

Infrared Absorption Spectrum of Carbon Disulfide

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The infrared absorption spectrum of carbon disulfide has been remeasured in the region from 2 to 24 μ with cells up to 5 mm in thickness. Fifteen bands were observed, some however being of low intensity. The strongest band for the liquid occurs at 6.62 μ , and the second harmonic of this band was observed at 2.22 μ , but the first harmonic, which should be at about 3.33 μ , was not observed, in accordance with the selection rules for a symmetrical linear molecule. Four combination bands were observed between 3 and 5 μ , whose wavelengths were in good agreement with the calculated values. A combination band, which is represented by the difference between two fundamentals, occurs as a broad, moderately strong band in the region of 11.6 μ . A weak band, observed at 15.27 μ , corresponds with the wavelength of the inactive vibration of the molecule. However, when this region was studied with a 140 cm cell filled with the saturated vapor of CS₂ at room temperature, no band was observed. In the vapor state a total of six bands were found at wavelengths less than 20 μ . The fundamental band at 6.5 μ shows a side branch that is probably due to the isotopic effect produced by C¹³. Some small bands that were observed may be attributed to the C¹²S³²S³⁴ molecule. As would be expected for this molecular configuration, the spectrum of CS₂ as observed may be classified into an array of terms analogous to those of CO₂. A band at 12.7 μ has different intensities for samples obtained from two different sources and may be caused by an impurity. This band did not appear when the cell containing the vapor was used.

I. Introduction

The infrared absorption spectrum of carbon disulfide has been measured by many observers [1, 2, 3].¹ The present work has been undertaken primarily to extend the observations to the short-wavelength region, also to compare the spectrum of the liquid with the vapor. In the near-infrared region CS₂ is quite transparent, and cell thicknesses of several centimeters may be used with only a small loss in energy. However, because of the presence of strong bands at 4.6 and 6.5 μ , and other bands at 3.4 and 3.55 μ , very thick cells are almost opaque beyond 3.3 μ . Many substances have strong absorption bands in the region between 7 and 15 μ . For this region, layers 0.1 mm in thickness are quite transparent, and carbon disulfide may be used as a solvent in the study of the

absorption spectrum of compounds. Carbon tetrachloride, another commonly used substance, is quite absorbing from 12 to 15 μ , and is not as satisfactory as CS₂ for use as a solvent when absorption measurements are made in this part of the spectrum.

The absorption spectrum of the vapor of CS₂ has been measured by Bailey and Cassie [2] and by Dennison and Wright [3], and the molecular structure has been determined to be of the type of CO₂. That is, the molecule is linear, and the carbon atom is at the center. Further work by Sanderson [4] on the fine structure of the 4.6 μ band has revealed that the rotational lines are equally spaced, which is further proof that the molecule is linear. Also, Lieberman [5] has resolved a band in the ultraviolet and found that the rotational lines were equally spaced. The Raman spectrum of CS₂ has been measured by a number of observers,

¹ Figures in brackets indicate the literature references at the end of this paper.

and such data are of great assistance in interpreting the energy levels.

The selection rules for the energy-level transitions in a linear symmetrical molecule are well known. Many of the energy transitions are inactive. In this work on the absorption of the material in the liquid state, a number of bands are found that have not been observed for the gaseous state. This will be discussed after the experimental results are given.

II. Experimental Results

A Perkin-Elmer infrared spectrometer was used to measure the absorption spectrum of carbon disulfide. In addition to the rock-salt prism, a LiF prism was used in the region from 3.3 to 3.7 μ and a KBr prism from 15 to 24 μ . A slit-control device, which has been described before [6], was found to simplify the measurements, especially in the long-wavelength region. The experimental arrangements were the same as formerly used, and the description will not be repeated here. Several cell thicknesses were used in various regions

of the spectrum. In figure 1 the results for cells 5.0 mm and 0.10 mm in thickness have been plotted on the same graph. The 5.0-mm cell showed all the bands that were observed, but in the region of 6.6 and 4.6 μ , the bottoms of the bands were broad, and the positions of maximum absorption could not be accurately determined. In table 1 the wavelengths of all the observed bands are given. The values of the observed wavelengths are obtained by taking the average of a number of observations.

Different cell thicknesses were used to display the different bands to best advantage; for example, the band at 2.22 μ absorbs about 15 percent of the radiation with a cell thickness of 5.0 mm, whereas the 4.6- and 6.6- μ bands absorb 100 percent for a cell 0.10 mm in thickness. The 3.55- μ band showed a slight side band on the long-wavelength side. When this region was investigated with a LiF prism, figure 2, the two bands were resolved and separated by about 23 cm^{-1} . The band at 6.62 μ is very intense and showed zero transmission from 6.50 to 6.70 μ with a 0.05-mm cell. The

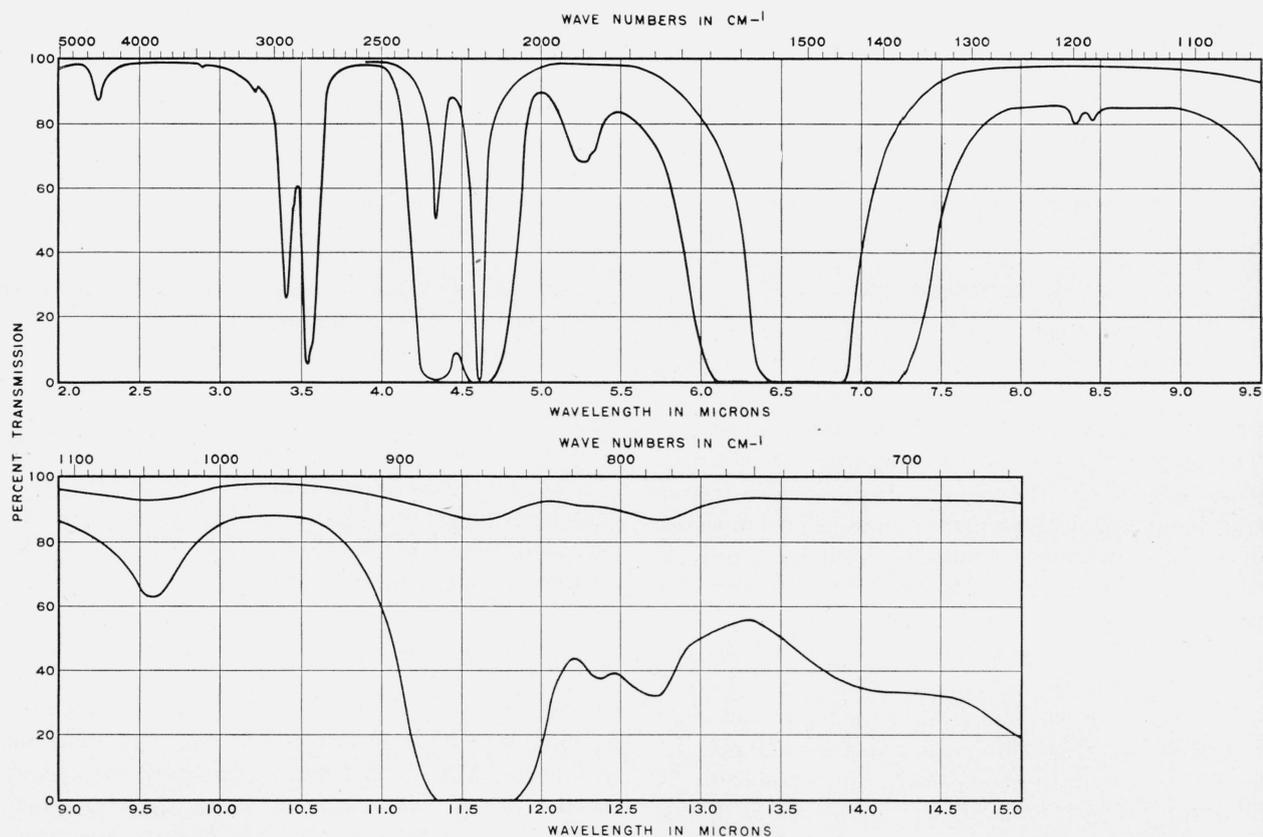


FIGURE 1.—Infrared transmission of liquid CS_2 for cells of 5 mm and 0.1 mm in thickness.

bands, as observed with a rock-salt prism are fairly sharp and are probably not over 0.02μ in error. The bands at 11.68 and 12.77μ are broad, and it is somewhat difficult to determine accurately their maxima of absorption. In the region of 14μ there is an indication of a band when a 5.0-mm cell is used, but with thinner cells no band was observed. For the thick cells there is considerable general absorption in this region. This is partly due to a band at 15.27μ . This was the only band observed beyond 15μ . There is a small dip at 20μ , but this was not sufficient to be considered as a band, especially as it occurs in a region of general absorption and may be due to experimental error. The percentage transmission is decreasing as the long-wavelength region is reached, and this is caused by the $25\text{-}\mu$ band.

TABLE 1.—Observed and calculated bands of carbon disulfide

Term	Wave number		Wave-length observed μ
	Observed	Calculated	
	<i>cm⁻¹</i>	<i>cm⁻¹</i>	
ν_1 -----	655	¹ 655	15.27
ν_2 -----		¹ 397	
ν_3 -----	1,510	¹ 1,510	6.64
$\nu_1 + \nu_2$ -----	1,048	1,052	9.54
$2\nu_2$ -----	807	794	12.39
	783	-----	12.77
$\nu_3 - \nu_1$ -----	855	855	11.66
	1,197	1,191	8.35
$3\nu_2$ -----	1,180	-----	8.47
$\nu_2 + \nu_3$ -----	1,910	1,907	5.23
$\nu_1 + \nu_3$ -----	2,163	2,165	4.62
$\nu_3 + 2\nu_2$ -----	2,303	2,304	4.34
$\nu_3 + 2\nu_1$ -----	2,815	2,820	3.55
$\nu_3 + 2\nu_1$ (C ¹² S ³² S ³⁴)-----	2,793	2,796	3.58
$\nu_1 + \nu_3 + 2\nu_2$ -----	2,949	2,960	3.39
$\nu_3 + 4\nu_2$ -----	3,105	3,098	3.22
$\nu_3 + 3\nu_1$ -----	3,472	3,475	2.88
$3\nu_3$ -----	4,504	4,530	2.22

¹ These values used in calculating other terms.

The transmission for cells of 1.5 and 5.0 mm in thickness is shown in figure 3 for the long-wavelength region. The CS_2 samples used in these measurements were obtained from the firms, J. T. Baker Chemical Co., and Merck & Co. The Merck product was marked "highly purified." The CS_2 obtained from Baker was labeled "Baker's Analyzed," and it was rated very pure. Although the absorption-spectra characteristic of the two samples were essentially identical, an observable difference was apparent. This was especially noteworthy for the band at wave number 783 cm^{-1} (12.77μ). In figure 4 are shown the ob-

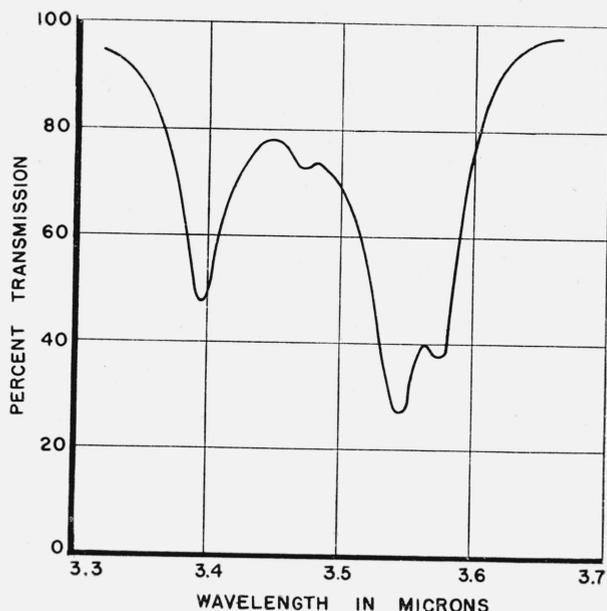


FIGURE 2.—Spectrum of liquid CS_2 in the region of 3.5μ as measured with a LiF prism (cell thickness about 1.2 mm).

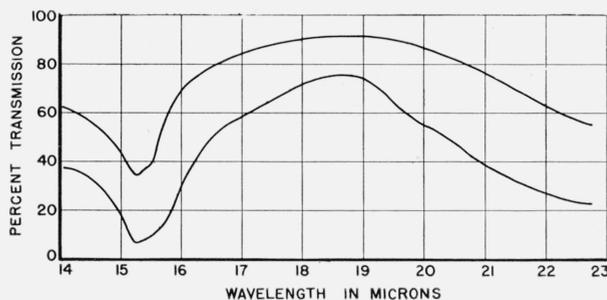


FIGURE 3.—Transmission of liquid CS_2 from 14 to 23μ as measured with a KBr prism (cells 1.5 and 5.0 mm in thickness were used).

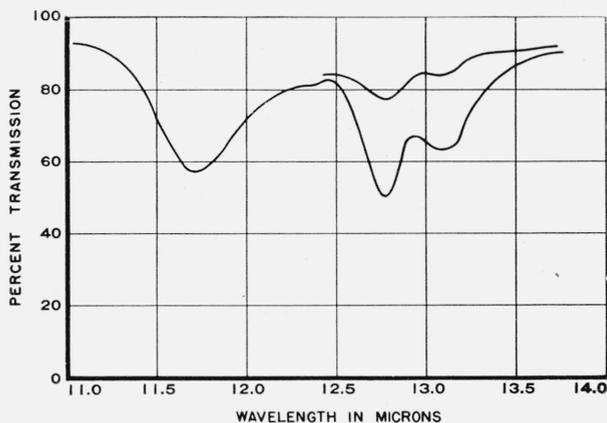


FIGURE 4.—Absorption spectra of two samples of liquid CS_2 for a cell, 0.4 mm in thickness.

served bands for this region for the two samples. It will be observed that the band at $12.77\ \mu$ is much more intense for the Merck sample than for the Baker product. The cell was $0.40\ \mu$ in thickness for each sample. It should be added that the Merck sample had been on a shelf for several years and that the bottle was only partially filled. A deterioration or polymerization in the compound could have taken place. This band has been found by other observers [1], but the varying intensity with different samples has not been previously noted. The other bands do not show such changes, and it appears that this band is due to some other molecule. The possible sources of its origin will be discussed later.

The bands between 3 and $4\ \mu$ were measured with a LiF prism, and in figure 2 the experimental results are given. The band at $3.40\ \mu$ has a side band at $3.35\ \mu$, and there is a small band at $3.47\ \mu$. The two parts of the $3.55\text{-}\mu$ band are well resolved, and there is another very weak band at $3.60\ \mu$ observed when thick cells were used. The resolution of the LiF prism is much greater than that of the rock-salt prism in this region. In figure 5 is shown the absorption band at $6.5\ \mu$ for the vapor of CS_2 . The presence of a side band is detected on the long-wavelength side. The cell length was $60\ \text{cm}$, and the pressure of the vapor was reduced until it was possible to observe this side band. With the full pressure of the saturated vapor, this band was broad and no structure was observed. When the pressure of the CS_2 vapor was reduced to extremely low values, the side band was not observed, and only a double-type band with less absorption at the center appeared.

The band at $11.36\ \mu$ due to CS_2 vapor is shown in figure 6. The CS_2 in liquid form was put in the bottom of the 60-cm cell and allowed to stand for $2\ \text{hr}$ before measurement. The separation in wave numbers of the two regions of maximum absorption is about $13.5\ \text{cm}^{-1}$, which checks well with the value found by other observers. Herzberg [7] has questioned the existence of the band at $11.26\ \mu$ for the vapor state, but it is readily observed and is of medium intensity. Six bands were observed for the vapor state in the region from 3 to $15\ \mu$. They were located at 3.38 , 3.50 , 4.28 , 4.62 , 6.52 , and $11.36\ \mu$. A few isotopic bands, not fully resolved, are not included in this number. All the bands that were observed in the vapor include the

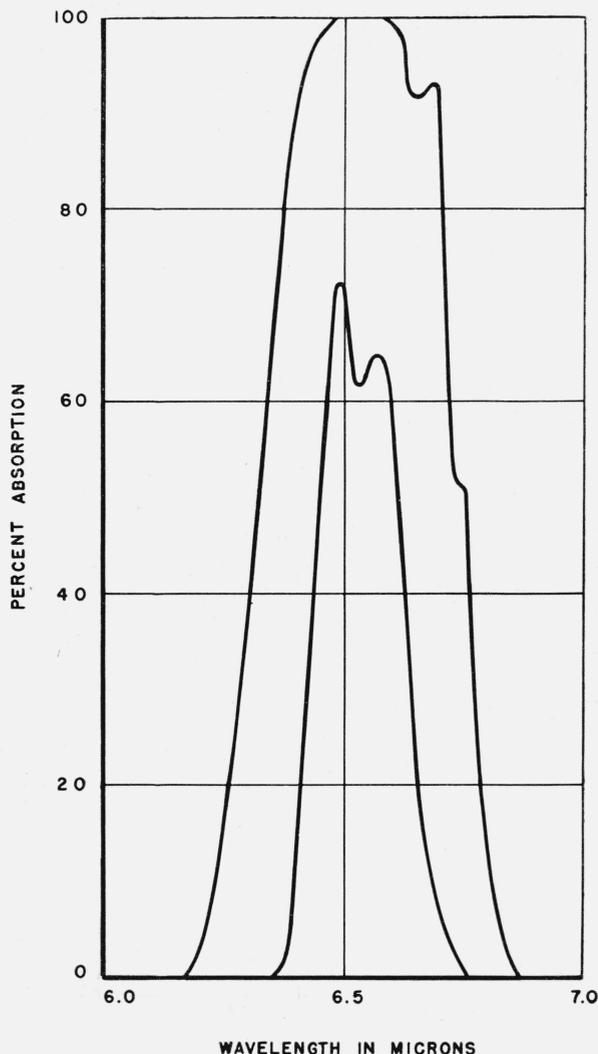


FIGURE 5.—Absorption of CS_2 vapor in the region of $6.5\ \mu$. Upper curve for 60-cm cell with reduced pressure. Lower curve obtained with a trace of CS_2 in the cell.

type of vibration, ν_3 . As ν_3 occurs at slightly shorter wavelengths in the vapor than in the liquid, all these bands are at shorter wavelengths than the corresponding bands for the liquid. The Raman spectrum indicates that the wavelength of the 15.27 band of CS_2 is not changed appreciably as the substance is measured in the liquid or vapor state.

The harmonic band, $2\nu_3$, was not observed in the vapor state, which is in agreement with the selection rules. The band, $3\nu_3$, which is allowed by the selection rules was not observed, but this band is of low intensity, and cell lengths greater than those used in this work would be needed for its observa-

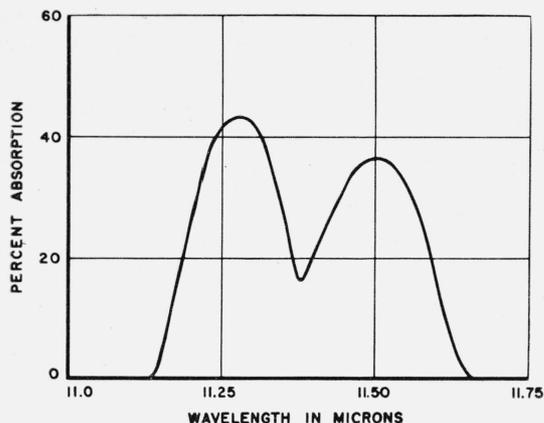


FIGURE 6.—Infrared absorption band of CS_2 vapor at 11.36μ . Saturated vapor at 23°C with a path length of 60 cm was used.

tion. The band at 11.36μ , corresponding to a wave number 879 cm^{-1} , is probably due to the combination $\nu_3 - \nu_1$, that is, it is a difference band. By calculation based on previously available data, this band should be located at the wave number 868 cm^{-1} , or 11 cm^{-1} less than its observed value. This difference is greater than the experimental error, and it appears that either this difference band is out of position or that the previously accepted location of ν_3 is not correct. The measurements herein reported permit the explanation and elimination of this discrepancy. This explanation follows.

As ν_1 is inactive in the infrared, the wave number of 655 is taken from results obtained by the Raman spectrum. Several observers [7] have measured this band, and their results agree to one or two wave numbers. The band corresponding to ν_3 is very intense, and also there exists a side band on the long-wavelength side. Several different amounts of gas were used, and with very small amounts the two branches of the band were observed, as shown in figure 5. The center of the band is located at $1,535 \pm 2 \text{ cm}^{-1}$. This is 12 cm^{-1} greater than the value accepted on the basis of data to date. The value $1,535 \text{ cm}^{-1}$ also gives better agreement for the band $\nu_1 + \nu_3$. This band is observed at $2,184 \text{ cm}^{-1}$. The calculated value, without the introduction of correction terms, is $2,190 \text{ cm}^{-1}$. The value $1,535 \text{ cm}^{-1}$ for ν_3 also removes the difficulty in regard to the position of the difference band $\nu_3 - \nu_1$. The calculated value is 880 cm^{-1} , and the observed value is 879 cm^{-1} . This is within the experimental error.

III. Discussion of Results

CS_2 , in the vapor state, has been measured by Bailey and Cassie [2] and by Dennison and Wright [3]. From the spectrum it was concluded that CS_2 was a linear symmetrical molecule, and that the selection rules that Dennison had previously worked out for CO_2 should apply to carbon disulfide. Adel and Dennison [8] were able to classify, with excellent agreement, a large number of bands of CO_2 that had been observed with long absorbing paths. By the use of a 5-mm cell of CS_2 in the liquid state, the percentage absorption should be as large in the bands as for several meters of the vapor. Some changes in the spectra may be produced by the closeness and association of the molecules in the liquid state. Also, the selection rules, which forecast zero intensity for some transitions, may not hold rigidly for the liquid state because of forces between neighboring molecules changing the high degree of symmetry of this type of molecule.

The first difference between the spectra of the liquid and the vapor, which has already been noted, is the change in frequency of band ν_3 at $1,535 \text{ cm}^{-1}$. Also, the band ν_1 at 655 cm^{-1} , which is very intense in the Raman spectrum, is in the spectrum of the liquid. This band was not observed for the vapor state, and should be inactive in a molecule of this type. The band could arise from a small amount of another substance as thick cells are necessary for its observation. But it is more probably produced by a lack of symmetry introduced by the forces of neighboring molecules. By the use of thick cells, the impurities in the substance become of great importance. One-tenth of 1 percent of some substances in solution in CS_2 would give rise to appreciable absorption in certain regions of the spectrum when observed with 5.0-mm cells. In fact, some differences in the spectrum of CS_2 were noted with the two different samples. A number of the small bands beyond 7μ showed slight differences, but such a difference was quite in evidence at 12.77μ . Guilotto and Caldirola [9] used CS_2 from Merck & Co. and obtained this band in the Raman spectrum. By the variation of the intensity of this band in different samples, it is evident that it is produced by another substance as yet unknown. Several of the observed bands of CS_2 correspond with the positions of the

bands of COS [10], and it may be possible that a small amount of this material is present.

The observed and calculated wave numbers of the observed bands and the corresponding terms are given in table 1. The observed values were not of sufficient accuracy to warrant the calculation of higher-order correction terms. No importance should be attached to the fact that the calculated and observed values agree to less than 5 cm^{-1} for some terms, as this variation is less than the error in the experimental values for bands of wavelength less than 5μ . The correction terms are small, and this may, in part, account for the rapid decrease in intensity of the harmonics and combination bands.

The harmonic, $2\nu_2$, which arises from the transition, $(02^0 \leftarrow 00^0)$, from the ground level, should be inactive and is not observed in the liquid state. However, $2\nu_2$, which arises from transition, $(03^1 0 \leftarrow 01^1 0)$, of one state above the ground level is observed and occurs at 807 cm^{-1} . Both these bands are observed in the Raman spectrum. The band at 807 cm^{-1} is somewhat displaced from the frequency 794 cm^{-1} because of the Fermi resonance. Sirkar [11] has found that the Raman spectrum of CS_2 in the solid state does not contain the 807 cm^{-1} band. This is in accordance with the interpretation that this band arises from a higher state and not the ground state. At room temperature, a considerable number of the molecules would be out of the lowest level for the band of lowest frequency.

The very intense band at 6.62μ does not have a first harmonic. There is observed a band at 3.39μ , but this is displaced from the position of the harmonic and the location of this band corresponds closely to the combination $\nu_1 + \nu_3 + 2\nu_2$. This type of combination gives rise to a band of medium intensity in CO_2 . The second harmonic is present and is observed at 2.22μ . The combination $\nu_1 + \nu_3$ is observed at 4.62μ , and is a very intense band; a 0.05-mm cell showed 100-percent absorption at the center of this band. A small side band was observed on the long-wavelength side of the combination $\nu_1 + \nu_3$, in both the liquid and the vapor. It is separated from the major band by about 14 cm^{-1} and is attributed to the isotope $\text{C}^{12}\text{S}^{32}\text{S}^{34}$.

Two small bands were observed with wave numbers 1,180 and $1,197 \text{ cm}^{-1}$. With different samples there was a variation in intensity, but the

band with wave number $1,197 \text{ cm}^{-1}$ was the more intense in the CS_2 from Baker. The $1,180\text{-cm}^{-1}$ band is probably due to $3\nu_2$. A weak band was observed at 5.23μ and checks well with the combination $\nu_2 + \nu_3$. This band should be inactive by the selection rules and may be due to the isotope $\text{CS}^{32}\text{S}^{34}$. The combination $\nu_1 - 2\nu_2$, which is observed in the spectrum of CO_2 does not appear in the spectrum of CS_2 for the cell thickness used.

There does not appear to be any evidence for the isomeric form of CS_2 with the carbon at one end position. If this molecule were present in appreciable quantities, there should be observed three active fundamentals, both in the infrared and Raman spectra.

A weak band at 397 cm^{-1} has been observed in the Raman spectrum by Wood and Collins [12] and by Venkateswaran [13]. For a linear symmetrical molecule this band should not be active in the Raman spectrum. However, the isotope $\text{CS}^{32}\text{S}^{34}$ would be active, and would produce a band at near the same wave number. A Raman band corresponding to ν_3 was observed at 642 cm^{-1} by Guilotto and Caldirola, and it was attributed to the isotopic molecule.

IV. Isotope Effect

There are three sulfur atoms with atomic weights of 32, 33, and 34, and two carbon atoms with atomic weights of 12 and 13. With these isotopes, 12 molecules could be formed with the carbon atom in the center position. Because of the variation in amount of each isotope, there are only four molecules of CS_2 of appreciable amount; these are $\text{C}^{12}\text{S}^{32}_2$, $\text{C}^{12}\text{S}^{32}\text{S}^{33}$, $\text{C}^{12}\text{S}^{32}\text{S}^{34}$, and $\text{C}^{13}\text{S}^{32}_2$. $\text{C}^{12}\text{S}^{32}\text{S}^{34}$ makes up about 8 percent of the total quantity, and the other two isotopic molecules are approximately 1 percent in amount. The shift in the bands due to the isotope S^{34} is small in ν_2 and ν_3 , but amounts to 10 cm^{-1} in ν_1 . The C^{13} does not produce any change in the frequency of ν_1 , but in ν_3 the shift in wave numbers on substitution of C^{13} is 49 cm^{-1} . The substitution of S^{34} produces a shift of only 4 cm^{-1} in ν_3 . For this reason the band observed on the long-wavelength side of ν_3 in the vapor state is attributed to $\text{C}^{13}\text{S}^{32}_2$.

The equations for the end and central isotope effect for linear triatomic molecules of the CS_2 type have been derived by Salant and Rosenthal [14]. Unfortunately, the designation of the three funda-

mentals by them does not agree with the notation of Dennison [3]. In table 2 are shown the term designations as given by Dennison, and also the calculated wave number of the band for each isotopic molecule. In most cases the change in position due to the presence of S³⁴ is small. It amounts to 1 cm⁻¹ in ν_2 and 4 cm⁻¹ in ν_3 . The bands arising from the less abundant isotopic forms of CS₂ are greatly overlapped by the bands due to C¹²S³²₂, so that many of them are not easily seen. However, in the band $\nu_3+2\nu_1$ at 3.55 μ , the shift amounts to 24 cm⁻¹ and is just recognized as a side band at low resolution. With the LiF prism the band is separated from the main branch, and it is found to be about 23 cm⁻¹ less in wave numbers.

TABLE 2.—Isotope effect in carbon disulfide fundamental frequencies for the liquid state

Wave-length	Wave number cm ⁻¹	Term	End effect			Central effect
			C ¹² S ³² S ³²	C ¹² S ³² S ³⁴	C ¹² S ³² S ³³	
25.19	397	ν_2	$\frac{\Delta\nu_2}{\nu_2}$	—	—	—
			ν_2	418	823	31
			$\Delta\nu_2$	-1	-0.5	-13
			$\nu_2+\Delta\nu_2$	396	396.5	384
			$\frac{\Delta\nu_1}{\nu_1}$	—	—	0
15.27	655	ν_1	$\frac{\Delta\nu_1}{\nu_1}$	—	—	—
			ν_1	66	130	0
			$\Delta\nu_1$	-10	-5	0
			$\nu_1+\Delta\nu_1$	645	650	655
			$\frac{\Delta\nu_3}{\nu_3}$	—	—	—
6.62	1,510	ν_3	ν_3	418	823	31
			$\Delta\nu_3$	-4	-2	-49
			$\nu_3+\Delta\nu_3$	1,506	1,508	1,461

The band at 12.77 μ , which has been observed in both infrared and Raman spectra, was considered by Guilotto and Caldirola [9] to be the isotopic band of CS³²S³⁴ corresponding to $2\nu_2$. They point out that it is displaced from 794 cm⁻¹ by 11 cm⁻¹, and that the isotope effect as calculated by them should amount to 10 cm⁻¹. However, $2\nu_2$ should have a change of 2 cm⁻¹ for the end isotope effect and 26 cm⁻¹ for the central isotope effect, and it is seen that the isotope effect does not explain the presence of the band at 12.77 μ or wave number 783 cm⁻¹. As has been pointed out before, this band is due to an impurity or to a polymer of CS₂. Several very weak bands were observed in the region 7 to 15 μ . These bands may

be due to the isotopic molecules or to impurities. These bands were of the order of magnitude in intensity of the band at 2.88 μ . This weak band was included because it corresponded to the combination term, $\nu_3+3\nu_1$, which also was observed for cells of considerable length in CO₂.

V. Conclusion

The spectrum of liquid CS₂ has been classified in terms and combinations analogous to those that have been found to exist for CO₂. All the intense bands except one, fall into the forecast terms. Some weak bands are also classified. The spectrum supports the conclusion that the molecular configuration of CS₂ is linear and symmetrical. The selection rules are followed very well, but not in all cases. As forecast by theory, $2\nu_2$ at 794 cm⁻¹ and $2\nu_3$ at 3,014 cm⁻¹ are not observed, but $3\nu_2$ and $3\nu_3$ are present as weak bands.

Except for the region of 4.6 and 6.6 μ , thin cells of CS₂ are fairly transparent from the visible region to 24 μ . For this reason it is useful as a solvent in infrared measurements.

VI. References

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