

## Raman Spectrum of Carbon Disulphide

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frared intensities. Attention may be called to the possibility of interesting results with polyatomic as well as diatomic molecules. For example, although  $\text{H}_2\text{O}$  is known to have a large permanent electric moment, available data on its infrared absorption bands<sup>7</sup> indicate that terms analogous to the coefficient of  $\xi$  in Eq. (1) are relatively small. That is,  $\mu_z$ , the component of the electric moment in the direction of the symmetry axis, is apparently near a maximum just as in HI, as regards symmetrical vibrations of the molecule: only a few weak bands are observed which correspond to an electric moment varying in the  $z$  direction ( $\Delta v_3 = \text{even}$ ). For those infrared bands ( $\Delta v_3 = \text{odd}$ , where  $v_3$  is the quantum number asso-

ciated with the normal coordinate corresponding to asymmetrical vibrations) whose intensity depends on a moment ( $\mu_y$ ) perpendicular to the symmetry axis, the intensities are high, indicating that for  $\mu_y$  the coefficient analogous to that of  $\xi$  in Eq. (1) is high.<sup>8</sup> For a non-vibrating molecule,  $\mu_y = 0$ , of course. The available data are unfortunately too qualitative in character to permit of a satisfactory interpretation in relation to the electronic structure of  $\text{H}_2\text{O}$ ; such a correlation, it may be pointed out, should involve relations between the coefficients of the expansion for  $\mu_y$  as a function of the normal coordinates, and those of the similar  $\mu_z$  expansion.

<sup>7</sup> R. Mecke and collaborators: *Zeits. f. Physik* **81**, 313, 445, 465 (1933); *Phys. Zeits.* **33**, 833 (1932).

<sup>8</sup> The fact that bands with  $\Delta v_3 = \text{odd}$  depend on  $\mu_y$ , those with  $\Delta v_3 = \text{even}$  on  $\mu_z$ , is easily deduced by group theory methods (procedure of L. Tisza, *Zeits. f. Physik* **82**, 48 (1933)). Cf. also W. Weizel, *Zeits. f. Physik* **88**, 214 (1934).

## Raman Spectrum of Carbon Disulphide

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The Raman spectrum of liquid carbon disulphide has been investigated with high dispersion. In addition to the lines already known, five very faint lines have been observed. The intensities of the stronger lines were measured and, with a spectrograph of low dispersion, the degrees of depolarization of the two principal bands were determined. The results are in accord with the assumption made by Fermi, Dennison and Placzek that large perturbations of some of the energy levels occur on account of the approximate coincidence of  $\nu_1$  with  $2\nu_2$ . The values  $\Delta = -120 \text{ cm}^{-1}$  and  $|P| = 17.8 \text{ cm}^{-1}$  are obtained for the difference  $\Delta = \nu_1 - 2\nu_2$  and for the coupling constant  $P = \beta h^{\frac{1}{2}} / 4\pi^2 \mu_1^{\frac{1}{2}} \mu_2 (\nu_1 + 2\nu_2)^{\frac{1}{2}}$ .

THE Raman spectrum of carbon disulphide has been studied by a number of investigators. The earlier workers<sup>1, 2, 3, 4</sup> found a strong band near  $656 \text{ cm}^{-1}$  and a less intense band around  $800 \text{ cm}^{-1}$ . Krishnamurti<sup>5</sup> observed

that the stronger of these two principal bands has a weak companion at  $647 \text{ cm}^{-1}$ . This was confirmed by Bhagavantam,<sup>6</sup> Matossi and Aderhold,<sup>7</sup> and Mesnage.<sup>8</sup> The latter, employing a spectrograph of high dispersion, resolved the  $800 \text{ cm}^{-1}$  band into a band at  $796.3 \text{ cm}^{-1}$  and a weaker companion at  $810.9 \text{ cm}^{-1}$ . Pienkowski<sup>9</sup>

<sup>1</sup> C. V. Raman and K. S. Krishnan, *Nature* **122**, 882 (1928).

<sup>2</sup> A. Petriakaln and J. Hochberg, *Zeits. f. physik. Chemie* **B3**, 217, 405 (1929).

<sup>3</sup> A. S. Ganesan and S. Ventekateswaran, *Nature* **124**, 57 (1929); *Ind. J. Phys.* **4**, 196 (1929).

<sup>4</sup> Cl. Schaefer, F. Matossi and H. Aderhold, *Phys. Zeits.* **30**, 581 (1929).

<sup>5</sup> P. Krishnamurti, *Ind. J. Phys.* **5**, 105 (1930).

<sup>6</sup> S. Bhagavantam, *Ind. J. Phys.* **5**, 35, 59 (1930); *Nature* **126**, 995 (1930); *Phys. Rev.* **39**, 1029 (1932).

<sup>7</sup> F. Matossi and H. Aderhold, *Zeits. f. Physik* **68**, 683 (1931).

<sup>8</sup> P. L. Mesnage, *J. de Phys. et le Rad.* **2**, 403 (1931).

<sup>9</sup> S. Pienkowski, *Acta. Phys. Pol.* **1**, 87 (1932).

determined the relative intensities of the principal bands, obtaining the ratio 3.1. The degree of depolarization of these bands has been measured by Bhagavantam,<sup>6</sup> Pienkowski,<sup>9</sup> Cabannes and Rousset,<sup>10</sup> and Ventekateswaran.<sup>11</sup> Hanle,<sup>12</sup> by observation on circular polarization, determined an upper limit for the depolarizations. Besides the afore-mentioned bands, three very feeble bands were observed by Bhagavantam<sup>6</sup> at  $400\text{ cm}^{-1}$ ,  $1229\text{ cm}^{-1}$ , and  $1577\text{ cm}^{-1}$ . The presence of the  $400\text{ cm}^{-1}$  band has been confirmed by Ventekateswaran<sup>11</sup> who also determined its depolarization.

The smallness of the dipole moment of  $\text{CS}_2$ , as well as other evidence,<sup>13</sup> suggests that the carbon disulphide molecule is linear and symmetrical. This assumption was shown by Placzek<sup>14</sup> to form a suitable basis for the interpretation of the Raman spectrum and has been definitely confirmed by the recent work of Dennison and Wright<sup>15</sup> and Bailey and Cassie<sup>16</sup> on the infrared absorption spectrum.

In view of the simple structure of linear triatomic molecules, it seemed desirable to obtain as accurate and detailed data on their Raman spectra as possible. We have, therefore, reexamined the Raman spectra of several molecules of this not very numerous class. In the present paper the results obtained with carbon disulphide will be reported.

### FREQUENCY SHIFTS

The carbon disulphide ("Merck C.P."), after being purified by shaking with mercuric chloride and by fractional distillation, was illuminated by four glass mercury arcs, each 32 cm long and surrounded by a reflector of proper shape. A 6 mm thick layer of a solution of quinine sulphate in water was interposed between the mercury

lamps and the tube containing the carbon disulphide.

The scattered spectrum was photographed with a four-prism glass spectrograph having a linear dispersion of 7A per mm at 4400A. Agfa Isochrome plates and a fine-grain developer were used. The exposure time varied between 20 and 48 hours. No observable photochemical decomposition of the carbon disulphide occurred.

The measured frequency shifts are listed in the first column of Table I. All frequency shifts

TABLE I.

Raman frequency	Intensity	Depolarization	Transition	Infrared frequency
383 $\text{cm}^{-1}$	—	0.8*	$(0000) \rightarrow (010 \pm 1)$	389.4 $\text{cm}^{-1}$
395	0.05			396.8
403	—			405.8
640.9	—	0.15	$(010 \pm 1) \rightarrow \{(110 \pm 1)(030 \pm 1)\}$ $(0000) \rightarrow \{(1000)(0200)\}$	645
648.3	4.2			
656.5	18.9			
787.7	0.1	0.18	$(0000) \rightarrow \{(0200)(1000)\}$ $(010 \pm 1) \rightarrow \{(030 \pm 1)(110 \pm 1)\}$  $(0000) \rightarrow (0010)$	807
796.0	1.5			
804.9	0.5			
812.6	0.1			
				1523

\* Determined by S. Ventekateswaran (reference 11).

were observed as Raman lines excited by the 4358A mercury line. The most intense shifts were observed also as produced by the mercury lines 4348A, 4916A and 5461A, and as anti-Stokesian lines due to 4358A. The values found for the shifts  $656.5\text{ cm}^{-1}$  and  $796.0\text{ cm}^{-1}$  should be accurate to  $\pm 0.5\text{ cm}^{-1}$ . Because of their proximity to the strong lines and to their lower intensity, the accuracy in the measurement of the satellites is somewhat smaller. The three very faint lines in the neighborhood of  $400\text{ cm}^{-1}$  are probably measured correctly to  $\pm 3\text{ cm}^{-1}$ . The observation of these lines was difficult because of the presence of a continuous background which was not entirely removed even after repeated purification of the carbon disulphide.

The frequencies  $656.5\text{ cm}^{-1}$  and  $796.0\text{ cm}^{-1}$  agree well with the measurements of previous observers but should be more accurate. The frequency  $648.3\text{ cm}^{-1}$ , while in good accord with the value  $647\text{ cm}^{-1}$  reported by Krishnamurti, differs markedly from the value  $642.6\text{ cm}^{-1}$  found by Mesnage. There is a similar discrepancy between the frequency  $810.9\text{ cm}^{-1}$  reported by

<sup>10</sup> J. Cabannes and A. Rousset, *Ann. de Physique* **19**, 229 (1933).

<sup>11</sup> S. Ventekateswaran, *Phil. Mag.* **15**, 263 (1933).

<sup>12</sup> W. Hanle, *Ann. d. Physik* **15**, 345 (1932).

<sup>13</sup> Cf. P. N. Gosh and P. C. Mahanti, *Phys. Zeits.* **30**, 531 (1929).

<sup>14</sup> G. Placzek, *Zeits. f. Physik* **70**, 84 (1931).

<sup>15</sup> D. M. Dennison and N. Wright, *Phys. Rev.* **38**, 2077 (1931).

<sup>16</sup> C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. A* **132**, 236 (1931); **A140**, 605 (1933).

Mesnage and our value  $804.9\text{ cm}^{-1}$ . We were unable, even with long exposures, to confirm the lines  $1229\text{ cm}^{-1}$  and  $1577\text{ cm}^{-1}$  reported by Bhagavantam.

#### INTENSITIES

It is a very difficult problem to measure the relative intensities of Raman bands. In most cases the rotational structure of the bands is not resolved well enough to separate the *Q*-branch completely from the rotational branches, and this may lead to serious error, especially when the Raman bands differ greatly in structure. To reduce this error, a spectrograph of high dispersion should be employed. Indeed, even with such an instrument, it will generally be necessary to use a considerably narrower slit than is ordinarily used when intensities of spectral lines are measured. This has the disadvantage that the peaks in the photometer record do not have the flat tops desirable for accurate measurement of the photographic blackening. Another source of error is the continuous background, so often present, which reduces the accuracy with which weak bands may be measured.

The Raman bands of carbon disulphide excited by the 4358A mercury line lie in a spectral region in which the variation with wave-length of the photographic sensitivity is very small. In addition, the principal bands lie rather close together. Hence, the methods of homogeneous spectrophotometry may be employed. The scattered spectrum was photographed with the previously mentioned four-prism spectrograph. The slit was  $0.03\text{ mm}$  wide, the focal lengths of collimator and camera objectives being  $50\text{ cm}$  and  $75\text{ cm}$ , respectively. Intensity marks were put on the plate by means of a continuous light source and a step-weakeners with six steps which had been calibrated by the aid of a Nuttall colorimeter. The step-weakeners was placed on the axis of the collimator of the spectrograph about  $1.5\text{ m}$  from the slit, and an image of it was formed on the slit. The light bulb serving as the source of continuous light was enclosed in a box having a window of variable size. A plate of white alabaster glass was placed between step-weakeners and light bulb, and the intensity of illumination was adjusted so that the same exposure time could be used in photographing the intensity

marks and the Raman spectrum. The photographic blackening was measured with a Moll, Type A, microphotometer, the slit in front of the thermoelement having in most cases a width of  $0.10\text{ mm}$ . Fig. 1 shows a typical photometer record of the principal bands together with a reproduction to the same scale of the spectrum. The corresponding energy distribution is plotted in Fig. 2a and Fig. 2b, the curve for the weaker of the two principal bands being drawn to ten times as large a scale as that for the stronger band. The correction for the continuous background amounted to 17 percent of the maximum intensity in the case of the former curve, while it was less than one percent of the maximum intensity in the case of the latter curve.

The curves show a considerable difference in the structure of the two bands, and the question arises whether this difference is real, or whether it may be the result of experimental errors. We have made photometer records of three plates and have varied the speed of motion of the plate as well as other details of the procedure but have always obtained practically the same results. Furthermore, the difference in the shape of the curves cannot be explained by an error in the correction for the continuous background. For, the error required to reduce the two curves to approximately the same shape would have to be more than 200 percent of the computed correction. We must conclude, therefore, that the difference in the structure of the two bands is real.

The energy distribution curves indicate beyond doubt that each group of bands consists of more than two bands. We have attempted to analyze the groups into component bands, as indicated by the dotted curves in Fig. 2. This analysis is to some extent arbitrary, especially in the case of the weaker group, and the accuracy is not great. It is now a question how the curves, obtained in the manner described, may be used for determining the relative intensities of the bands. The values listed in the second column of Table I are simply the maximum ordinates of each of the dotted peaks. If we assume that these values represent the relative intensities, we find the value 12.7 for the ratio between the intensities of the  $656.5\text{ cm}^{-1}$  and  $796.0\text{ cm}^{-1}$  bands. On the other hand, if we assume that the intensities are represented by the areas under the curves, we

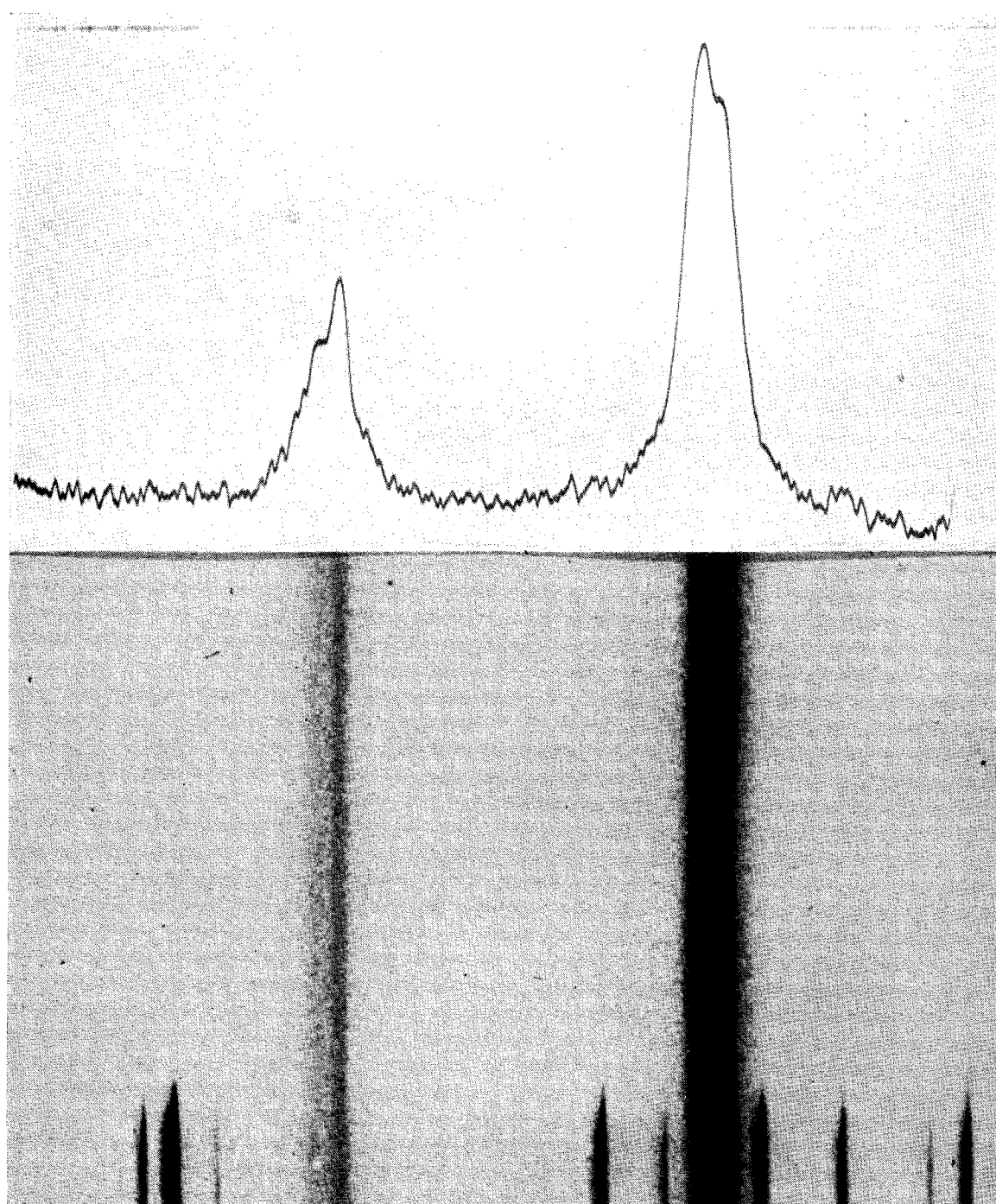
R 151 CS<sub>2</sub> III

FIG. 1. Photometer record and reproduction of the principal Raman bands of carbon disulphide. *R* 151, CS<sub>2</sub> III.

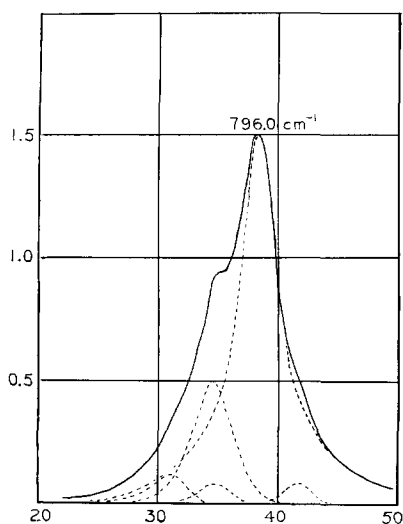


FIG. 2a.

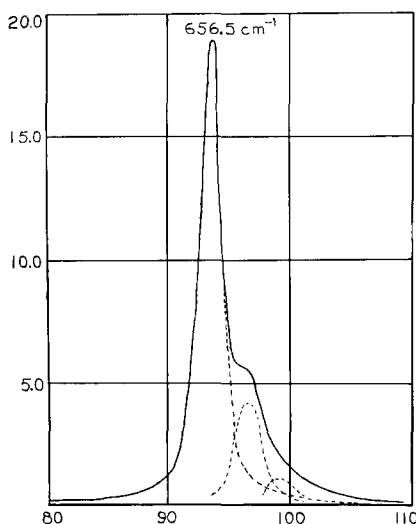


FIG. 2b.

FIG. 2. Energy distribution in the principal Raman bands of carbon disulphide.

get for the intensity ratio the value 3.0 which is in excellent agreement with the value 3.1 reported by Pienkowski. Unfortunately, Pienkowski does not give complete information regarding experimental details, so it is uncertain what weight should be attached to this agreement. It may be concluded from our curves with reasonable certainty that a measurement made in the usual way with a spectrograph of low dispersion will give a value in the neighborhood of 3.0 for the ratio of the intensities of the  $656.5\text{ cm}^{-1}$  and the  $796.0\text{ cm}^{-1}$  bands whereas a similar measurement with an instrument of high dispersion will yield a value as high as 12.7, or even slightly higher. We assume, therefore, that the latter value represents fairly well the true intensity ratio of the  $Q$ -branches.

A rough verification of this assumption may be obtained as follows. As indicated in Table I, the satellites  $648.3\text{ cm}^{-1}$  and  $804.9\text{ cm}^{-1}$  are due to transitions similar to those giving rise to the principal bands, the only difference being that the scattering molecules are in the excited  $(010 \pm 1)$ -state rather than in the state of lowest energy. Hence, it is possible to compute the ratio between the intensities of the principal band and its satellite. Taking into account the double statistical weight of the  $(010 \pm 1)$ -state, and assuming that the temperature is  $300^\circ\text{K}$ , we find the value 3.37. The ratios derived from the

intensities listed in Table I, namely 4.5 and 3.0, are in fair agreement with this value.

The depolarization measurements described below, which were made with a spectrograph of low dispersion, lead to a determination of the ratio between the intensities of the  $656\text{ cm}^{-1}$  and  $796\text{ cm}^{-1}$  groups of bands. The average value found is  $8.3 \pm 0.3$ . The fact that this is considerably lower than the value 12.7 is undoubtedly a consequence of the smaller dispersion used in the polarization measurements.

#### POLARIZATION

The difficulties met with in intensity measurements are magnified when one turns to the problem of measuring the degree of depolarization of Raman lines. Since the incident light must have a well-defined direction in polarization experiments, only a small part of the light emitted by the source can be utilized for illumination. Hence, the scattered light will be very weak and this makes necessary the use of a fast spectrograph which will, generally, have a low dispersion. It will not always be possible, therefore, to separate the  $Q$ -branch completely from the rotational branches, and this may cause serious error on account of the large difference usually existing between the polarization of the rotational branches and that of the  $Q$ -branch. The extent to which the  $Q$ -branch is separated

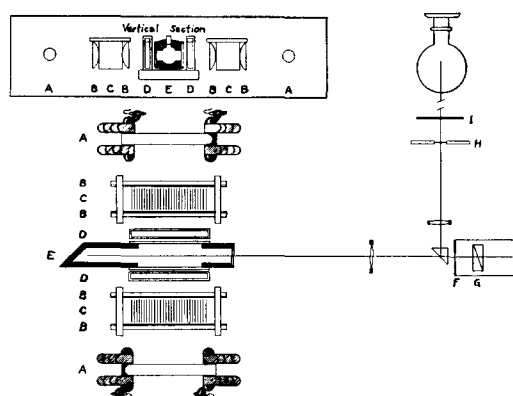


FIG. 3. Experimental arrangement for polarization measurements. A, Hg lamp; B, cylindrical lens; C, screens; D, filter; E, Raman tube; F, spectrograph slit; G, Wollaston prism; H, step-weaker; I, alabaster glass.

from the rotational branches and, hence, the observed depolarization will depend upon the width of the spectrograph slit. Usually, one cannot at the same time use a slit narrow enough to get the greatest possible resolution and wide enough to attain the maximum accuracy in the photometry.

The experimental arrangement used for measuring the degree of depolarization of the principal Raman lines of carbon disulphide is shown in Fig. 3. The liquid was contained in a suitably constructed porcelain tube *E* with black glazing on the inside surface and with cemented glass windows. Two 220-volt quartz mercury lamps *AA*, placed on opposite sides of the container, served as the sources of illumination. In order to reduce the continuous emission, the series resistances were increased to three times their normal value. The direction of the incident light should be perpendicular to the axis of the collimator and to the slit of the spectrograph. As has been shown by Ramakrishna Rao,<sup>17</sup> however, when the light source is of small extension and the proper precautions are taken, a lens may be used for focussing the light upon the scattering substance, thus increasing greatly the intensity of illumination. This fact was utilized in the following manner. Between each mercury lamp and the container were mounted two plano-cylindrical lenses *BB* which focussed the axis of the lamp at the axis of the container. Care was

taken that lamps and lenses were accurately parallel to the collimator of the spectrograph and in the proper height. Between the lenses forming a pair were placed a series of blackened screens, 5 cm wide and 5 mm apart, which prevented the light not approximately at right angles to the collimator axis from reaching the container. Before entering the carbon disulphide, the light was filtered through a solution *DD* of 1 g meta-dinitrobenzene in 100 cm<sup>3</sup> carbon tetrachloride. This filter, which has been proposed by Bär,<sup>18</sup> removes the 4046Å and 4078Å mercury lines without absorbing the 4358Å line appreciably.

The spectrograph had a collimator lens of 60 mm clear aperture and 60 cm focal length. The dispersive system consisted of a 65° hollow prism filled with ethyl cinnamate, the glass windows being large enough to transmit the entire beam of light. The camera lens was a Tessar of diameter 60 mm and focal length 21 cm. A quartz Wollaston prism was placed in the collimator tube 3 cm behind the slit with its refracting edges accurately parallel to the slit. Each spectral line was thus split up into two components lying side by side, one being polarized parallel and the other at right angles to the slit. Apart from the correction for the polarization produced by the refraction in the prism, the ratio between the intensity of the latter component to that of the former is equal to the degree of depolarization. Intensity marks were put on the plate by means of a step-weaker *H* illuminated by a continuous light source, the light passing through a plate *I* of alabaster glass. An image of the step-weaker was formed on the slit by means of an achromatic lens and a totally reflecting prism. The correction for the polarization produced by the prism was determined by letting unpolarized light from a Geissler tube containing helium enter the spectrograph and measuring the relative intensities of the perpendicular and parallel components. The correction varied only slightly with wavelength and amounted to 36 percent for the principal Raman lines excited by 4358Å. The width of the spectrograph slit was either 0.05 mm or 0.10 mm, essentially the same value being obtained for the depolarization in both cases.

<sup>17</sup> J. Ramakrishna Rao, Ind. J. Phys. 2, 61 (1927).

<sup>18</sup> R. Bär, Helv. Phys. Acta. 5, 174 (1932).

The exposure time varied between  $1\frac{3}{4}$  and 4 hours.

Under these conditions, the band at  $648.3\text{ cm}^{-1}$  is not separated from the principal band at  $656.5\text{ cm}^{-1}$ , and the satellite at  $804.9\text{ cm}^{-1}$  is fused with the principal band at  $796.0\text{ cm}^{-1}$ . Also, the  $Q$ -branches are not completely separated from the rotational branches.

The values obtained for the degree of depolarization  $\rho_n$  (the subscript  $n$  indicating that the incident light was unpolarized) are listed in the third column of Table I. These values could be duplicated to within 5 percent. Because of the imperfect resolution, however, they are undoubtedly somewhat higher than the true depolarizations of the  $Q$ -branches of the  $656.5\text{ cm}^{-1}$  and  $796.0\text{ cm}^{-1}$  bands. On the other hand, the depolarizations, 0.13 and 0.18, found by us are considerably lower than those found by previous observers. Indeed, Pienkowski<sup>9</sup> found 0.27 and 0.29 for the  $656.5\text{ cm}^{-1}$  and  $796.0\text{ cm}^{-1}$  bands, respectively. Bhagavantam,<sup>6</sup> and also Cabannes and Rousset,<sup>10</sup> found the value 0.25, and Ventekateswaran<sup>11</sup> the value 0.2, for both lines. Only Cabannes and Rousset give sufficient experimental detail to permit of an estimate as to the reason for the difference between their results and ours. While this difference cannot arise from the fact that the incident light was somewhat less accurately parallel in their experimental arrangement than in ours, it may be due to their using a spectrograph slit four times as wide as the widest slit used by us.

#### DISCUSSION OF RESULTS

A linear and symmetrical triatomic molecule will, in general, have only one strong Raman band.<sup>14</sup> The presence of two nearly equally intense bands in the Raman spectrum of carbon dioxide was explained by Fermi<sup>19</sup> as the result of an abnormally large perturbation arising from the approximate coincidence of  $\nu_1$  with  $2\nu_2$ . In the Raman spectrum of carbon disulphide, there are also two strong bands, which, however, differ much more in intensity than do the two strong  $\text{CO}_2$ -bands, and it has been suggested by Fermi that the same accidental degeneracy, although

not as complete, occurs in the  $\text{CS}_2$ -molecule as in  $\text{CO}_2$ . The theory has been worked out in greater detail by Dennison<sup>20</sup> and by Placzek,<sup>21</sup> and these authors have also discussed the experimental evidence.<sup>22</sup>

Our results are in good accord with this view regarding the origin of the principal Raman bands of  $\text{CS}_2$ . In the fourth column of Table I are indicated the transitions assumed to give rise to the stronger bands. The vibrational states are characterized by the quantum numbers  $V_1$ ,  $V_2$ ,  $V_3$ , and  $i$ , introduced by Dennison.<sup>23</sup> The symbols  $\{(1000)(0200)\}$  and  $\{(0200)(1000)\}$  are used to represent the states produced by partial fusion of the (1000)- and (0200)-states, the component having the largest numerical factor in the resulting wave function being written first. The symbols  $\{(110\pm 1)(030\pm 1)\}$  and  $\{(030\pm 1)(110\pm 1)\}$  have similar meanings.

In the last column of Table I are listed the frequencies determined from the infrared absorption spectrum. The three frequencies in the neighborhood of  $400\text{ cm}^{-1}$  were measured by Dennison and Wright,<sup>15</sup> and the other frequencies are obtained from the measurements of Bailey and Cassie.<sup>16</sup> The agreement between the Raman and infrared frequencies is satisfactory when the experimental errors and the fact that the infrared frequencies were obtained with  $\text{CS}_2$  in the gaseous form are taken into consideration.

If we assume that the perturbation term  $\beta q r^2$  produces an effect which is large compared with that of all other perturbation terms, we may use the measured frequencies of the principal Raman bands and their satellites to compute the difference  $\Delta = \nu_1 - 2\nu_2$ , the frequency  $\nu_2$ , and the numerical value of the quantity

$$P = \beta \hbar^{\frac{1}{2}} / 4\pi^2 \mu_1^{\frac{1}{2}} \mu_2 (\nu_1 + 2\nu_2)^{\frac{1}{2}}$$

where  $\mu_1$  and  $\mu_2$  are the reduced masses associated with the vibrations  $\nu_1$  and  $\nu_2$ , respectively.<sup>24</sup>

<sup>20</sup> D. M. Dennison, Phys. Rev. **41**, 304 (1932).

<sup>21</sup> G. Placzek, *Rayleigh-Streuung und Raman-Effekt*, Marx: Handbuch der Radiologie, 2nd ed., Vol. 4, Part II. We are indebted to Dr. Placzek for the opportunity of seeing this article before its publication.

<sup>22</sup> Cf. also A. B. D. Cassie and C. R. Bailey, Zeits. f. Physik **79**, 35 (1932).

<sup>23</sup> D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1930).

<sup>24</sup> Cf. Reference 21, pp. 324–325.

<sup>19</sup> Fermi, Zeits. f. Physik **71**, 250 (1931).



In fact, we have

$$(\Delta^2 + 16P^2)^{\frac{1}{2}} = 796.0 - 656.5 = 139.5 \text{ cm}^{-1},$$

$$(\Delta^2 + 32P^2)^{\frac{1}{2}} = 804.9 - 648.3 = 156.6 \text{ cm}^{-1},$$

and

$$\begin{aligned} \nu_1 + 2\nu_2 &\leq 796.0 + 656.5 \leq 804.9 + 648.3 \\ &\leq 1452.8 \text{ cm}^{-1}. \end{aligned}$$

Solving these equations, we obtain

$$\Delta = -120 \text{ cm}^{-1}, |P| = 17.8 \text{ cm}^{-1}, \nu_2 = 393.2 \text{ cm}^{-1}.$$

The agreement between the computed and the observed values of  $\nu_2$  is very satisfactory. The values for  $\Delta$  and  $|P|$  are more satisfactory than the values  $\Delta = -136.7 \text{ cm}^{-1}$  and  $|P| = 7.0 \text{ cm}^{-1}$  computed by Dennison<sup>20</sup> from Krishnamurti's measurements of the principal Raman bands and the value  $\nu_2$  determined by Dennison and Wright in the infrared absorption. Also, the values for  $\Delta$ ,  $|P|$ , and  $\nu_2$ , derived from our measurements should be more accurate than the values  $\Delta = 106 \text{ cm}^{-1}$ ,  $|P| = 33 \text{ cm}^{-1}$ , and  $\nu_2 = 389.5 \text{ cm}^{-1}$ , computed by Placzek<sup>21</sup> from the data of Mesnage.

If it be assumed that the matrix elements  $\alpha_1 = (0000|\alpha|1000)$  and  $\alpha_2 = (0000|\alpha|0200)$  of the polarizability tensor have approximately the same relative anisotropy, it is possible,<sup>25</sup> from the measured ratio between the intensities of the  $656.5 \text{ cm}^{-1}$  and  $796.0 \text{ cm}^{-1}$  bands and the value of  $\Delta$ , to estimate the value of the quantity  $|\alpha_1/\alpha_2|^2$  which would represent the ratio between the probabilities of the transitions  $(0000) \rightarrow (1000)$  and  $(0000) \rightarrow (0200)$  if no accidental

degeneracy were present. Taking the value 12.7 for the intensity ratio, we find  $|\alpha_1/\alpha_2|^2 = 40,000$ , a value which is of the order of magnitude to be expected.

From the interpretation of the bands, one would expect the depolarization of the  $656.5 \text{ cm}^{-1}$  band to be smaller than that of the  $796.0 \text{ cm}^{-1}$  band, and also both depolarizations to be small. The measured values are in good accord with this expectation. However, until the depolarizations have been measured for the principal lines and the satellites separately, it is impossible to draw quantitative conclusions.

It is an interesting fact that the band  $(0000) \rightarrow (010 \pm 1)$ , which is forbidden in the Raman spectrum on account of the antisymmetry of the  $\nu_2$ -vibration, is observed, although with low intensity. The presence of this band is undoubtedly connected with the fact that the carbon disulphide has been studied in the liquid rather than in the gaseous form. The depolarization 0.8 found by Ventekateswaran for this band is in good agreement with the value 6/7 to be expected from theory. The very faint and broad lines  $383 \text{ cm}^{-1}$  and  $403 \text{ cm}^{-1}$  probably represent the maxima of unresolved rotational branches. Considering the low intensity, the frequencies are in fair agreement with those found by Dennison and Wright in the infrared.

The faint lines  $640.9 \text{ cm}^{-1}$ ,  $787.7 \text{ cm}^{-1}$ , and  $812.6 \text{ cm}^{-1}$ , may be due to transitions from the excited levels  $\{(1000)(0200)\}$ ,  $\{(0200)(1000)\}$ , and  $(020 \pm 2)$ . An unambiguous interpretation is not possible, however, until we have a more complete knowledge of the vibrational levels of the  $\text{CS}_2$ -molecule.

<sup>25</sup> Cf. reference 21, p. 321.