The Infrared Absorption Spectrum of Carbon Suboxide

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The infrared absorption spectrum of carbon suboxide vapor has been studied under low dispersion in the region from 2μ to 25μ. The vibrational bands observed may be satisfactorily accounted for on the basis of a linear symmetric structure for the carbon suboxide molecule, in agreement with evidence obtained from Raman spectra and from electron diffraction investigations.

R ECENT studies of the structure of the carbon suboxide molecule by electron diffraction[1,2] and by ultraviolet absorption and Raman spectra[3-5] have made desirable an investigation of the molecule's absorption spectrum in the infrared region. The information to be gained from such an investigation should be particularly helpful since the spectroscopic and electron diffraction evidence indicates that the most probable form of the carbon suboxide molecule is one possessing a symmetry center. For such a structure the Raman and infrared absorption spectra are complementary, the fundamental frequencies active in either type of spectrum being inactive in the other.

We have studied the absorption by carbon suboxide vapor under various pressures in the region between 2μ and 25μ. The absorption curves were made with the KBr prism, vacuum, recording spectrometer of Randall and Strong[6] operated in conjunction with the periodic amplifier described by Firestone.[7] The cell containing the absorbing gas was 12 cm in length, with plane polished KBr windows cemented to each end. The customary Nernst glower furnished the infrared radiation.

Professor J. O. Halford kindly supplied several samples of liquid carbon suboxide, of two or three cubic centimeters each, for our use. The

material was prepared by the pyrolysis of diacetyl tartaric anhydride[8] and was purified by two distillations in an all-glass system. Measurements of the vapor pressure of the suboxide over a range of temperatures up to 0°C agreed satisfactorily with those in the literature.[9] The absorption cell was filled by distilling the *middle* fraction of the particular sample at hand into the evacuated cell, the desired pressure being obtained by surrounding the distilling vessel with a bath of acetone of the proper temperature.

While in every instance we were satisfied before making the absorption measurements that the carbon suboxide in the cell was of suitable purity, each absorption curve was examined for the presence of bands due to foreign

TABLE I. *Absorption bands of carbon suboxide.*

WAVE-LENGTH IN μ	WAVE-NUMBER IN CM^{-1}	PERCENT ABSORPTION		
		$p = 14$ mm	67 mm	200 mm
2.18	4590		5	
2.64	3790		30	
2.96	3380		5	
3.17	3150	—	30	40
4.15	2410 ⎫			
4.37	2290 ⎬	80	90	95
4.57	2190 ⎭			
5.05	1980	—	10	unresolved
5.41	1850	—	5	unresolved
5.68	1760	25*	40	80
5.98	1670		40	80
6.37	1570	25	75	95
6.80	1470	5	10	25
7.21	1387	20	30	70
8.16	1225	—	2	15
8.88	1126	—	10	35
9.76	1024	—	5	20
11.00	909	10	30	65
11.24	889	—	25	60
12.84	779	—	20	40
15.70	637	15	60	75
17.94	557		75	
18.18	550	50	65†	90
18.40	544		70	

Spectral range: 14 mm: $3\mu-20\mu$; 67 mm: $2\mu-25\mu$; 200 mm: $3\mu-25\mu$.
* Water vapor band on a blank run with source intensity comparable to that used for the 14 mm run absorbs some 20 percent at this point. Most of this band in the 14 mm curve is doubtless due to water.
† Central minimum of this band resolved only in 67 mm curve.

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[1] Brockway and Pauling, Proc. Nat. Acad. Sci. 19, 860 (1933).

[2] Boersch, Naturwiss. 22, 172 (1934); Wien Ber. 144 (IIb) 1 (1935).

[3] Badger and Barton, Proc. Nat. Acad. Sci. 20, 166 (1934).

[4] Thompson and Healey, Proc. Roy. Soc. (London) A157, 331 (1936).

[5] Engler and Kohlrausch, Zeits. f. physik. Chemie B34, 214 (1936).

[6] H. M. Randall and J. Strong, Rev. Sci. Inst. 2, 585 (1931).

[7] F. A. Firestone, Rev. Sci. Inst. 3, 163 (1932).

[8] Hurd and Pilgrim, J. Am. Chem. Soc. 55, 757 (1933).
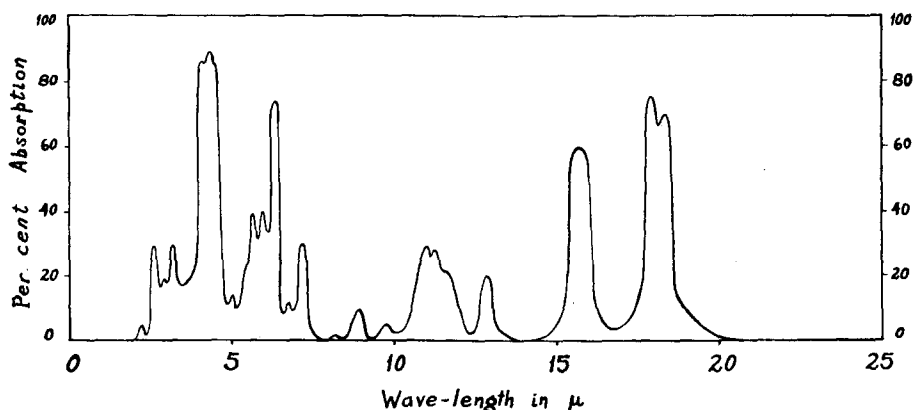
[9] E.g., reference 4, p. 332.

FIG. 1. Infrared absorption of carbon suboxide vapor. Cell length, 12 cm; pressure, 67 mm.

gases. Absorption bands in the region $3.2–3.5\mu$ were either extremely weak or nonexistent. Since compounds with the $C-H$ linkage exhibit rather powerful absorption in this region, the concentration of such possible impurities as ketene, acetic acid and other pyrolytic products with $C-H$ groups must have been very small. The weak carbon dioxide bands present in the absorption curves were of the intensity to be expected from the amount of carbon dioxide in the air path of the incident radiation. The fundamental band of carbon monoxide, if present in the absorption curves, would have been masked by the strong and rather wide absorption band found at 4.4μ.

In the paper of Thompson and Healey,[4] attention is called to the possibility that carbon suboxide prepared by the pyrolytic method may be contaminated with a small amount of sulfur dioxide. There is no trace in our absorption curves of the strong sulfur dioxide fundamental at 8.67μ. The other strong fundamental, at 7.40μ, might be partially obscured by the 7.21μ band of the carbon suboxide spectrum, but the shape of the latter band gives no indication of a satellite on the long wave-length side. The remaining sulfur dioxide bands are of lower intensity, and of these, the ones which do not coincide with the bands of the suboxide make no appearance on the absorption records.

It might be of interest to remark that at no time did we experience difficulty due to polymerization of the carbon suboxide vapor in the absorption cell. Measurement of the pressure of the gas after it had remained in the cell for several days

always led to the value, within a millimeter or two, of the initial pressure with which the cell had been filled. When the cell was filled for the first time (at about 700 mm pressure), a very faint fogging of the windows was observed after a few hours. This cloudiness did not increase with time, however. The windows were not visibly less transparent after the cell had been filled and emptied several times than at the time when the fogging was first observed. The absorption of the clouded windows was tested with the cell exhausted to an oil pump vacuum. Only those absorption bands due to the carbon dioxide and water vapor in the 50 cm airpath outside the spectrometer were observed. No trace of the strong bands of carbon suboxide appeared.

Absorption curves were made with the carbon suboxide under pressures of 14, 67, 200 and 700 mm. The absorption of the gas under 700 mm was not studied over the whole available range of the spectrograph because in the region first explored, from 10 to 20μ, it was found that absorption was too strong to allow satisfactory resolution of the individual bands. Table I lists the wave-lengths and wave numbers of the observed bands, together with the approximate percentages of absorption under the several pressures. Of these pressures, 67 mm was found to be the most favorable for resolution of the structures of the various bands. The curve for 67 mm is reproduced in Fig. 1. As the figure indicates, no absorption bands were found between 20 and 25μ.
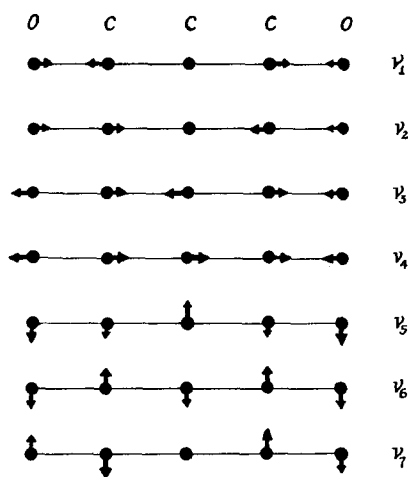
FIG. 2. Modes of vibration for linear carbon suboxide molecule.

DISCUSSION OF RESULTS

To interpret the infrared absorption data, one may make profitable use of some preconceptions about the structure of the carbon suboxide molecule. From the electron diffraction studies,[1, 2] it appears very likely that all the atoms in carbon suboxide are on a line, and furthermore that the oxygen atoms and two of the carbon atoms are symmetrically disposed about the third carbon atom. Valence requirements dictate that the oxygen atoms occupy the two outermost positions.

The interatomic distances C−O and C−C as determined from the diffraction patterns lead to a calculated moment of inertia of 390×10^{-40} gram-cm^2 for the linear model. The spacing of the rotational lines for such a molecule will have the hopelessly small value of 0.14 cm^{-1}, and even the "spread" in the maxima of the P and R branch envelopes will amount to no more than 11 cm^{-1} at room temperature. Since the envelope maxima are not at all sharp, one would hardly expect the prism spectrometer to resolve the vibration bands into their rotational components, at least not those bands having wavelengths less than about 15μ. The rotational structure of the absorption bands will therefore not concern us, and we shall consider only their vibrational interpretation.

The essential elements of symmetry of the suggested structure are the figure axis and the symmetry center. A pentatomic molecule of this symmetry has seven vibration frequencies, three of which are doubly degenerate. The vibrational modes are shown in Fig. 2. Our frequency enumeration follows that of Engler and Kohlrausch.[5] These authors, as well as Thompson and Healey,[4] give both the vibration forms and also equations for the frequencies based on simple potential systems of the valence force type.

The four nondegenerate frequencies, which preserve the figure axis as an element of symmetry, may be classified as symmetrical (ν_1 and ν_2) and antisymmetrical (ν_3 and ν_4) to the symmetry center. The totally-symmetrical ν_1 and ν_2 may appear in the Raman effect, while ν_3 and ν_4, which produce temporary electric moments along the figure axis, should be active in infrared absorption. By estimating force constants from analogous frequencies in carbon dioxide and allene, Engler and Kohlrausch calculate that ν_1 and ν_2 should appear, respectively, at about 2200 cm^{-1} and 800 cm^{-1}. They are thus able to identify the Raman frequencies observed at 2200 cm^{-1} and 843 cm^{-1} with these vibrations. Having accomplished this assignment, they can then compute accurate values of the force constants and predict that ν_3 should lie at 2458 cm^{-1} and ν_4 at 1627 cm^{-1}. This prediction enables us to assign with some assurance the very strong infrared band at 2290 cm^{-1} to ν_3 and the strong band at 1570 cm^{-1} to ν_4.

The Engler-Kohlrausch frequency equations for the linear vibrations involve four constants, which measure the forces required to: (1) stretch the C−O bond; (2) stretch the C−C bond; (3) enlarge the distance between an oxygen atom and the central carbon; (4) enlarge the distance between the two noncentral carbons. It is of interest to calculate these constants with the help of the infrared data. If one makes the assumption that the constants (3) and (4) are negligibly small, calculation of (1) and (2) may be made independently from the Raman and from the infrared frequencies. In both instances one finds that the observed frequencies lead to imaginary values for (1) and (2), an indication that the simple valence force picture is an inadequate one. Straightforward solution of the four equations gives for the constants: (1) 13.7; (2) 9.1; (3) 1.2 and (4) 2.5, all in units of 10^5

dynes per cm. These may be compared with the values found from carbon dioxide: (1) 14.1; (3) 1.3 and from allene: (2) 9.5. No particular physical significance is to be attributed to the constants (3) and (4), save that their sizes indicate the extent to which the respective valence bond forces depart from quasi-elastic form.

Of the three degenerate frequencies, ν_7 alone is to be expected in the Raman effect. Since this vibration involves only the distortion of the $C-C-O$ bond angle, its frequency may be estimated with the help of the constant for the distortion of the $O-C-O$ angle in carbon dioxide. The calculated value lies very close to 586 cm^{-1}, the frequency of a line in the Raman spectrum. Engler and Kohlrausch have therefore assigned the latter to ν_7. These authors then proceed to compute the remaining degenerate frequencies by assuming that the constants for bending the $C-C-C$ angle and the $C-C-O$ angle are about equal. In this way they find $\nu_5 = 227$ cm^{-1} and $\nu_6 = 937$ cm^{-1}.

It should be noted here that the useful supposition of the equality of the two distortion constants, while necessary because further information is wanting, is a very rough assumption. One should therefore regard the calculated values of ν_5 and ν_6 simply as guides to the general spectral region in which these frequencies are likely to appear. In addition it is by no means safe to assume that the "constant" for the distortion of the $C-C-O$ angle will have the same value in ν_5 and ν_6 as in ν_7. In closely analogous vibrations in acetylene and in benzene, it has been found that the corresponding bending "constants" are numerically quite different for frequencies of different symmetry types.[10]

Unless something is quite seriously wrong with the assumptions which have been made in order to calculate ν_5, that frequency should lie in the range 40–50μ, i.e., well beyond the limit of our spectrograph. Thus ν_5 will occur in our absorption curves only in combination tones. On the other hand ν_6 should appear at about 11μ, and

there is actually observed at this point a rather wide band of medium intensity. One might attribute this band confidently to ν_6 if it were not for certain disquieting features of the absorption spectrum between 15 and 20μ. In this range are found two bands whose intensities are very large in comparison with the 11μ band. Assignment of either of these bands to ν_6 is not ruled out by calculations as rough as those which placed ν_6 at 11μ. If ν_6 be identified with either band, however, the other must still be interpreted and some alternative explanation worked out for the 11μ band. It is thus essential to consider the frequencies at which it is possible for overtones to appear.

Fortunately the appearance of overtones is considerably restricted by molecular symmetry. In the infrared absorption spectrum of a linear molecule with a symmetry center, all combinations tones must involve one or more fundamental frequencies antisymmetric to the symmetry center, and the changes in the quantum numbers of these antisymmetric frequencies must add up to an odd integer.[11] From this rule it follows readily that no observed band is the sum of or difference between other observed bands, and that the even overtones (e.g., $2\nu_5$, $4\nu_5$) of the active fundamentals never appear. The selection rule is a "strong" rule, for it follows from the symmetry properties of the molecular potential function and does not depend on assumptions of harmonic forces or on neglect of higher terms in the power series development for the vibrating electric moment.

The selection principle requires that binary combinations tones (i.e. tones in which the quantum numbers of only two frequencies change, each by one unit) be composed of one Raman active and one infrared active vibration. The binary combinations may be either summation or difference frequencies, but it must be kept in mind that the latter will have appreciable intensities only for combinations involving ν_5, since only for ν_5 should the Boltzmann factor have a value large enough to be comparable to unity. Binary tones involving ν_3 and ν_4 will therefore be observed below 5μ, and our interpretation of the region from 5 to 20μ must consider only combinations with ν_5 and ν_6.

[10] Compare the acetylene vibrations ν_4 and ν_5 (Colby, Phys. Rev. **47**, 388 (1935)) which are analogous to $\nu_{5, 6}$ and ν_7 in carbon suboxide. Difficulties with the calculation of the corresponding frequencies in benzene, ν_{11} and ν_{10}, have been pointed out by Kohlrausch, Zeits. f. physik. Chemie **B30**, 313 (1935) and by Lord and Andrews, J. Phys. Chem. **41**, 151 (1937).

[11] See Dennison, Rev. Mod. Phys. **3**, 297 (1931).

Table II. *Allowed combination tones involving ν_6.*

Combination	Calculated, $\nu_6 = 550$ cm⁻¹	Observed Band at:	Calculated, $\nu_6 = 900$ cm⁻¹	Observed Band at:
Binary:				
$\nu_1 + \nu_6$	2750	—	3100	3150
$\nu_2 + \nu_6$	1390	1387	1740	1760*
$\nu_7 + \nu_6$	1130	1126	1480	1470
Ternary:				
$3\nu_6$	1650	1670*	2700	—
$2\nu_6 + \nu_3$	3390	3380*	4100	—
$2\nu_6 + \nu_4$	2670	—	3370	3380*
$2\nu_6 + \nu_5$	1290	—	1990	1980
$2\nu_6 - \nu_5$	910	909	1610	1670*
$\nu_6 + 2\nu_2$	2230	2290	2580	—
$\nu_6 + 2\nu_4$	3690	—	4040	—
$\nu_6 + 2\nu_5$	930	909	1280	—
$\nu_6 - 2\nu_5$	180	—	520	550
$\nu_6 + 2\nu_7$	1720	1760*	2070	1980
$\nu_1 + \nu_2 + \nu_6$	3590	—	3940	—
$\nu_1 + \nu_6 + \nu_7$	3340	3380*	3680	3790
$\nu_2 + \nu_6 + \nu_7$	1980	1980	2330	2290

All observed bands except those marked * may be satisfactorily interpreted independently of ν_6.

Assuming for the moment that the estimated value of ν_5 is correct, we should expect the band $\nu_7 + \nu_5$ at about 800 cm⁻¹, $\nu_2 + \nu_5$ at 1060, $\nu_1 + \nu_5$ at 2420, $\nu_7 - \nu_5$ at 360 cm⁻¹, $\nu_2 - \nu_5$ at 620 and $\nu_1 - \nu_5$ at 1970. Intensity maxima are actually observed at 779 cm⁻¹, 1024, 2410, 637 and 1980. (360 cm⁻¹ is not within the range of the spectrometer.) The absorption spectrum thus indicates that the frequency calculated for ν_5 is probably roughly correct but somewhat large. The combination tones place ν_5 at 200 cm⁻¹.

If the wide band at 900 cm⁻¹ be assigned to ν_6, the very strong absorption at 550 cm⁻¹ must be given an interpretation involving ν_5. Since we have already seen that the binary tone $2\nu_5$ is forbidden, it is quite reasonable to interpret the band as the first allowed overtone to ν_5, namely $3\nu_5$. This interpretation implies a ν_5 of about 185 cm⁻¹, in fair agreement with the value suggested by the assignment of the binary tones. The intensity of this band is remarkably high for an overtone, and indicates that the fundamental should exhibit extremely strong absorption. The corresponding overtone in CO_2 was found by Barker and Wu by using a pressure of about an atmosphere and a cell seven feet long.[12]

If $3\nu_5$ shows such strong absorption, it is quite possible that $5\nu_5$ should appear with

appreciable intensity. The roughly calculated frequency of $5\nu_5$ is 920 cm⁻¹, which lies just in the region of the absorption band we have ascribed to ν_6. This unfortunate coincidence is the source of considerable trouble, for it prevents a clear-cut decision on the origin of the 900 cm⁻¹ band. Assuming provisionally that the band is due *only* to $5\nu_5$ we may use the observed frequency of the band in conjunction with that of the 550 cm⁻¹ band to calculate the frequency of the fundamental. The two bands provide the data required to solve an anharmonic frequency formula[13] for the necessary constants. The frequency obtained is $\nu_5 = 190$ cm⁻¹.

The anharmonicity expression also helps to account for the doublet structure exhibited by the two bands. The doublets might be explained as rotational branches except that: (1) a Q branch ought also to be present; (2) the maxima of the P and R branches should be 11 cm⁻¹ apart, while the observed spacing is 14 cm⁻¹ in the 550 band and 20 cm⁻¹ at 900 cm⁻¹. On the other hand if it be assumed that the low frequency maximum in each doublet is due to transition from the first excited vibrational level, the spacings calculated from the anharmonicity formula are 12 cm⁻¹ and 19 cm⁻¹, respectively. The shoulder on the low frequency slope of the 900 cm⁻¹ band and the broadness of the 550 cm⁻¹ absorption may be contributed by transitions from the second excited level. The first and second excited levels have population factors of 0.80 and 0.46, referred to the ground state population.

An alternative explanation of these bands has been suggested to us by Professor Dennison. If the 550 band be assigned to ν_6, resonance degeneracy may occur between ν_6 and $3\nu_5$. Such an accidental degeneracy would lead to a small splitting of the 550 frequency and would account for the observed doublet structure of that band. In addition the doublet nature and the intensity (which is rather large for so high an overtone) of the band at 900 cm⁻¹ are understandable on the basis of resonance degeneracy.[14] It is clear that a study of these bands under high

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[12] Barker and Wu, Phys. Rev. **45**, 1 (1934).

[13] Cf. Dennison, reference 11, p. 296.

[14] Cf. the relatively high intensity of the overtones at 3610 and 3717 cm⁻¹ in CO_2. This pair of bands constitutes a resonance doublet.

TABLE III. *Interpretation of observed bands.*

Observed Band:		CALCULATED FREQUENCY IN CM⁻¹	INTERPRETATION
λ in μ	$\bar{\nu}$ in cm⁻¹		
18.12	550	[550]*	$[\nu_6](3\nu_5)$*
15.70	637	650	$\nu_2 - \nu_5$
12.84	779	780	$\nu_5 + \nu_7$
11.00	909	930 (900)	$\nu_6 + 2\nu_5(\nu_6)$
9.76	1024	1030; 980	$\nu_2 + \nu_5;\ 2\nu_7 - \nu_5$
8.88	1126	1140 (1140)	$\nu_6 + \nu_7(3\nu_5 + \nu_7)$
8.16	1225	1190; 1240	$\nu_4 - 2\nu_5;\ \nu_2 + \nu_7 - \nu_5$
7.21	1387	1390 (1390); 1360	$\nu_2 + \nu_6(\nu_2 + 3\nu_5);\ \nu_5 + 2\nu_7$
6.80	1470	1500 (1490)	$2\nu_2 - \nu_5(\nu_6 + \nu_7)$
6.37	1570	[1570]	$[\nu_4]$
5.98	1670	1650; 1720 (1610; 1720)	$3\nu_6;\ 2\nu_7 + \nu_6(2\nu_6 - \nu_5;\ 2\nu_7 + 3\nu_5)$
5.68	1760	1720 (1740)	$2\nu_7 + \nu_6(\nu_2 + \nu_6)$
5.41	1850	1880; 1910	$2\nu_2 + \nu_5;\ \nu_3 - 2\nu_5$
5.05	1980	1910; 2010 (1990)	$\nu_3 - 2\nu_5;\ \nu_1 - \nu_5(\nu_5 + 2\nu_6)$
4.57	2190	2160 (2070)	$\nu_4 + \nu_7(\nu_6 + 2\nu_7)$
4.37	2290	[2290]	$[\nu_3]$
4.15	2410	2390; 2410	$\nu_1 + \nu_5;\ \nu_2 + \nu_4$
3.17	3150	3130 (3100)	$\nu_2 + \nu_3(\nu_1 + \nu_6)$
2.96	3380	3340; 3390 (3370)	$\nu_1 + \nu_6 + \nu_7;\ 2\nu_6 + \nu_3(2\nu_6 + \nu_4)$
2.64	3790	3770 (3690)	$\nu_1 + \nu_4(\nu_1 + \nu_6 + \nu_7)$
2.18	4590	4490	$\nu_1 + \nu_3$

* The interpretation enclosed in parentheses is that for $\nu_6 = 900$ cm⁻¹. Frequencies calculated on this interpretation are also put within parentheses. The square brackets enclose fundamental frequencies whose values were used in finding the calculated frequencies. We have used for the Raman active frequencies: $\nu_1 = 2200$ cm⁻¹; $\nu_2 = 843$ cm⁻¹; $\nu_7 = 586$ cm⁻¹.

resolution is prerequisite to a satisfactory interpretation of them.

Because the strong bands which might be attributed to ν_6 may also be accounted for in other ways, we must resort to combination tones to find a value for ν_6. Table II lists the allowed binary tones and such ternary tones involving ν_6 as should appear in the spectroscopic region we have studied. With two exceptions the difference tones have been excluded from the Table because their Boltzmann factors are too small (<0.1). The frequencies of the indicated combinations have been calculated for $\nu_6 = 550$ cm⁻¹ and 900 cm⁻¹, and the frequencies of bands near the calculated values listed for comparison. It is apparent that neither assumed value of ν_6 is clearly superior to the other in interpreting those bands (marked with an asterisk) for which no alternative explanation is possible. The assignment $\nu_6 = 550$ is favored by the fact that the 1670 band, of fairly strong absorption, is attributed to the lowest allowed overtone of a strong fundamental. The interpretation of this band for $\nu_6 = 900$ is not particularly convincing because it involves a difference tone for which the corresponding summation frequency is quite weak. On the other hand, several frequencies

predicted by the 550 interpretation are missing from the spectrum, in particular $\nu_1 + \nu_6$ and $2\nu_6 + \nu_5$. These bands should be expected to have appreciable intensity.

Under the 900 cm⁻¹ assignment, absorption bands are observed for all the binary combinations. One of these bands can be interpreted only with the help of ν_6. The expected ternary combinations are found experimentally except for the important bands $3\nu_6$ and $2\nu_5 + \nu_6$.

On the whole it does not seem possible to make a definite assignment for ν_6 on the basis of the data we have obtained. Further argument in favor of assignment to the 550 frequency is to be found in the remarkable intensity of this band, which seems surprisingly strong for a third overtone. In addition when $\nu_6 = 550$ cm⁻¹, all the interpretations involving $3\nu_5$ (see Table II) apply equally well if $3\nu_5$ be replaced by ν_6 so that none of these interpretations is invalidated by such an assignment.

If ν_6 be in truth at 900 cm⁻¹ it must be weak enough so that it becomes confused with the other frequencies in the 11μ band. One should point out, however, that the low intensity of ν_6 is readily understandable from the form of the vibration. Suppose that in the distortion vibra-

tions the center of one electrical charge, either positive or negative, be at the central carbon atom and two centers of the other charge on the oxygen atoms. The vibrating electric moment in ν_6 should then be small because both the positive and negative charges move in the *same* direction and about the same amount. On the other hand ν_5 should have a large vibrating moment on this basis, and ν_5 should be quite intense. The latter fact is compatible with the assignment of $3\nu_5$ to the band at 550 cm^{-1}.

The presence of two apparent overtones at 1114 and 1174 cm^{-1} in the Raman spectrum of carbon suboxide might assist our assignment of ν_6. The latter line is very probably $2\nu_7$ and is of no help. $2\nu_6$ is also an allowed overtone in the Raman effect, and if this interpretation be placed on the 1114 cm^{-1} frequency, we obtain $\nu_6 = 557$, in excellent agreement with the absorption band at 550 cm^{-1}. Unhappily for this argument, however, the combination tone $\nu_5 + \nu_6$ is also allowed in the Raman effect, and if ν_6 be given a value slightly larger than 900 cm^{-1}, we find $\nu_5 + \nu_6 = 1114$ cm^{-1}. The Raman spectrum thus does not permit an unequivocal decision.

In passing it might be remarked that the suggestion of Engler and Kohlrausch[5] of resonance splitting to account for these weak lines is probably not acceptable. The proposed interaction of $\nu_5 + \nu_6$ with $2\nu_7$ satisfies symmetry requirements, but such a perturbation is a second-order effect and should result in a splitting of a few wave-numbers at the most, rather than the observed 60 cm^{-1}. The large splitting of 103 cm^{-1} in the Raman spectrum of CO_2 is due to a first-order perturbation.

Patently further experimental study will be required to settle the assignment of ν_6. It would be of great assistance if the region from 2 to 7μ and the bands at 11μ and 18μ could be examined under considerably higher resolution. If a clearer notion of the individual components of these bands could be obtained, a definite decision about ν_6 might be possible. Direct experimental confirmation of the fundamental at 52μ would also be of interest.

We have assembled in Table III the complete interpretation of the observed bands. The interpretation is double for some bands because of

our indecision with respect to ν_6. Since one or two quaternary bands may be found in the Table, we should state that we have examined systematically the three hundred or more possible quaternary tones. Nearly all of these may be rejected without further consideration because of one or more of these reasons: (1) wavelength outside the 2–25μ region; (2) Boltzmann factor too small (for difference bands); (3) very low predicted intensity, from consideration of observed intensities in analogous but simpler tones.

Despite our failure to assign definite values to all of the infrared active fundamentals, we have produced forceful evidence in favor of the symmetric linear structure for carbon suboxide. In the first place, there is no indication of the presence of Raman active frequencies in the absorption curve. Any sign of ν_1 would be obscured by the ν_3 band, but if there is absorption due to a frequency at 843 cm^{-1} (ν_2) it should certainly appear definitely close to 12μ. The long wave-length slope of the 11μ band shows no trace of an absorption band near 12μ. There is absolutely no indication of an absorption band at 586 cm^{-1} (ν_7). Similarly no sign of the strong infrared bands at 550, 635, 900, 1570 and 2290 cm^{-1} appears in the Raman spectrum. This is an excellent indication that the molecule in question contains a center of symmetry.

We have remarked previously that no band in the absorption spectrum of a symmetric linear molecule should be expressible, except by accident, as the sum of two other bands. Examination of the spectrum of carbon suboxide shows that this rule holds in the region of the spectrum where resolution is good enough to make the bands fairly narrow and the maxima sharp. For example, no absorption occurs at the sum of the two strong bands 550 and 635, at 550 plus 779, at twice 550 or at twice 635. This is further evidence for the postulated structure.

Finally the unmistakable appearance of the linear frequencies ν_3 and ν_4 close to the predicted points is an indication that the equations developed for a linear structure are valid for carbon suboxide. Agreement of the force constants with the analogous constants in the carbon dioxide molecule also supports the linear model.

In our opinion the preceding evidence is

sufficient to rule out any nonlinear or asymmetric structure for carbon suboxide. It is disappointing that we cannot make a complete vibrational analysis of the absorption spectrum, but it appears quite probable that absorption studies made under higher resolution will enable the

analysis to be completed. We are grateful to Professor Halford for his kindness in furnishing us with the carbon suboxide, to Professor Randall for placing the spectrometer at our disposal and particularly to Professor Dennison for helpful discussions.

Calculation of the Heat Capacity Curves of Crystalline Benzene and Benzene-d₆

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The heat capacity curve for solid benzene has been computed with the help of the set of internal frequencies previously proposed by Lord and Andrews. The agreement with experiment is satisfactory over the entire temperature range in which the internal frequencies contribute, indicating that the frequency values are essentially correct. A prediction of the heat capacity of benzene-d₆ has also been made.

THE existence of a complete set[1] of values for the internal frequencies of the benzene molecule makes it possible for the first time to calculate directly the contribution of these degrees of freedom to the heat capacity of crystalline benzene. Earlier attempts[2] to carry out computations of this sort involved empirical and rather rough estimates of these frequencies, and led only to qualitative information concerning the specific heat of the crystal. A precise calculation of the heat capacity of solid benzene is of interest, particularly in view of the experimental data obtained at "helium" temperatures recently by Ahlberg, Blanchard and Lundberg[3] and the other excellent values at higher temperatures which can be compared with calculated values. Our discussion will be concerned with this calculation and the conclusions to be drawn from such a comparison.

When thermal energy is absorbed at constant pressure by a crystalline solid such as benzene, this energy is distributed among: (1) the oscilla-

tions of the crystal lattice; (2) the internal vibrations of the molecules composing the lattice; and (3) the work of expanding the lattice. Before discussing these three components of the specific heat, we must emphasize that our ultimate interest lies in the contribution (2). Contributions (1) and (3) will be evaluated as accurately as possible by means of the traditional expressions for them, but it is not our purpose to improve these expressions or to criticize their theoretical origins.

Experience has shown that the share of the lattice vibrations in the specific heat of a crystal is ordinarily described rather accurately by the familiar Debye function $D(x)$:

$$C_v \text{ (lattice)} = 3RD(x),$$

$$D(x) = \frac{12}{x^3} \int_0^x \frac{z^3 dz}{e^z - 1} - \frac{3x}{e^x - 1}, \quad (2)$$

in which x is the parameter $(h\nu_D/kT)$. ν_D is the well-known Debye characteristic frequency which must be determined in some way if we are to utilize the function $D(x)$.

The physical significance of ν_D has been the subject of much discussion. In a recent critique

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[1] Lord and Andrews, J. Phys. Chem. 41, 149 (1937).
[2] D. H. Andrews, Proc. Roy. Soc. Amst. 29, 744 (1926); Chem. Rev. 5, 533 (1928); E. O. Salant, Proc. Nat. Acad. Sci. 12, 334, 370 (1926).
[3] J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, J. Chem. Phys. 5, 539 (1937).