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Infrared Spectra of Bromochloromethane, Dibromomethane, Tribromochloromethane, and Tetrabromomethane

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The infrared spectra of bromochloromethane, dibromomethane, tribromochloromethane, and tetrabromomethane have been measured from 2 to 36 microns. By the use of the results of other workers in Raman spectra it has been possible to classify all the strong bands that have been observed. Many of the weaker bands were classified as combinations and overtones. Only a few of the bands of tetrabromomethane were observed, on account of the breaking down of the compound in solutions of carbon disulfide and carbon tetrachloride. The intense bands of dibromomethane and tetrabromomethane were measured in the vapor state. The infrared absorption bands of these compounds had not previously been measured over an extended range of wavelengths, and these measurements were undertaken to determine the positions of weak bands so that a more complete classification of the spectra of these molecules could be made.

I. Introduction

Other workers have measured the vibrational bands of a number of substituted methanes in the infrared region, and also the frequencies have been determined by Raman spectra. From theory it has been determined that molecules of the type of CX_4 show two active and two inactive fundamentals. Where interaction occurs the inactive frequencies also appear in the infrared spectrum. When the substituted atoms are of more than one species, the degeneracy is removed and nine fundamentals are present in the spectrum. In a molecule of the type CXY_3, the degeneracy is only partly removed and six fundamentals are found in the spectrum.

The four substituted methanes, bromochloromethane, dibromomethane, tribromochloromethane, and carbon tetrabromide, represent the the three types of molecules that give nine, six, and two active fundamentals in the infrared spectrum. The infrared bands of these compounds had not previously been measured over an extended range of wavelengths, and these measurements were undertaken to determine the positions of the weak bands so that the combination bands could be classified.

II. Experimental Observations

A Perkin-Elmer spectrometer was used for all measurements with lithium fluoride, potassium bromide, sodium chloride, and thallium bromide-iodide prisms to cover the wavelength range of 2 to 36 μ. In the spectral region of 2 to 24 μ, cell thicknesses of 0.2, 0.1, and 0.05 mm were used to bring out most of the bands. For very strong bands the compounds were diluted either in carbon tetrachloride or in carbon disulfide, or liquid films with a thickness of 0.01 mm or less were formed between two potassium bromide windows. In the thallium bromide-iodide region between 24 and 36 μ it was necessary to use cell thicknesses of 1.5 mm to bring out the weaker absorption bands. The method of measurement and the reducing of data have been described in a previous paper [1].[1] Bromochloromethane, dibromomethane, and tribromochloromethane were obtained from the Dow

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

Chemical Company and tetrabromomethane from the Eastman Kodak Company.

Purification consisted of treatments until an examination of the products indicated satisfactory agreement with accepted physical constants. To avoid any effect of oxygen, the infrared measurements were made as quickly as possible after purification.

Figure 1 shows the absorption spectra of the four halogenated methane derivatives in the region from 2 to 15 μ. The cell thicknesses and other conditions of the measurements are given on the figure and in the captions. The intense bands were observed by use of a cell that contained a thin layer of the material. The cell was made by placing a small quantity of the liquid on a plate of potassium bromide and then pressing another plate on the top without the use of a shim. The thicknesses of the cells made in this manner were not measured, but it is estimated that they were of the order of 0.005 mm. This estimate of the thickness was made on the basis of the percentage absorption that was observed in a 0.1-mm cell when the compound had been diluted with a transparent solvent. The reason that the thin cell was employed was to locate the position of the band accurately for the pure liquid in regions of intense absorption. In figure 1 the portions of the absorption curves represented by broken lines indicate that small details could not be accurately determined on account of the absorption of the solvents or the absorption of atmospheric bands.

As tribromochloromethane and tetrabromomethane are solids at room temperature, their spectra were determined in solutions of carbon tetrachloride and carbon disulfide. There was a tendency for the solutions of tetrabromomethane to darken on standing, and the absorption spectrum was

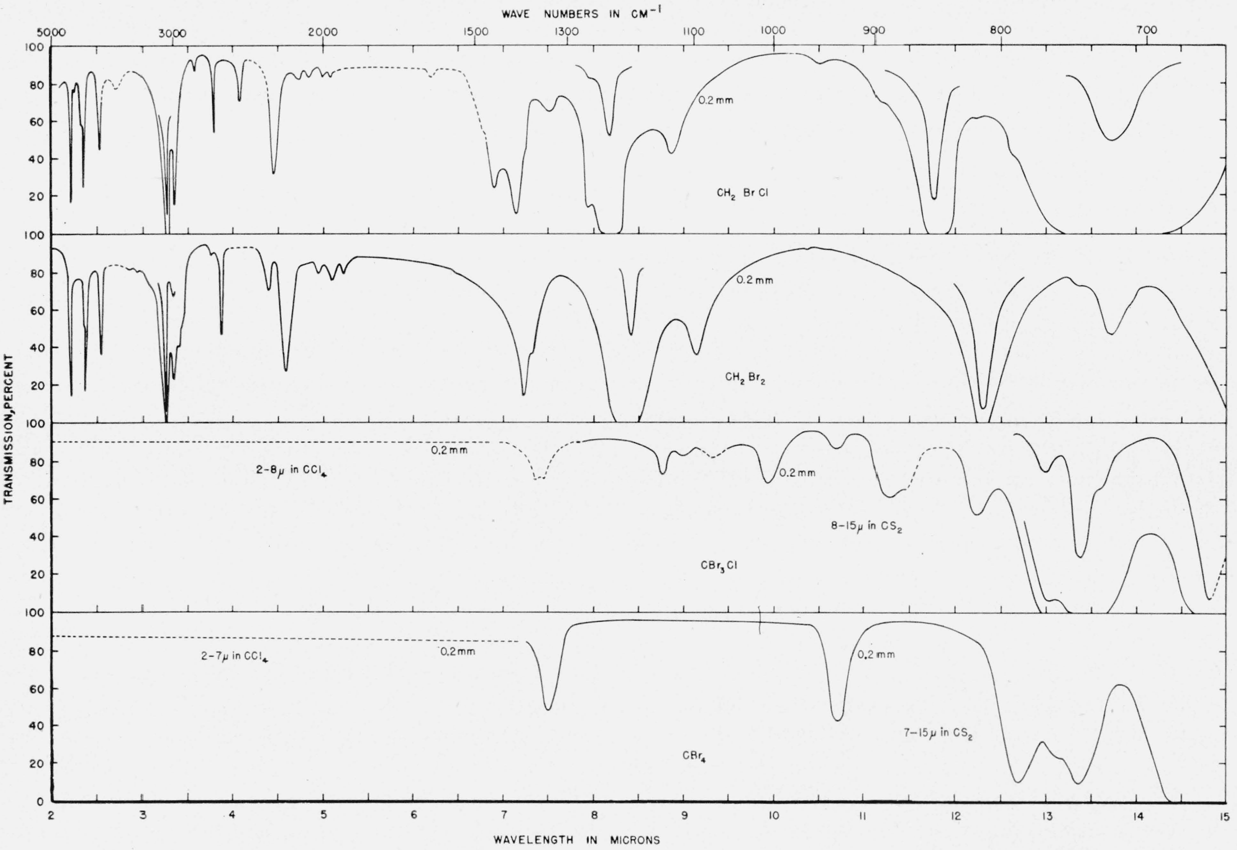

FIGURE 1. *Infrared absorption spectra of bromochloromethane, dibromomethane, tribromochloromethane, and tetrabromomethane.*

Tribromochloromethane and tetrabromomethane were dissolved in carbon tetrachloride and carbon disulfide. The solution concentration of tribromochloromethane in carbon tetrachloride is 3.1 g/ml, and in carbon disulfide, 2.4 g/ml for the observations in 0.2-mm cell. For the insert bands the concentration is 0.14 g/ml. Saturated solutions of tetrabromomethane were prepared in each solvent.

measured immediately after their preparation. The observations were repeated several times and the same bands were always found. Since it was possible to account for all the observed bands as combinations, overtones, or fundamentals, it does not seem probable that any of the observed bands were produced by products of decomposition or oxidation in the solution.

Figure 2 shows the long wavelength spectra of the four substituted methanes from 14 to 36 μ. Some general absorption was observed in the spectra of bromochloromethane and dibromomethane from 28 to 36 μ, but no definite bands could be found in this region. For the measurement of tribromochloromethane in the region of 24 to 36 μ, a saturated solution in methylcyclohexane was used. The methylcyclohexane has a high transmittance in this region, and its spectrum shows only one absorption band when a cell 1.5 mm thick is used.

In figures 3 and 4 are shown some of the absorption bands of dibromomethane and tetrabromomethane measured in the vapor state. The substances were placed in the bottom of a cell 40 cm long, which was not evacuated, and allowed to remain in the cell for several hours. On repeating the measurements 6 hours later, it was found that the bands did not increase in intensity. It is probable that the vapors were at a saturated condition in the air of the cell at 25° C.

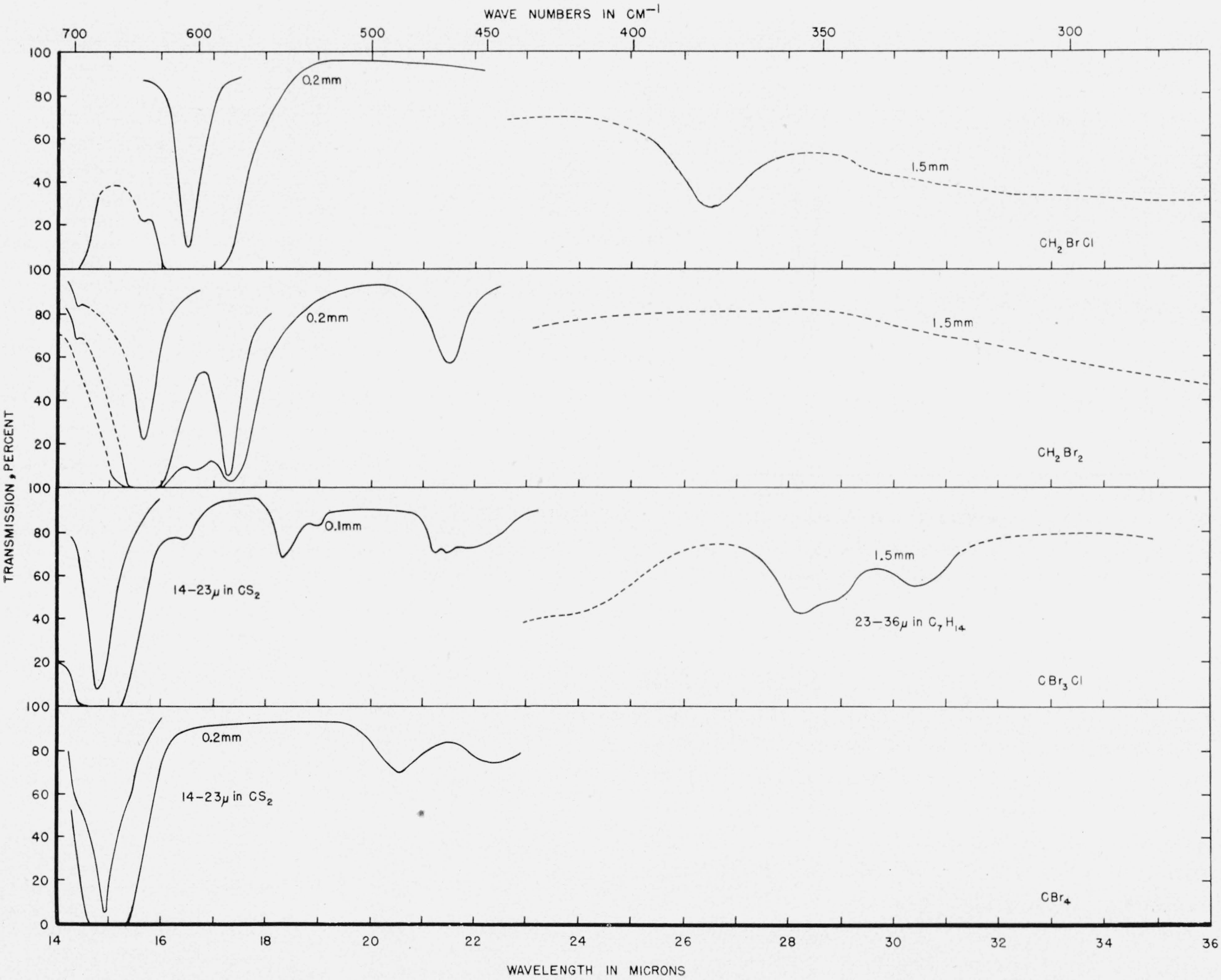

FIGURE 2. *Absorption spectra of bromochloromethane, dibromomethane, tribromochloromethane, and tetrabromomethane in the region from 14 to 36 μ.*

A solution concentration of 4.0 g/ml in carbon disulfide was used for tribromochloromethane with the 0.1-mm cell. A concentration of 0.14 g/ml was used in the 0.05-mm cell. A saturated solution in methylcyclohexane was used in the region of 24 to 36 μ.

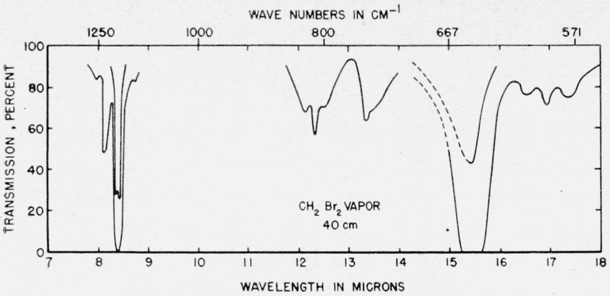

Figure 3. *Absorption spectrum of dibromomethane vapor from 7 to 18 μ.*

The more intense absorption is for the saturated vapor (45 mm of Hg at 25° C).

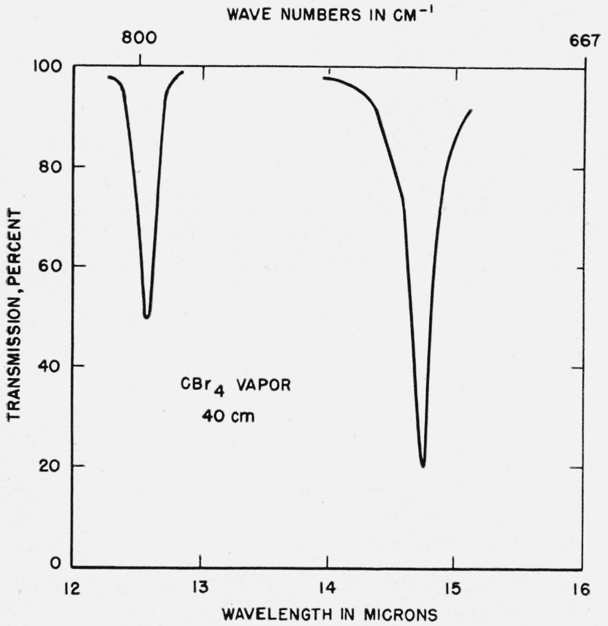

Figure 4. *Absorption bands at 12.6 and 14.9 μ for saturated vapor of tetrabromomethane at room temperature.*

III. Discussion

In table 1 are given the wavelengths and frequencies of the observed bands. These bands have been interpreted as fundamentals, combinations, and harmonics. The numbering of the levels is in accordance with that adopted for correlation of a large number of molecules of different symmetries, as will be discussed in a forthcoming paper by Plyler and Benedict. Eight of the infrared active fundamentals of bromochloromethane have been observed, and the other, occurring at 226 cm^{-1}, was outside the range of the thallium bromide-iodide prism. In the determination of the combination bands for this compound the Raman value was used from the work of W. Bacher and J. Wagner [2]. The other fundamental bands, as determined by Raman spectra, check within a few wavenumbers with infrared measurements given in table 1, except ν_7, which was estimated by them at 724 cm^{-1} from Raman

Table 1. *Observed frequencies of the infrared bands of bromochloromethane, dibromomethane, tribromochloromethane, tetrabromomethane, and their assignments*

Classification	ν	λ
BROMOCHLOROMETHANE		
	cm $^{-1}$	*Microns*
ν_4	[a] 226(R)	44. 2
ν_2	606	16. 51
ν_9	728	13. 73
ν_7	852	11. 76
ν_5	1, 130	8. 85
ν_8	1, 225	8. 16
ν_3	1, 402	7. 13
ν_1	2, 987	3. 348
ν_6	3, 060	3. 268
$\nu_2-\nu_4$	377	26. 5
$\nu_7-\nu_4$	638	15. 65
$\nu_4+\nu_9$	950	10. 52
?	1, 261	7. 93
$\nu_2+\nu_7$	1, 331	7. 51
$2\nu_9$	1, 453	6. 88
$\nu_5+\nu_8$	1, 969	5. 08
$\nu_2+\nu_3$	2, 004	4. 99
$\nu_7+\nu_8$	2, 006	4. 84
$\nu_3+\nu_9$	2, 119	4. 72
$\nu_3+\nu_7$	2, 242	4. 460
$2\nu_8$	2, 450	4. 082
$\nu_3+\nu_8$	2, 639	3. 789
$2\nu_3$	2, 803	3. 568
$\nu_1+\nu_9$	3, 751	2. 665
$\nu_6+\nu_7$	3, 939	2. 539
$\nu_1+\nu_8$	4, 228	2. 365
$\nu_3+\nu_6$	4, 502	2. 221
DIBROMOMETHANE		
ν_4	[a] 174(R)	57. 5
ν_2	579	17. 27
ν_9	639	15. 66
ν_7	813	12. 29
ν_5	1, 096	9. 12
ν_8	1, 190	8. 40
ν_3	1, 385	7. 22
ν_1	2, 988	3. 347
ν_6	3, 065	3. 263
$\nu_9-\nu_4$	466	21. 5
?	729	13. 71
$\nu_5-\nu_4$	922	10. 85
$\nu_4+\nu_8$	1, 366	7. 32
$\nu_5+\nu_7$	1, 912	5. 23
$\nu_3+\nu_2$	1, 961	5. 10
$\nu_3+\nu_9$	2, 020	4. 95
$2\nu_5$	2, 179	4. 59
$\nu_3+\nu_8$	2, 587	3. 866
$\nu_6+\nu_7$	3, 909	2. 558
$\nu_1+\nu_8$	4, 195	2. 384
$\nu_3+\nu_6$	4, 488	2. 228
DIBROMETHANE VAPOR		
	cm $^{-1}$	*Microns*
?	1, 233	8. 11
ν_8	1, 195	8. 37
ν_7	810	12. 34
?	745	13. 42
ν_9	648	------
ν_2	591	------
TRIBROMOCHLOROMETHANE		
ν_{25}	[a] 141(R)	70. 9
ν_{79}	[a] 214(R)	46. 7
ν_4	215(calc.)	46. 5
ν_3	329	30. 4
ν_{68}	675	14. 81
ν_1	747	13. 39
$\nu_{25}+\nu_{79}$	355	28. 2
$2\nu_4$, $2\nu_{79}$	436	22. 9
$\nu_3+\nu_{25}$	467	21. 4
$\nu_1-\nu_4$	525	19. 01
$\nu_3+\nu_{79}$	545	18. 35
$\nu_1-\nu_{25}$	608	16. 44
?	735	13. 61
$2\nu_4+\nu_3$	769	13. 00
$\nu_{68}+\nu_{25}$	817	12. 24
$\nu_{79}+\nu_{18}$	872	11. 47
$\nu_{68}+\nu_4$	886	11. 28
?	933	10. 69
$\nu_{68}+\nu_3$	1, 006	9. 94
$\nu_1+\nu_3$	1, 068	9. 33
$\nu_1+\nu_{25}+\nu_{79}$	1, 114	8. 98
$\nu_3+\nu_{25}+\nu_{68}$	1, 141	8. 76
$2\nu_{68}$	1, 350	7. 40
TETRABROMOMETHANE		
ν_{25}	[a] 123(R)	81. 3
ν_{479}	[a] 183(R)	54. 6
ν_3	[a] 267(R)	37. 4
ν_{168}	669	14. 95
$\nu_{168}+\nu_3+\nu_{479}$	748	13. 36
$\nu_{25}+\nu_{168}$	787	12. 70
$\nu_3+\nu_{168}$	934	10. 71
$2\nu_{168}$	133	7. 50
TETRABROMOMETHANE VAPOR		
$\nu_{25}+\nu_{168}$	796	12. 57
ν_{168}	678	14. 74

[a] (R) indicates Raman value obtained from literature.

spectra, and has been observed by us in the infrared spectra as a strong band at 852 cm^{-1}.

All of the fundamental bands of dibromomethane have been observed in the infrared spectrum except ν_4 at 174 cm^{-1}. This value has been determined by Dadieu and Kohlrausch and several other workers in Raman spectra [3]. The Raman spectra for the remaining eight fundamentals check well with these observations, except that ν_7 and ν_8 are found at 813 and 1,190 cm^{-1}, respectively, in the infrared as compared to 723 and 1,133 cm^{-1}, respectively, in the Raman spectrum as reported by Dadieu and Kohlrausch. The other observed bands, except for a few weak ones, have been classified on the basis of the nine fundamentals.

A close similarity between the spectrum of dibromomethane and of bromochloromethane is observed. The effect of replacing the chlorine in bromochloromethane by the heavier atom bromine is to shift corresponding vibrations to longer wavelengths. The shift is observed for all frequencies except those involving primarily C—H stretching vibrations. As can be seen from table 1, the values of ν_1 and of ν_6 for the two compounds fall within 5 cm^{-1} of each other. This difference in wavenumber is almost within the limit of experimental error for this region of the spectrum.

The spectrum of dibromomethane was also determined in the vapor state for some of the intense bands, so that a comparison could be made with the liquid state. The type of bands at 1,195 and 648 cm^{-1} could not be determined with the prism instrument available. For the band at 1,190 cm^{-1} in the liquid state there is a small shift to 1,195 cm^{-1} in the vapor state. The other band shifted from 639 to 648 cm^{-1}. Two of the remaining bands located at 810 and 591 cm^{-1} show definite zero branches when measured in the vapor state. These bands have shifted from 813 and 579 cm^{-1}, respectively, as measured in the liquid state. The vapor band at 745 cm^{-1} is shifted 16 cm^{-1} from the liquid band at 729 cm^{-1} and may have a zero branch. The comparison of the positions of the bands in the liquid and in the vapor states shows that there is a small change in the frequencies when measured in the two different states.

Of the six active infrared fundamentals of tribromochloromethane, only three bands, ν_1, ν_{68}, and ν_3, were observed in the infrared region that was covered in these measurements. The other three fundamentals fall beyond the range of the thallium bromide-iodide prism. Calculations show that two of these bands, ν_{79} and ν_4, should have frequencies at 214 and 215 cm^{-1}, respectively. The calculated values are in good agreement with the wavenumber of a single Raman line determined by Lecomte and coworkers [4].

For the classification of the combination and harmonic bands, the Raman values 141 and 214 cm^{-1} have been used. The three fundamentals observed in the infrared checked within 5 cm^{-1} with the Raman values of Lecomte. The differences between the infrared and Raman values may be attributed to the effect of the solvent carbon disulfide on the tribromochloromethane in producing a small shift in the bands, and also to the presence at 667 cm^{-1} of the absorption band of atmospheric CO_2, which made it difficult to locate accurately the position of the band at 675 cm^{-1}. The two absorption bands at 735 and 933 cm^{-1} could not be accounted for on the basis of the fundamentals.

In comparing the fundamentals of tribromochloromethane and tetrabromomethane, it is seen that the substitution of the bromine atom for the chlorine atom reduces the number of fundamentals from six to four. Only the two threefold degenerate vibrations, ν_{168} and ν_{479}, are infrared active. The remaining two appear in combination. One of these bands, ν_{168}, with frequency 669 cm^{-1}, was observed in the rocksalt region. This is 4 cm^{-1} greater than the Raman value as determined by Dadieu and Kohlrausch [5]. This difference can probably be attributed to error of observation caused by the presence at 667 cm^{-1} of the absorption band of atmospheric CO_2. The other bands in the observed spectrum, which are of low intensity, can be interpreted on the basis of the four fundamentals. Three of the fundamentals listed in table 1 are the Raman values determined by Dadieu and Kohlrausch.

The classification of the bands as given in table 1 accounts for most of the observed bands. The band observed at 729 cm^{-1} in dibromomethane was not classified and may have arisen from a small amount of bromochloromethane that was present as an impurity. There was observed an intense band in this region for bromochloromethane. When the vapor of dibromomethane was measured, the ratio of intensities of the bands at 735

cm^{-1} and 813 cm^{-1} were much different than in the liquid, and also a band at 1,233 cm^{-1} appeared. This is near the location of another intense band of bromochloromethane at 1,225 cm^{-1} as measured in the liquid state. Another sample of dibromomethane was measured that also contained these bands. According to mass spectrograph determinations it contained about 1 percent of chlorine. It is probable that a small amount of bromochloromethane is present in the dibromomethane and produces the bands that do not fall in the classification scheme. On further purification of dibromomethane it was found that the band in the region of 13.6 μ (729 cm^{-1}) disappeared when the compound was measured in cells 0.1 mm thick.

Without a study of the rotational structure of these bands the molecular constants cannot be obtained. Unpublished observations made with a different instrument show resolution of some of the near infrared bands of dibromomethane and bromochloromethane into a series of lines approximately 1.5 cm^{-1} apart. The spacing interval is less for dibromomethane than for bromochloromethane.

The authors thank W. S. Benedict of this Bureau for his discussions on the classification of the bands of these compounds.

IV. References

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