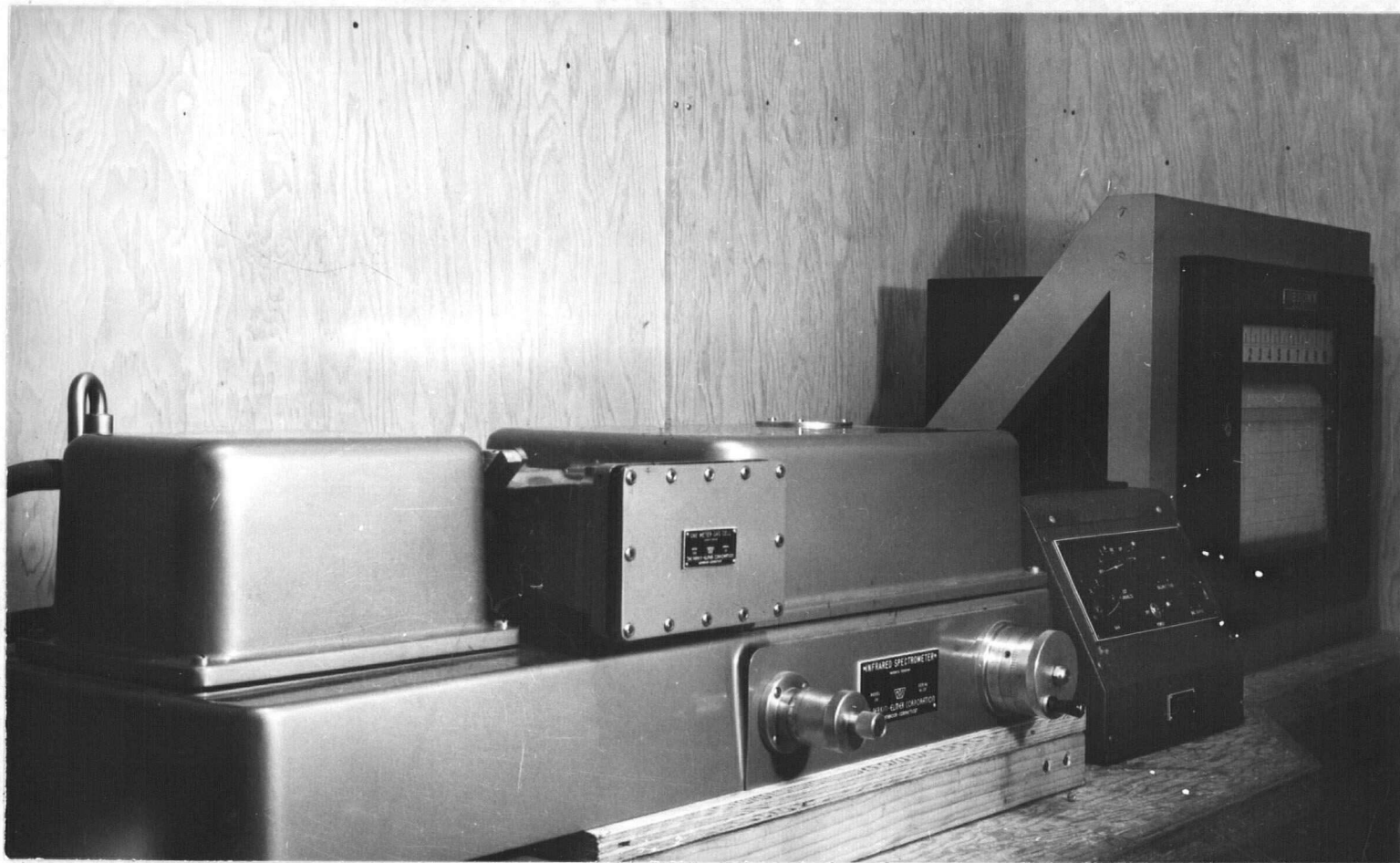
PHOTO IV   APPARATUS WITHOUT SHIELDING

ating the power supply on the floor.

Description and operation of the spectrometer and associated apparatus: FIGURES VII and IX and photo III show the arrangement of the equipment, which may be divided functionally into several sections-

1. a source of continuous infrared radiation.

2. a condensing unit which focuses this heterogeneous "white" light on the entrance slit.

3. sample cells which contain the material of which the absorption is to be examined, placed in the path of this "white" light.

4. the monachromator which disperses the white light from the entrance slit and selects a small range of wave-lengths to fall on the exit slit.

5. the receiver which takes this radiation and focuses it on the thermocouple.

6. the direct current amplifier which amplifies the minute D.C. thermocouple voltages to currents which are large enough to be recorded.

7. the Brown electronik recorder which measures the energy falling on the thermocouple and records it.

The source of infrared radiation is a 2" by 3/8" cylindrical rod of carborundum, which approximates black-body radiation, except at long wave-lengths. It operates at about 1000°C, on 200 watts. In cases where greater illumination is needed we have operated up to 280 watts, which is approximately the maximum power output of our sola transformer.

FIGURE IX

SPECTROMETER

D.S.

G   S   M_{II}   M_I   C

M_V   T_C   M_{VII}

S_I   S_{II}

M_{VI}   M_{IIII}

P

Ms   Mw
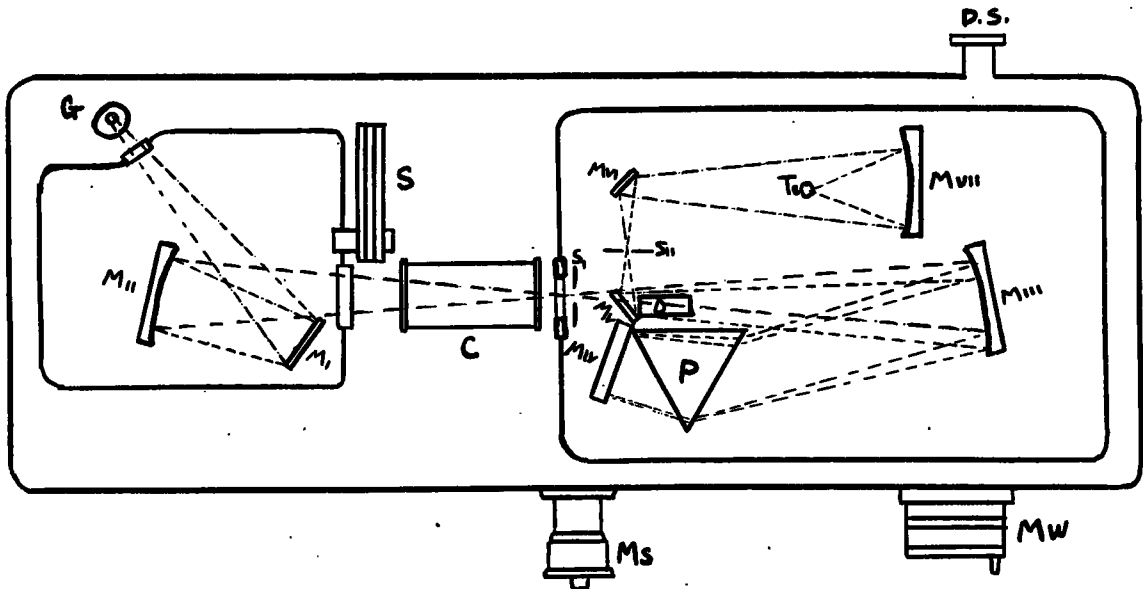
C   — SAMPLE CELL
G   — GLOBAR
M_{I, IV, V, VI}   — PLANE MIRRORS
M_{II}, M_{VII}   — SPHERICAL MIRRORS
M_{III}   — OFF-AXIS PARABOLA
Ms   — SLIT MICROMETER
Mw   — WAVE LENGTH MICROMETER
P   — PRISM
S   — SHUTTERS
S_I   — ENTRANCE SLIT
S_{II}   — EXIT SLIT
T_C   — THERMOCOUPLE
D   — TEMPERATURE COMPENSATOR
D.S.   — DRIVE SHAFT

In order to prevent chromatic aberration, which would be present if lenses were used, front surface aluminized mirrors are used throughout. This makes it possible to focus the apparatus with visible light and have it also in focus for the infrared region. MI and MVI are plane mirrors, known as diagonal flats, which are fixed in position. Their purpose is to change the direction of the light in order to reduce the bulk of the instrument. MII is a spherical mirror. MIII is an off-axis parabola (18°) of focal length 27 cm and aperture f 4.5. The resolving power of the instrument depends greatly on the accuracy of the surface of this mirror and its correct adjustment. MIV is a plane Littrow mirror operated by the wave-drive mechanism. MV is a plane mirror mounted on the prism table in such a way as to be rotated for temperature compensation. MVII is a spherical mirror.

The entrance slit S1 is 12 mm high, and is curved to compensate for curvature in the slit image caused by the prism. The exit slit SII is also 12 mm high, and is operated simultaneously with SI; both open bilaterally, are of equal width, and are read directly in thousandths of a mm on the slit micrometer.

Three mounts permit the use of filters or shutters. Generally one uses -
1. LiF filter - used from 5 to 9.5μ to reduce effects of scattered light, especially of shorter wave-lengths.

2. Glass filter - used from 9.5 to 15μ.

3. Opaque shutter of glass aluminised on both sides.

The prism consists in our case of a single crystal of rock salt (NaCl), of which the apex angle is 60° and face 60 by 75 mm. It is fixed in position, and consequently does not always operate in the position of minimum deviation. The instrument is designed to operate with any of the following three prisms, which are specially mounted on separate tables to facilitate interchangeability.

1. NaCl used from 2.5 to 15μ.

2. KBr used from 10 to 25μ.

3. LiF used from 2.5 to 5.5μ.

As the temperature coefficients of the refractive indices of the prisms are large, MV, mounted on the prism table, is rotated by means of a bimetallic strip to make the drum setting for a wave-length invariant with temperature. Each prism has its own table and mirror with the correct strip or element mounted on the table.

The thermocouple is a high vacuum type of thermocouple with a response time of one second. It is extremely sensitive, and is 95% compensated for temperature drift. It is accompanied by a carbon "getter bulb" to maintain a high vacuum, which increases sensitivity.

Mw is the wave-drive micrometer which rotates the Littrow mirror 9° of arc for 2000 divisions. D is the bimetallic strip temperature compensator mentioned above. C is the cell for gas absorption. The windows are of NaCl throughout, as

glass, quartz, etc. absorb strongly in the infrared.

Optical Path:

Radiation from the globar falls on MI, is reflected on to MII, and focused through the sample cell C on the entrance slit. The slit image then falls on MIII, the off-axis parabola, is collimated by it, dispersed by the prism onto the Littrow mirror, which returns it through the prism onto Parablic MIII, which focuses it, after reflection by MV, as a spectrum on the exit slit. This exit slit selects a certain range of wave-lengths depending on its setting, and with the aid of baffles prevents scattered light from passing onto the thermocouple. The light now falls on MVII, and is focused on one of two opposed thermocouple junctions. The purpose of these two junctions is to compensate for temperature drift by oppositely directed emfs. The total path length is 195 cms.

Amplification:

The emf generated by the thermocouple is led by a cable, which is shielded electrically, magnetically, and thermally, to the input side of our G.E. amplifier. This amplifier converts minute D.C. input voltages from the thermocouple to A.C. by means of a motor-driven circuit breaker, amplifies this small A.C. voltage, rectifies it by means of a second synchronous circuit breaker, and passes it through a filter to the recorder mechanism.

Recording:

Our recording unit is a Brown electronik recorder, consisting of a constant speed chart, (this speed is adjustable

by changing gear ratios), with recording pen operated by a self-balancing wheatstone bridge. The scale is linear in energy falling on the thermocouple.

Adjustment:

The Perkin-Elmer booklets recommend a rather long procedure for the assembly, adjustment, and optical alignment of the spectrometer. However, in view of the fact that the instrument is properly adjusted before leaving the factory, a more simple procedure is, in general, possible, and is advisable under ordinary circumstances.

Recommended Procedure:

1. Mount all NaCl windows and the shutters provided with great care, to prevent water vapour, marks, etc., from spoiling their surfaces.

2. Adjust the slits with precision, so that they are parallel and close to zero simultaneously, then adjust the slit micrometer to read zero at this position.

3. Check that the source image is focused on the entrance slit.

4.- Check that the entrance slit image falls directly on the exit slit.

5. Check that the exit slit image is focused on one of the thermocouple junctions.

If at any point the apparatus fails to satisfy one of these conditions, it is necessary to check the Perkin-Elmer procedure from then on, avoiding, wherever possible, the difficult adjustment of the collimating and focusing mirrors,

especially the off-axis parabola, upon whose performance the ultimate resolution of the instrument depends. The full Perkin-Elmer procedure is not given here since it is readily available and quite lengthy.

Perkin-Elmer suggests that when the instrument is properly adjusted, it will easily resolve the 4.2 μ CO_2 band into a nice doublet. That our instrument does so can be seen from photo VII. The 4.2μ band is the sharp minimum on the far left of the photo, occurring at a drum reading of about 1640.

The following procedure is recommended in using the infrared spectrometer, to obtain a chart of energy versus on the recorder.

1. Decide on the region to be scanned.
2. Decide what compromise between resolution and stability is to be made. Set the gain control accordingly.
3. Select the desired speed for the wave-length drive, remembering that the thermocouple response time is one second, and that resolution is inversely proportional to the speed, sensitivity is inversely proportional to the square of the speed. Set the wave-drive gear shift accordingly.
4. Select the proper shutter for the region.
5. Set the slit-width to such a value that upon scanning the region by hand, the separation of the maximum and minimum recorder readings is about 4/5 of full scale deflection.
6. Set the zero balance so that neither the maximum nor the minimum is off the scale.

7. Record all settings.

8. Start operation by means of the master switch.

9. Mark suitable wave-drive settings on the chart by means
    of the test-microvolt switch on the amplifier during the
    operation. This is known as a fiducial wave-length mark-
    er, as it provides us with a fixed basis of comparison.

In general, one may wish to scan the whole region in
steps, to locate bands in a substance's spectrum, or one may
wish to know the shape of the absorption versus ν curve.
For the former purpose the auto-stop switch is left on, and
will stop pen, chart, and motor after each 1000 divisions on
the micro-wave-drive drum. This allows for adjustments in
slit-width, etc., as may be expedient.

The preceding procedure is entirely satisfactory for
wave-length or frequency readings and checks, provided that
the bands do not fall among strong bands of atmospheric water
and CO_2, which form sharp maxima and minima on our black-body
radiation curve.

In cases where optical density or quantitative intensi-
ties of energy transmitted are desired to be measured, it is
necessary to compare the deflections with and without the
sample in the beam, without disturbing any of the settings.
The treatment of these readings will be given in the next
section.

The power setting of the globar is important in cases
where performances are to be repeated, in that the tempera-
ture of the globar determines both the shape of the black-

body radiation curve and the intensity in any given wave-length region. This is particularly true near the peak of the curve.

(D) Calibration of the spectrometer:

After the spectrometer was properly adjusted and tested for performance, the next step was to calibrate it, in such a way as to associate a wave-drive drum setting with a frequency in cm^{-1}.

The general procedure involved required a scanning of the spectrum from 3 to 15μ, with suitable absorbers in the optical path. These absorbers have absorption bands of which the general appearance and frequencies of absorption maxima are well known by virtue of previous work with gratings and spectrometers of comparable resolving power. This is important in order that frequencies given be of use for our calibration. We used the absorption bands of H_2O, CO_2, and NH_3; and identification was made from R.S.I. 13, 515, 1942, (ref. 9), where curves are shown for grating and spectrometer of comparable resolving power.

TABLE I shows the conditions under which the calibration charts were recorded.

SUBSTANCE	REGION	CELL LENGTH	PRESSURE	SLIT WIDTH	GAIN	PHOTO
CO_2	15 → 14μ	40 cm	150 mm	0.15 mm	10	V
NH_3	13 → 8μ	10 cm	100 mm	0.15 mm	9.6	VI
H_2O CO_2 }	8 → 4μ	in atmosphere		0.050mm	10	VII
NH_3 H_2O } CO_2	3 → 2.5μ {	10 cm in atmosphere 40 cm	300 mm low }	0.020mm	10	VIII

For the H_2O bands, that water present in the atmosphere at about 40% R.H. was sufficient throughout.

The CO_2 was introduced by means of a small tray of dry ice in the first housing, which has a path length of 40 cm. The pressure of the CO_2 would be low but is not critical for these readings.

In order to examine the NH_3 absorption bands, a gas-filling apparatus was constructed, consisting of a high-vacuum pump, a manometer, a cell-filling outlet, a $CaCl_2$ drying tube, and a NH_3 generator. FIGURE X shows this apparatus.

The 10 cm gas absorption cell was fitted with suitable inlet and outlet tubes and joined to the system, the whole of which was then evacuated. The pump was then cut off and the NH_4OH warmed until there was NH_3 at the desired pressure in the cell. The cell was then removed from the system and placed in its proper position on the spectrometer.

It is to be noted that some of the conditions of pressure, slit-width, globar power, amplifier gain, etc., may be varied from the values we used if suitable adjustments of the others are made. Generally speaking, the slit-widths used are the smallest which permit reasonable energies to reach the thermocouple, so that the signal to noise ratio may be high.

Four charts were obtained for sections in the region from 3 to 15 μ using the procedure outlined, carefully marking wave drive settings every 25 divisions by means of our fiducial wave-length marker. These charts are shown in photos V, VI, VII, and VIII.

FIGURE X

NH₃ FILLING SYSTEM

P - HYVAC PUMP

C - CELL

M - MANOMETER

D - DRYING TUBE

G - GENERATOR

T - TUBE TO REPLENISH NH_4OH

B - BUNSEN BURNER

S - STOP COCKS

720
675
650
625
600
575
550
525
500
475
450
425

720.7
667.0
699.7

CALIBRATION CHART

FOR P.E. INFRA-RED SPECTROMETER MODEL 12B SERIAL # 213
WITH NaCl PRISM IN THE REGION $\nu = 660 cm^{-1}$ TO $\nu = 720 cm^{-1}$
i.e. $\lambda = 14$ to 15μ CALIBRATION FROM THE 14.5μ CO_2 ABSORPTION
BAND PERFORMED MARCH 12, 1948 IDENTIFICATION FROM
R.S.I 13,515, 1942 SLIT WIDTH 0.15 m.m. TEMP 70°F
GLOBAR POWER 200 WATTS MAXIMUM GAIN 10 HUMIDITY 35%
WAVE-DRIVE SPEED 5'12" 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

PHOTO V

CALIBRATION CHART

For P.E. Infra Red Spectrometer Model 12 B Serial #215 with NaCl Prism in the Region ⩾=800 cm⁻¹ to ⩾ =1200 cm⁻¹ I.E. λ = 8 to 13 M Calibration from the 10 µ NH₃ Band Performed March 10, 1948. Identification from R.S.I. 13,515, 1942. Slit Width 0.15 mm. Temp. 70°F. Globar Power 150 watts Gain 9.6 Humidity 32 %. Wave Drive Speed 5' 10" per Rev. Cell Length 10 cm. Pressure 100 mm. Hg.

FIGURES BELOW CURVE ARE FREQUENCIES IN CM⁻¹
FIGURES ABOVE CURVE ARE WAVEDRIVE READINGS.

PHOTO VI

CALIBRATION CHART

For P.E. Infra-Red Spectrometer Model 12B Serial #213 with NaCl Prism, in the region $\nu = 1260 \text{ cm}^{-1}$ to $\nu = 2000 \text{ cm}^{-1}$ i.e. $\lambda = 5$ to 8μ. Calibration from the 6μ H_2O Absorption Band. Performed February 26, 1948. Identification from R.S.I. 13,515, 1942. Slit width 0.050 mm. Temp. 70°F. Globar Power 150 watts. Maximum gain 10. Humidity 40%. Minimum wave drive speed 10' 24" per rev.

Figures below curve are frequencies in cm⁻¹
Figures above curve are wave-drive readings

PHOTO VII

CALIBRRATION CHART

For P.E. Infra Red Spectrometer Model 12B Serial # 213
With NaCl Prism in the Range $v = 3200$ cm⁻¹ to $v = 3900$ cm⁻¹
i.e. $M = 2.5$ to $3M$ Calibration from the $3M$ NH_3, CO_2 & H_2O
Bands. Performed March 13, 1948 Identification from
R.S.I. 13, 515, 1942. Slit Width 0.020 mm Temp 70°F
Globar Power 200 Watts Maximum Gain 10 Humidity 38%
Minimum Wave-Drive Speed 10⁰²⁶" per Rev. H_2O in Atmosphere
CO_2 Cell Length 40 cm. Pressure not Critical
NH_3 Cell Length 10 cm. Pressure 300 mm Hg.
Figures below curve are Frequencies in cm⁻¹
Figures above curve are Wave-Drive Readings
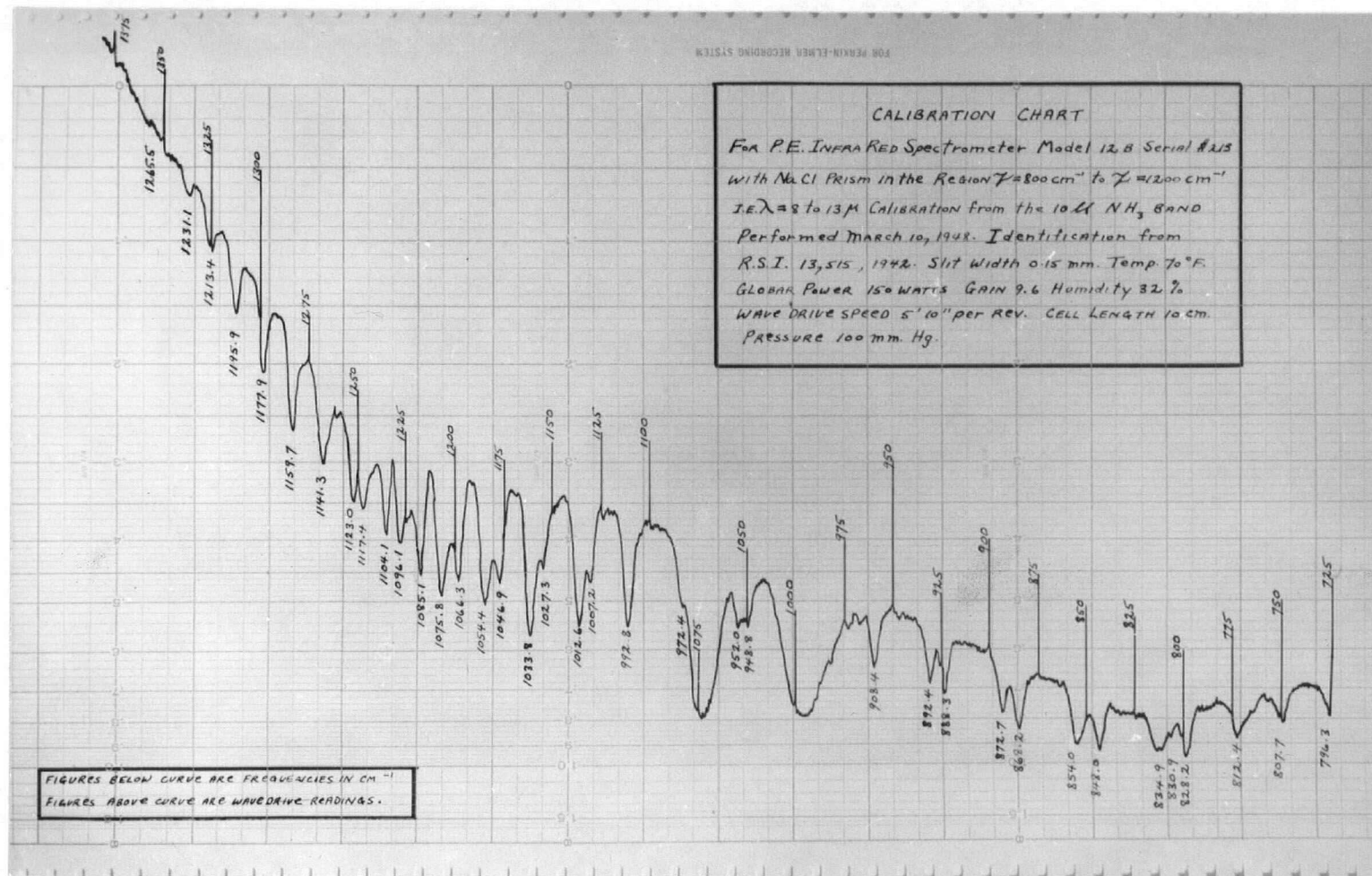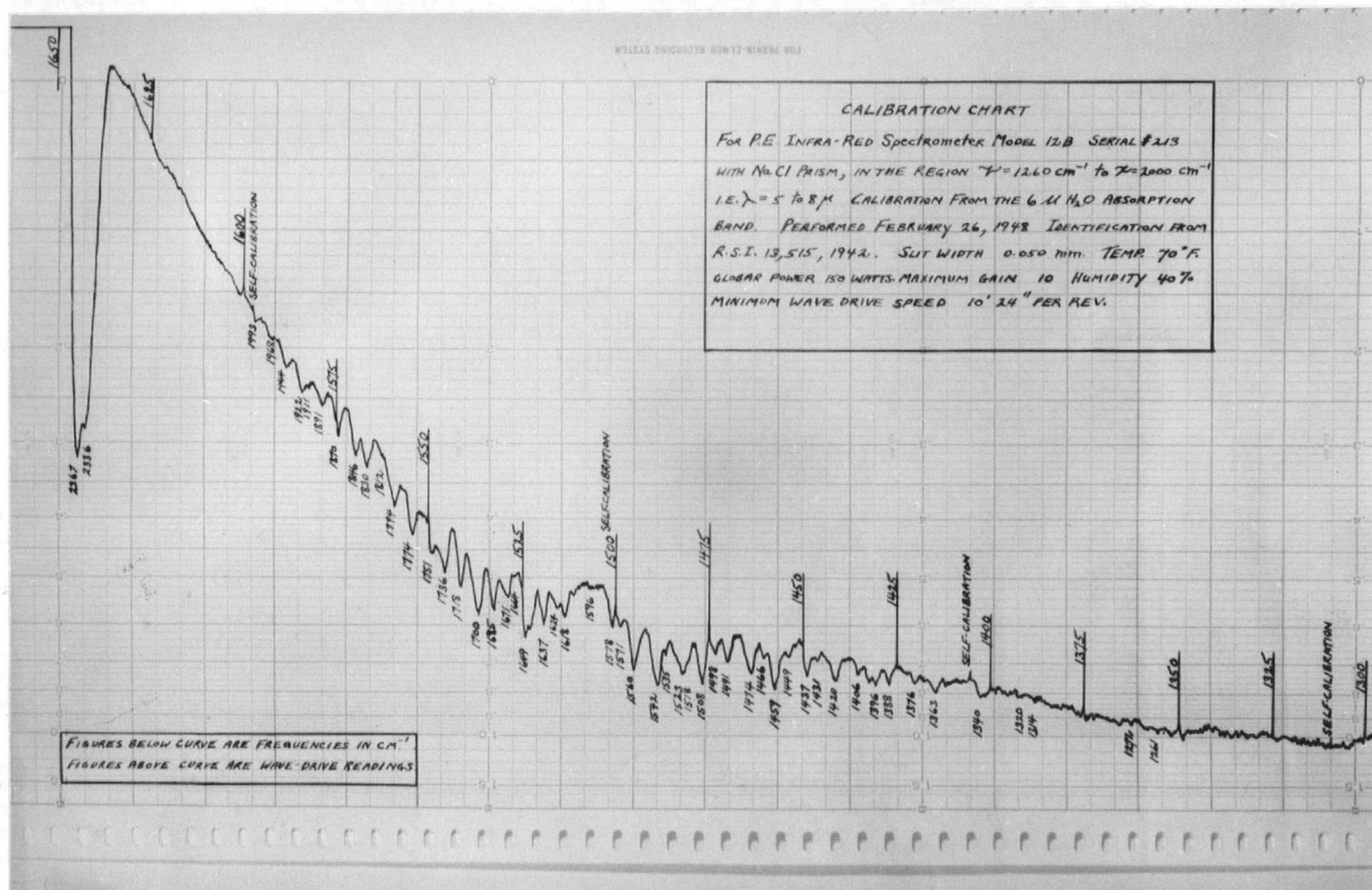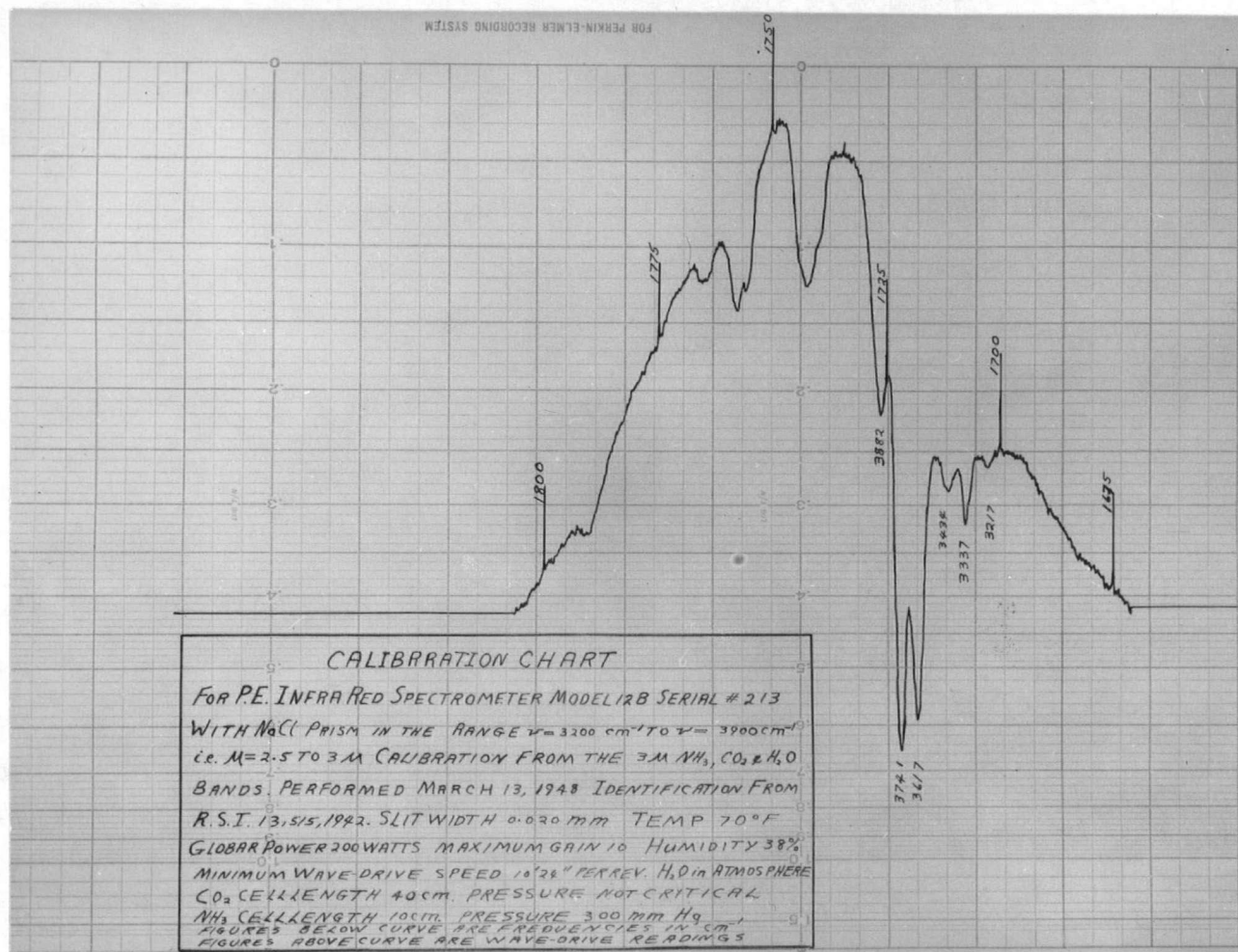
PHOTO VIII

TABLE II shows drum readings measured from these charts, versus frequencies in cm^{-1}.

DRUM READING	FREQUENCY in cm^{-1}	SUBSTANCE	PHOTO CHART	GRAPH
517	667.0	CO_2	V	–
589	720.7	CO_2	V	IX
748	807.7	NH_3	VI	IX
765	812.4	"	"	"
798	828.2	"	"	"
807	830.9	"	"	"
812	833.0	"	"	"
814	834.8	"	"	"
843	848.0	"	"	"
855	854.0	"	"	"
885	868.2	"	"	"
893	872.7	"	"	"
947	888.3	"	"	"
955	892.4	"	"	"
984	908.4	"	"	"
1049	948.8	"	"	"
1055	952.0	"	"	"
1082	972.4	"	"	"
1111	992.8	"	"	"
1131	1007.2	"	"	"
1136	1012.6	"	"	"
1155	1027.3	"	"	"
1161	1033.8	"	"	"
1177	1046.9	"	"	"
1184	1054.4	"	"	"
1198	1066.3	"	"	"
1207	1075.8	"	"	"
1218	1085.1	"	"	"
1228	1096.1	"	"	"
1236	1104.1	"	"	"
1248	1117.4	"	"	"
1253	1123.0	"	"	"
1268	1141.3	"	"	"
1284	1159.7	"	"	"
1298	1177.9	"	"	"
1313	1195.9	"	"	"
1325	1213.4	"	"	IX,X
1337	1231.1	"	"	" "
1355.7	1261	H_2O	VII	" "
1361.5	1272	"	"	" "
1389	1314	"	"	X
1391.6	1320	"	"	"
1403	1340	"	"	"
1415	1363	"	"	"
1420.3	1376	"	"	"
1427.5	1388	"	"	"
1430.7	1396	"	"	"

TABLE II continued

DRUM READING	FREQUENCY in cm^{-1}	SUBSTANCE	PHOTO CHART	GRAPH
1435	1406	H_2O	VII	X
1441.7	1420	"	"	"
1447	1431	"	"	"
1449	1437	"	"	"
1454.2	1449	"	"	"
1458	1459	"	"	"
1461	1466	"	"	"
1464.4	1474	"	"	"
1470.5	1491	"	"	"
1473.5	1498	"	"	"
1477	1508	"	"	"
1480.3	1518	"	"	"
1481.8	1523	"	"	"
1486.4	1535	"	"	"
1489	1542	"	"	"
1495	1560	"	"	"
1498.5	1571	"	"	"
1501.4	1578	"	"	"
1506.8	1596	"	"	"
1514	1618	"	"	"
1516	1624	"	"	"
1519.4	1637	"	"	"
1524	1649	"	"	"
1527.3	1664	"	"	"
1529.5	1671	"	"	"
1533	1685	"	"	"
1537	1700	"	"	"
1541.5	1718	"	"	"
1545.7	1736	"	"	"
1549	1751	"	"	"
1554.5	1774	"	"	"
1559.5	1794	"	"	X,XI
1562.5	1812	"	"	" "
1567	1830	"	"	" "
1570	1846	"	"	" "
1575	1870	"	CHART	" "
1579	1891	"	"	" "
1582.5	1911	"	"	" "
1585	1922	"	"	" "
1588.5	1944	"	"	" "
1592.3	1968	"	"	" "
1597	1993	"	"	" "
1640	2336	CO_2	"	XI
1644	2367	"	"	"
1703	3217	NH_3	VIII	"
1708	3337	"	"	"
1711	3434	"	"	"
1718	3617	H_2O	"	"
1722	3741	"	"	"
1726	3882	"	"	"

We have plotted these readings on three graphs for the regions 700 to 1300 cm^{-1}; 1200 to 2000 cm^{-1}; and 1800 to 3900 cm^{-1}. Photos IX, X, and XI show these graphs. From them we can obtain directly the frequency in cm^{-1} of any absorption maximum which we may observe at any wave-drive setting in the region calibrated. It is gratifying to note that a recent check indicated that the calibration has not shifted.

An attempt was made to fit a cubic equation to the central region of the calibration curve by the method of least squares, but the resulting equation was not accurate enough to be acceptable. Such an analytical expression would be desirable since our probable error would be smaller and more accurately known.

(E) The absorption spectrum of CS_2:

From the point of view of experimental difficulties, CS_2 is one of the more troublesome materials to work with. It is a highly volatile poisonous substance, which dissolves most greases, waxes, rubber, and other components used in filling systems and connections.

After considerable experimentation with greases we found silicone grease was useable in stop-cocks, although it must be replaced occasionally. The only wax we were able to find which was insoluble in CS_2 was high-pyseal, which is very brittle and fairly difficult to handle. We used it for all glass to metal seals. Most rubbers, natural and synthetic, are affected by CS_2. They swell to many times their natural size. Neoprene was the least affected in tests made by us,

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PHOTO IX

CALIBRATION CURVE

For P.E. Infra Red Spectrometer Model 12B
Serial # 213 with NaCl Prism, in the region
λ = 1260 cm⁻¹ to λ = 2000 cm⁻¹ = 14 μ - 5 μ = 5 μ
Calibration from the 6.1μ H₂O Absorption Band
Performed - February 26, 1948. Identification
from RSI 13,515, 1942.

PHOTO X

CALIBRATION CURVE
FOR P.E. INFRARED SPECTROMETER MODEL 12 B
SERIAL # 213 WITH NaCl PRISM IN THE REGION
$\nu = 1800\ cm^{-1}$ TO $\nu = 3900\ cm^{-1}$ i.e. 2.5 TO 6 μ
CALIBRATION FROM NH_3, CO_2, H_2O BANDS
PERFORMED MARCH 12, 1948   IDENTIFICATION
FROM R.S.I. 13, 515, 1942
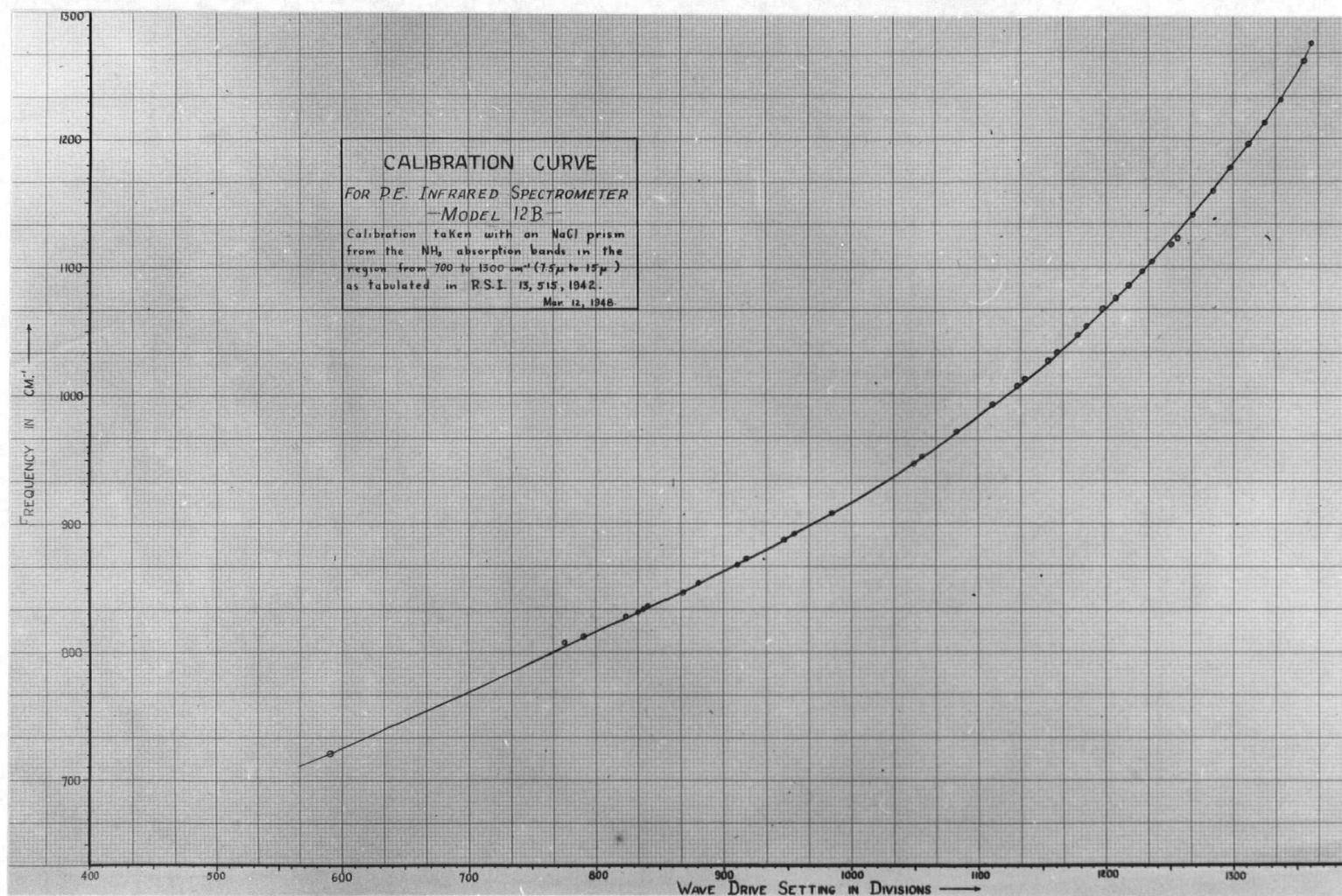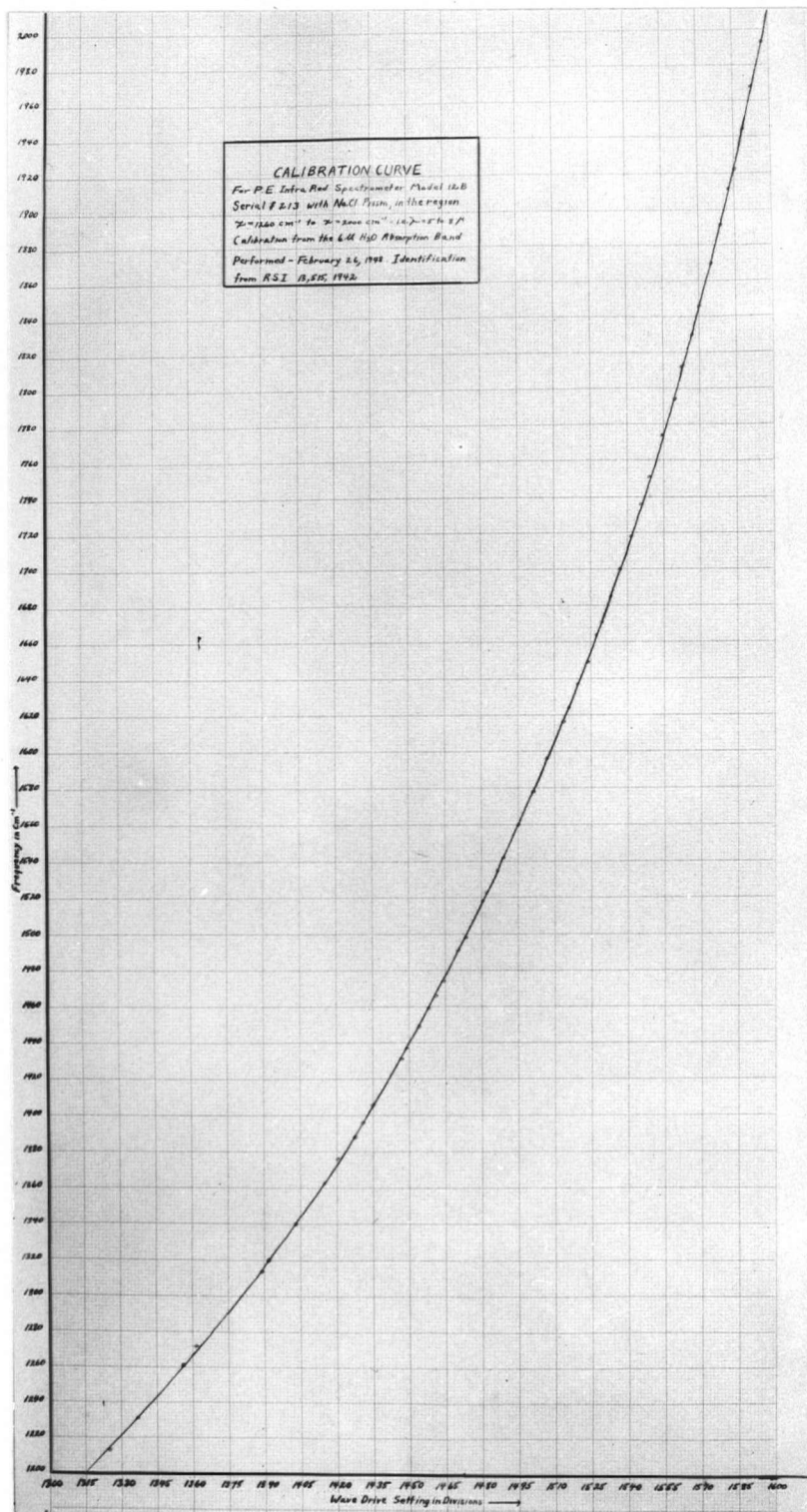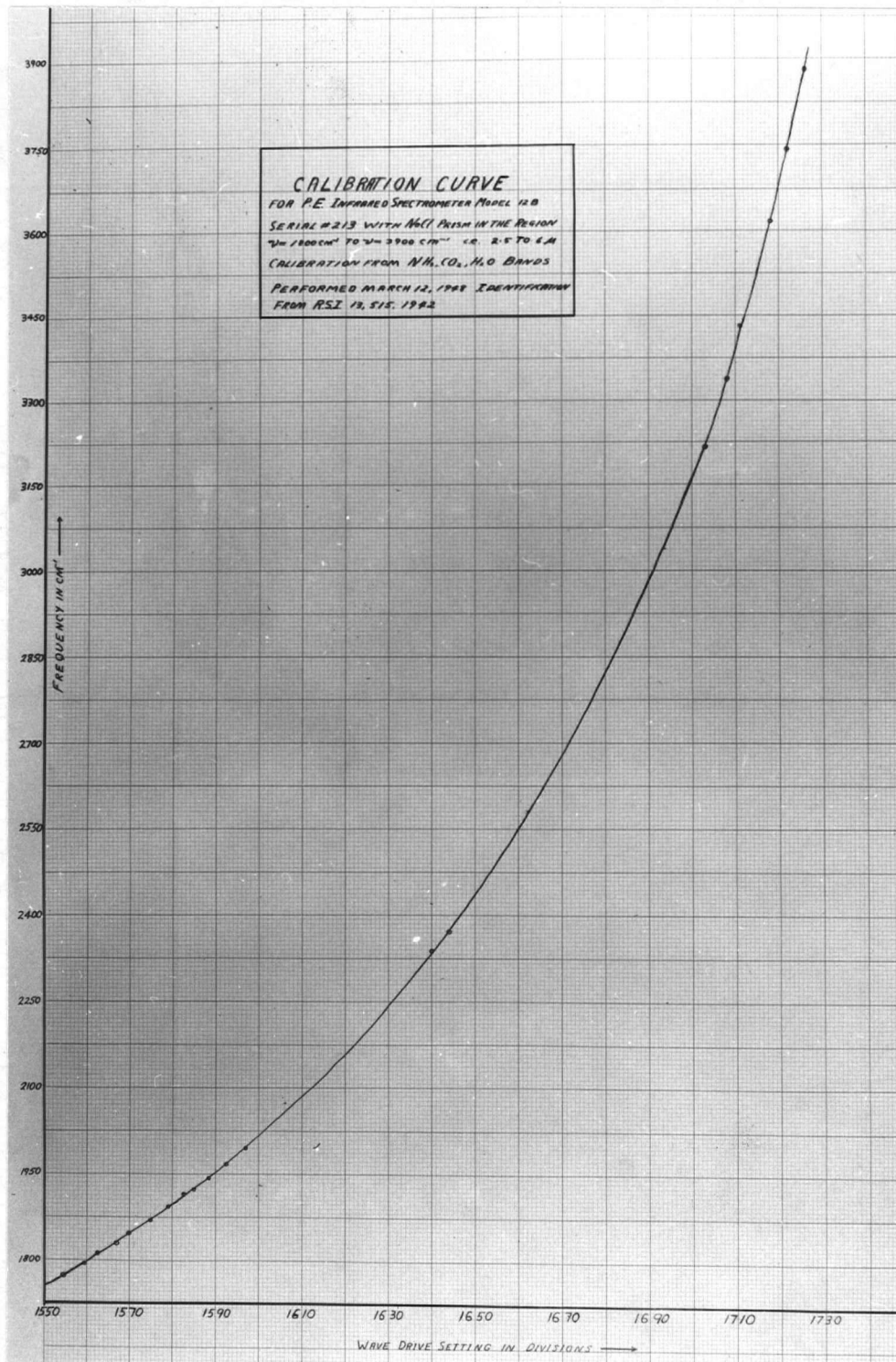
PHOTO XI

and therefore we used it for gaskets and flexible connections.

The method used to determine the frequencies of the CS_2 absorption bands is as follows:- successive "sweeps" of the entire region from 15μ to 2μ were made with and without CS_2 in the 10 cm cell. Comparison of the charts obtained indicated one very strong and two medium bands. A similar procedure with the one meter cell indicated three more bands which are fairly weak. Each of these bands was then examined carefully, using minimum useable slit-width, maximum power, maximum gain, and minimum speed, to give the best possible results.

For each band the instrument was run with shutter closed, both before and after the small region to be examined. The line joining these "end-traces" was then used as our base line from which to measure the intensity of radiation falling on the thermocouple in a given region. For ν_3 for instance, the machine was run from drum-reading 1465 to 1475 with shutter closed, from 1475 to 1495 with shutter open, and fiducial marks were made at 1481 and 1491 divisions by means of the test-microvolt switch on the amplifier. From charts taken with the cell evacuated and then filled with CS_2, we measured the energy transmitted (which is linear on the chart), for every $\frac{1}{4}$ wave-drum division. The % transmission for CS_2 is given by $\dfrac{CS_2\ reading}{vacuo\ rdg.} \times 100$. For each of the bands we plotted % transmission versus drum readings, which are convertible to frequencies by our calibration graphs.

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IV RESULTS

Six bands due to CS_2 were found between 12 and 3μ. Photos XII to XVI show the graphs of % transmission versus wave-drive reading for all six. Various pressures and cell-lengths were used, from a "trace" in the 10 cm cell for ν_3, to approximately 30 cm Hg in the one meter cell for $\nu_3 - \nu_1$.

The band at 6.52μ is by far the strongest, and hence may be expected to be one of the fundamentals. As ν_1 is inactive in the infrared, this band must be either ν_2 or ν_3. However, according to our theory (pages 16, 17, 18), ν_2 is a perpendicular band with a strong central Q branch, and ν_3 is a parallel band with the Q branch missing; hence ν_3 will appear as a doublet. On this basis the band at 6.5μ is ν_3, and the central peak transmission corresponds to the centre of the band. The side-band is attributed to the isotope effect.

All of the other bands can be written as simple combination or difference bands. TABLE III gives the six bands observed in CS_2 vapor.

BAND	DRUM READING	METHOD	FREQUENCY	PROBABLE ERROR
3.38μ	1688.5	2 rdgs.	2959 cm^{-1}	± 6 cm^{-1}
3.51μ	1681.0	2 rdgs.	2838 cm^{-1}	± 6 cm^{-1}
4.29μ	1640.0	1 rdg.	2332 cm^{-1}	± 5 cm^{-1}
4.58μ	1623.45	4 rdgs.	2185 cm^{-1}	± 5 cm^{-1}
6.52μ	1846.75	6 rdgs.	1535 cm^{-1}	± 2 cm^{-1}
11.4μ	928.0	1 rdg.	8877 cm^{-1}	± 1 cm^{-1}

THE COMBINATION BANDS

$\nu_3 + 2\nu_1$ AND $\nu_1 + 2\nu_2 + \nu_3$

Temperature : 20°C
Pressure : 20 cm
Cell Length : 100 cm.
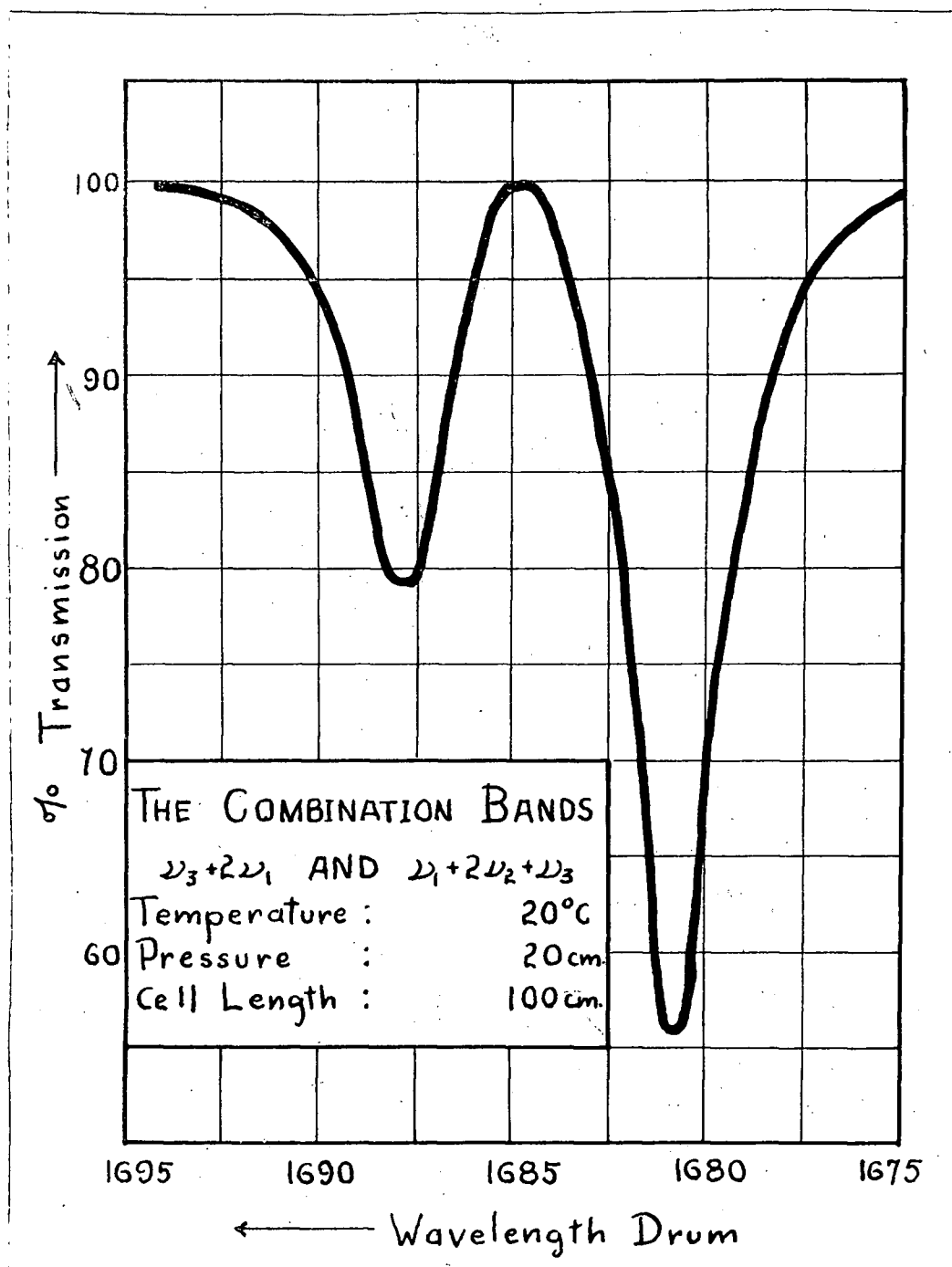
PHOTO XII

PHOTO XIII

PHOTO XIV

STRUCTURE OF THE
ν_3 BAND
Temperature: 20°C
Pressure   :   <1 m.m.
Cell Length: 10 cm.

% Transmission

Wavelength Drum

PHOTO XV

THE DIFFERENCE BAND
$\nu_3 - \nu_1$
Temperature : 20°C
Pressure : 30cm
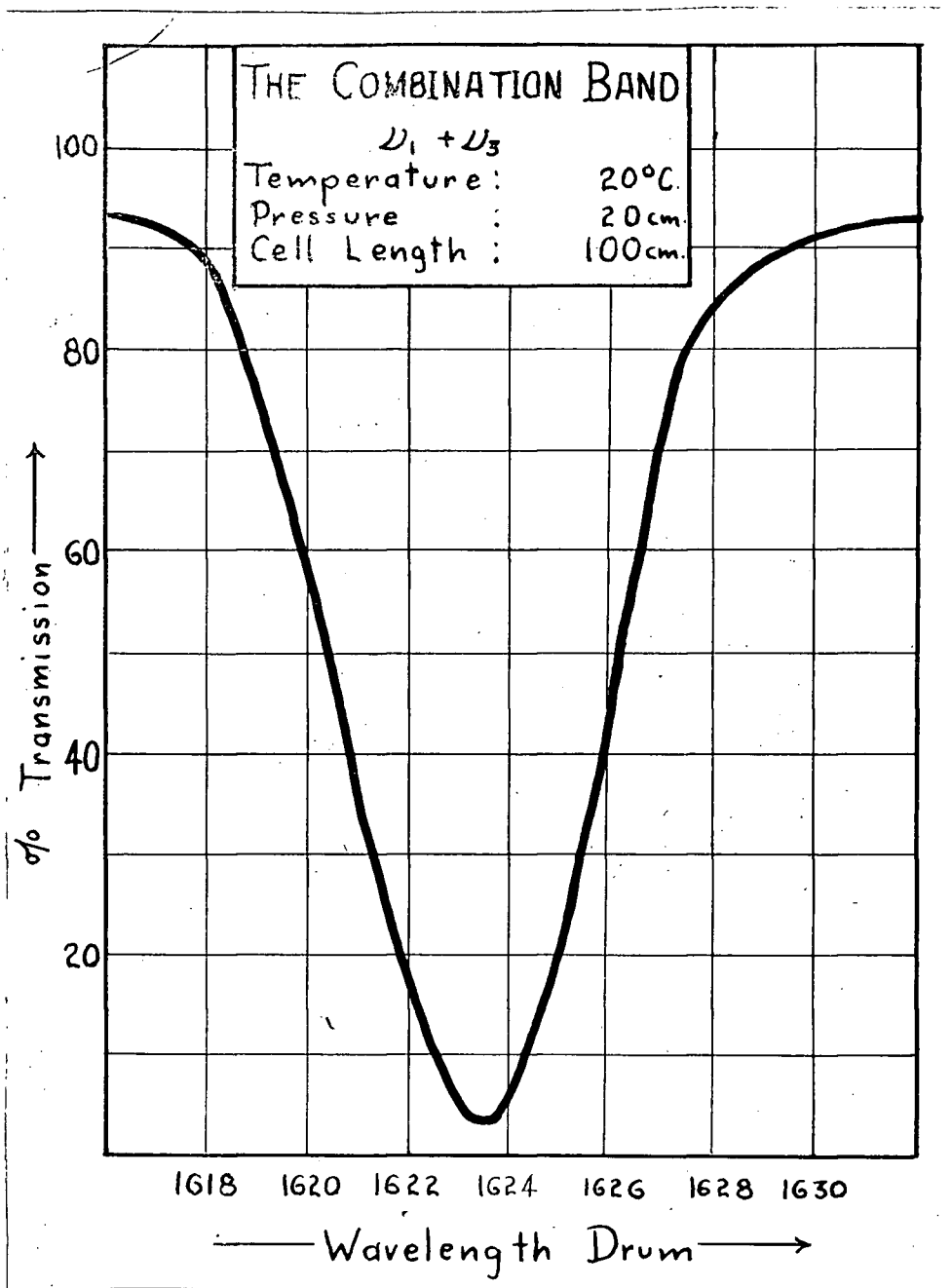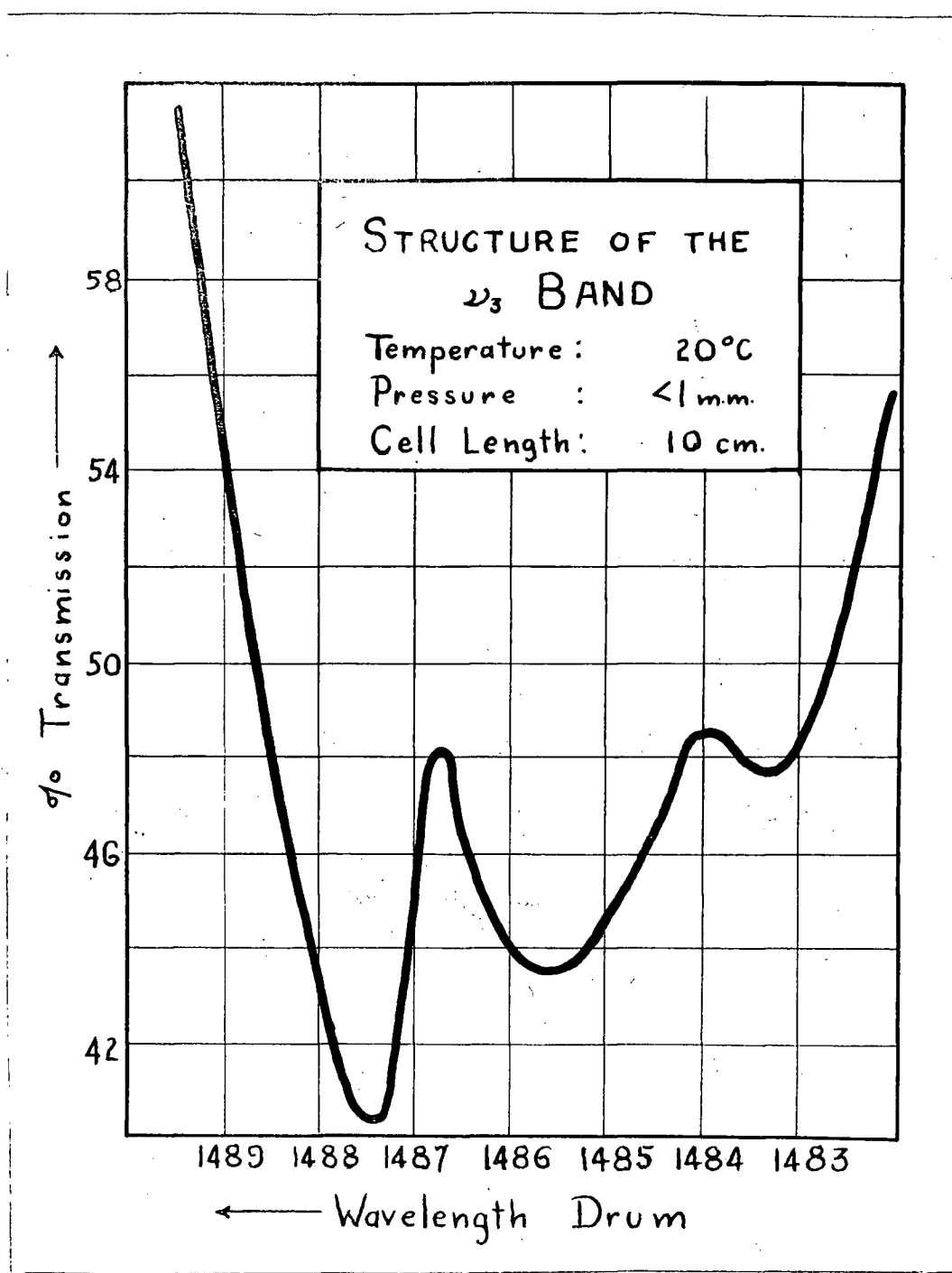Cell Length : 100cm

% Transmission
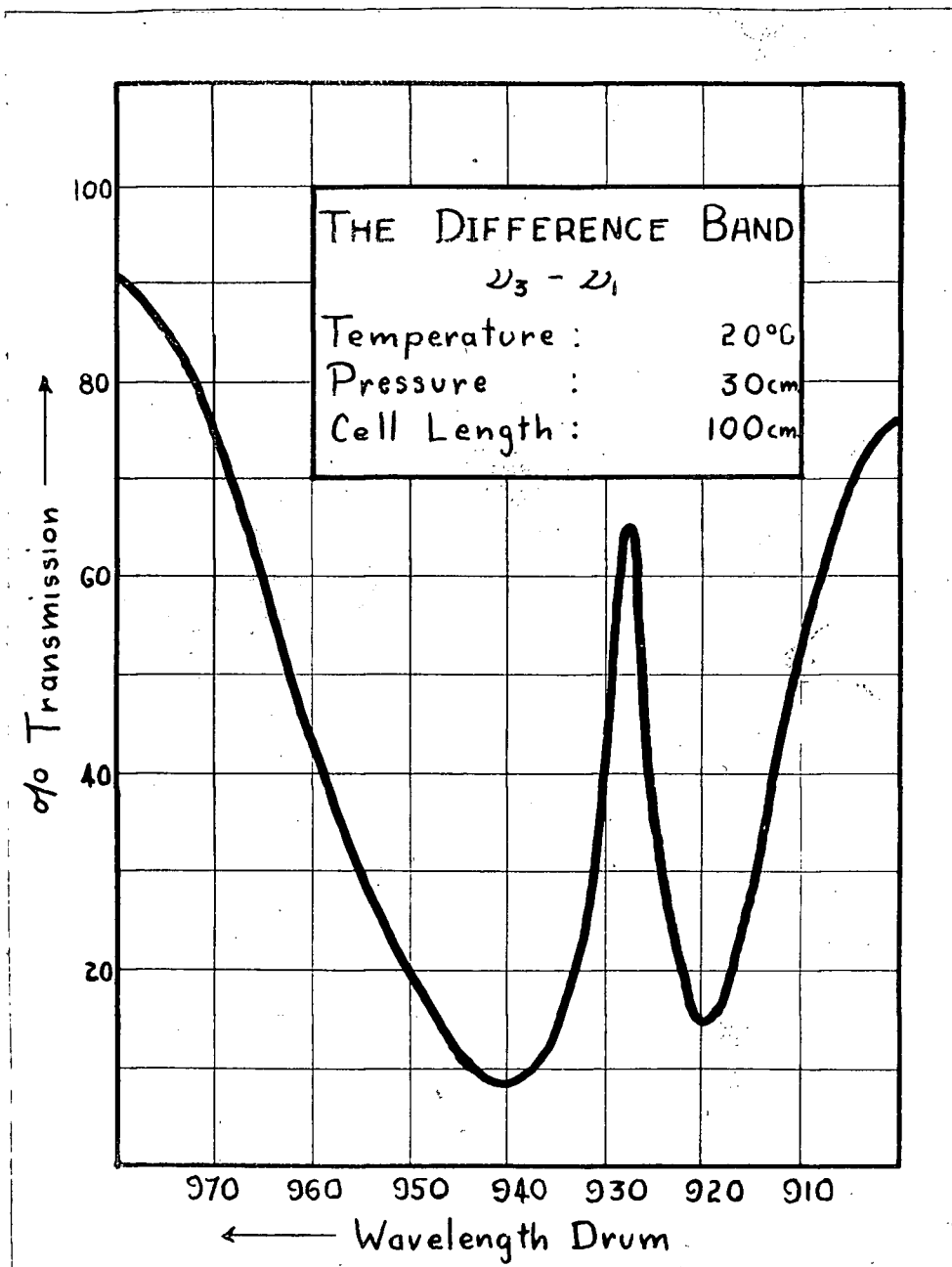
← Wavelength Drum
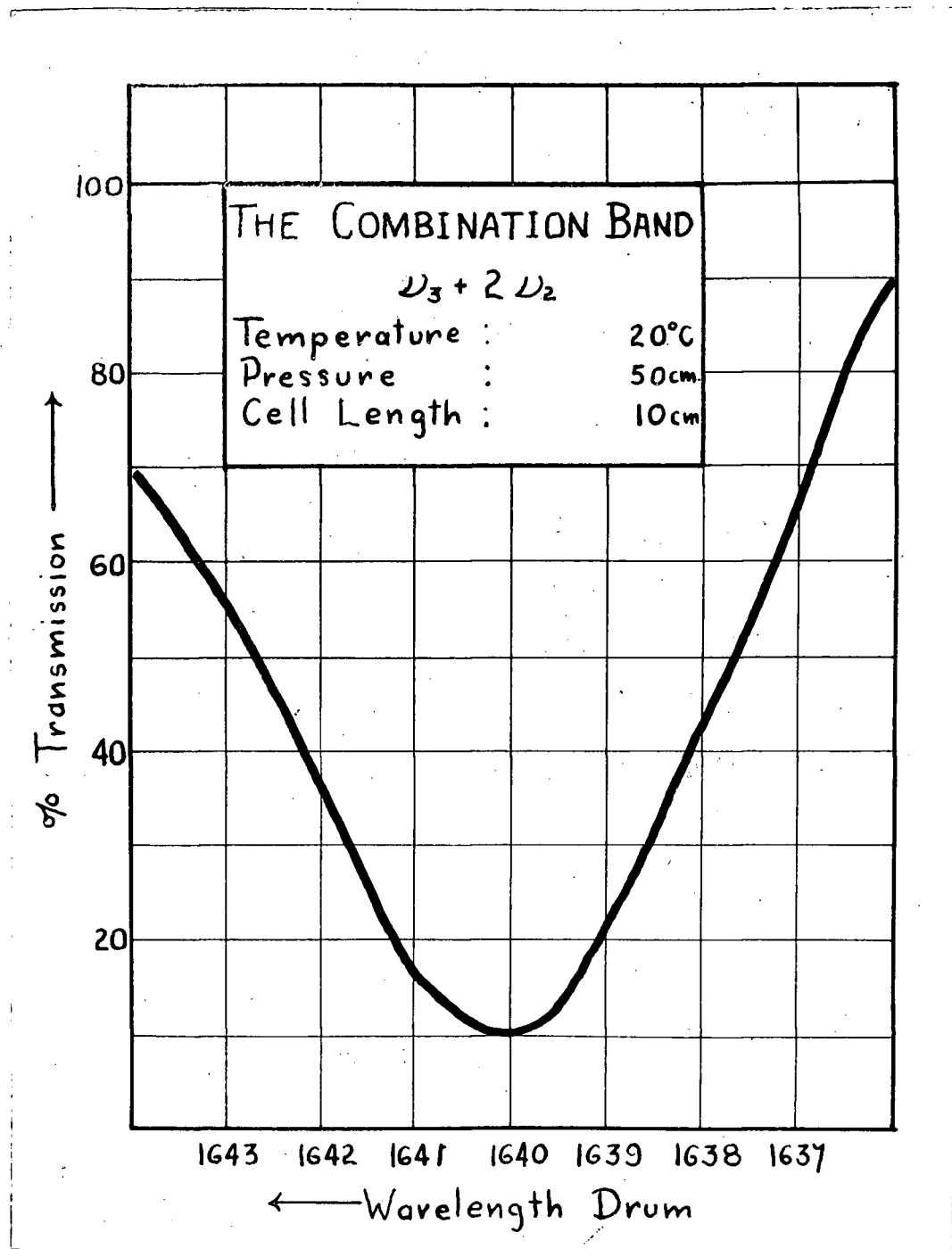
PHOTO XVI

TABLE IV gives these six bands, together with the two other

fundamentals ν_1 and ν_2.

BAND TERM	LOWER STATE $n_1 n_2 l n_3$	UPPER STATE $n_1 n_2 l n_3$	BEST VALUES to 1945 HERZBERG	1947 PLYLER & HUMPHREYS obs. calc.		EDWARDS MITCHNER & ROGERS obs.
ν_1	0 0 0 0	1 0 0 0	656.5	–	655*	–
ν_2	0 0 0 0	0 1 1 0	396.7	–	397*	–
ν_3	0 0 0 0	0 0 0 1	1523	1535	1535*	1535
$\nu_3 - \nu_1$	1 0 0 0	0 0 0 1	878	879	880	877
$\nu_1 + \nu_3$	0 0 0 0	1 0 0 1	2183.9	2184	2190	2185
$\nu_3 + 2\nu_2$	0 0 0 0	0 2 2 1	2329	2336	2329	2332
$\nu_3 + 2\nu_1$	0 0 0 0	2 0 0 1	–	2857	2845	2838
$\nu_1 + \nu_3 + 2\nu_2$	0 0 0 0	1 2 0 1	–	2959	2984	2959

* these values used to calculate frequencies of combination
and difference bands.

The calculated values of Plyler & Humphreys are obtained by

assuming that CS_2 is so heavy a molecule that anharmonicity

effects are small.

The values we obtained agree very well with the best

data obtainable. The one exception is our value of 2838 cm^{-1}

for $\nu_3 + 2\nu_1$. The experimental error is insufficient to ac-

count for the difference of 19 cm^{-1} between our value and

that of Plyler & Humphreys.

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V CONCLUSIONS

We have successfully set up the Perkin-Elmer spectrometer and associated instruments, calibrated it, and applied it to CS_2 in the vapor phase.

We have verified the frequencies at which six major vibrational bands of CS_2 occur in the vapor, as given by Plyler & Humphreys. Of particular importance is our confirmation of their value for ν_3. As shown on page 14, this $\nu_3 = 1535$ cm^{-1} gives a better value for the force constant k than is obtained by Herzberg from $\nu_3 = 1523$ cm^{-1}. The new value of $k_1 = 7.1 \times 10^5$ dynes/cm is in better agreement with the value obtained from ν_1, and shows that the valence force approximation method is justifiably applied to CS_2.

The work remaining to be done includes a search for nine more bands which fall in our region and were found by Plyler & Humphreys in the liquid only. In addition to these bands there should be side-bands due to isotope effects which could be measured.

Finally, the work at various pressures and temperatures remains to be done to determine the effects of association on the frequencies at which the bands appear.

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