

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

**The Infrared Spectra of Fifteen Organic Bromides from 500 to 800 Cm.<sup>-1</sup>**BY FORREST S. MORTIMER,<sup>1</sup> ROBERT B. BLODGETT<sup>1a</sup> AND FARRINGTON DANIELS

This investigation was undertaken in an attempt to find some correlation between shifts in the vibrational spectrum of a molecule and the relative reactivities of a chemical bond. The carbon-bromine bond was chosen because the large difference in the masses of the two atoms should lead to a fundamental mode of vibration which is due primarily to the stretching of this bond. The location of this frequency in the longer infrared was felt to be particularly favorable for study, because so few harmonics are found in this region of the spectrum. Overlapping spectra have rendered difficult the interpretation of infrared measurements on organic materials in the shorter infrared, but in the region near 560 cm.<sup>-1</sup> most of these complications disappear. However, the spectra of the compounds chosen for this study have shown other complications resulting in the fact that no single band can be assigned to the vibration of the carbon-bromine bond alone. For this reason the original purpose of the investigation has been postponed. However, the spectra which were recorded during the course of the study are not recorded elsewhere in the literature and for this reason the present paper has been written to present these spectra and a possible interpretation of the infrared bands involved.

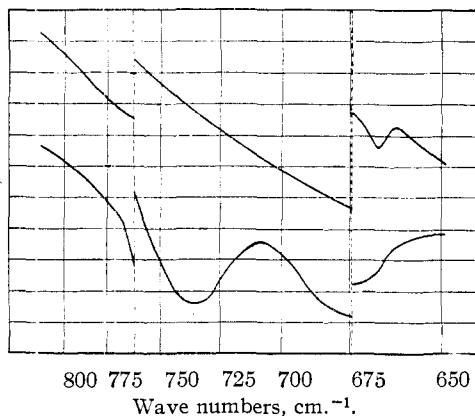


Fig. 1.—Galvanometer deflections as plotted against wave numbers taken from a typical measurement on bromobenzene. The upper curve gives incident radiation intensity. The lower curve gives transmitted intensity. The dotted lines indicate a change in amplification. The atmospheric absorption band for carbon dioxide at 14.97 $\mu$  can be seen at the right of the upper curve.

**Apparatus**

The monochromator used in the infrared spectrometer on which the spectra in this investiga-

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tion were recorded has been described by Cross and Daniels.<sup>1b</sup> It consists of a single prism in a conventional Wadsworth mounting. The light from a voltage-stabilized Nernst filament is focused by means of a spherical mirror on the entrance slit after passing through a cell, faced with potassium bromide windows, containing the sample. The energy passed by the second slit is focused on the receiver of a two-junction chromel-constantan thermopile constructed by Mr. Foerst, mechanician in the University of Wisconsin Department of Physics. The thermopile is mounted in an evacuated copper case connected to a charcoal trap immersed in liquid air.

Sodium chloride and potassium bromide prisms are mounted on separate removable tables which are set in place on the prism table by means of a hole, slot and plate kinematic mounting.

The amplified deflections of the primary galvanometer are recorded on photographic paper wound on a rotating drum. The amplifier is of the Barnes-Matossi type, using the general arrangement employed by Gershinowitz and Wilson.<sup>2</sup> The galvanometers are mounted on Müller supports so as to reduce vibration.<sup>3</sup> The recording of the spectrum is automatic, the prism being rotated in steps by a motor-driven typewriter ratchet. At each prism position the galvanometer deflection is recorded first with a blank, and then with the cell containing the sample in the light path. This complete sequence of operations is automatic and data can be taken at 150 different wave lengths in about two hours.<sup>4</sup> By recording the spectrum in this way the "zero" curve representing the energy incident upon the sample is obtained at the same time as the absorption curve. By plotting the ratio of the intensities of corresponding pairs of readings against frequency the transmission curves shown in Fig. 2 are obtained. An example of the type of record obtained is shown graphically in Fig. 1, where the intensities of the incident and transmitted radiation as recorded are plotted against frequency in cm.<sup>-1</sup>.

The spectrometer was calibrated as described by Cross<sup>5</sup> using the refractive index values for potassium bromide which are given by Gundelock<sup>6</sup> and Korth.<sup>7</sup> The standard wave length used for reference was the atmospheric absorption band of

(1b) Cross and Daniels, *J. Chem. Phys.*, **1**, 48 (1933).

(2) Gershinowitz and Wilson, *J. Chem. Phys.*, **6**, 197 (1938).

(3) Strong, "Procedures in Experimental Physics," Prentice-Hall Co., New York, 1937, p. 328.

(4) For further details, see Ph.D. thesis of Robert M. Blodgett, University of Wisconsin, 1940.

(5) Cross, *Rev. Sci. Inst.*, **4**, 179 (1933).

(6) Gundelock, *Z. Physik.*, **66**, 776 (1930).

(7) Korth, *ibid.*, **84**, 677 (1933).

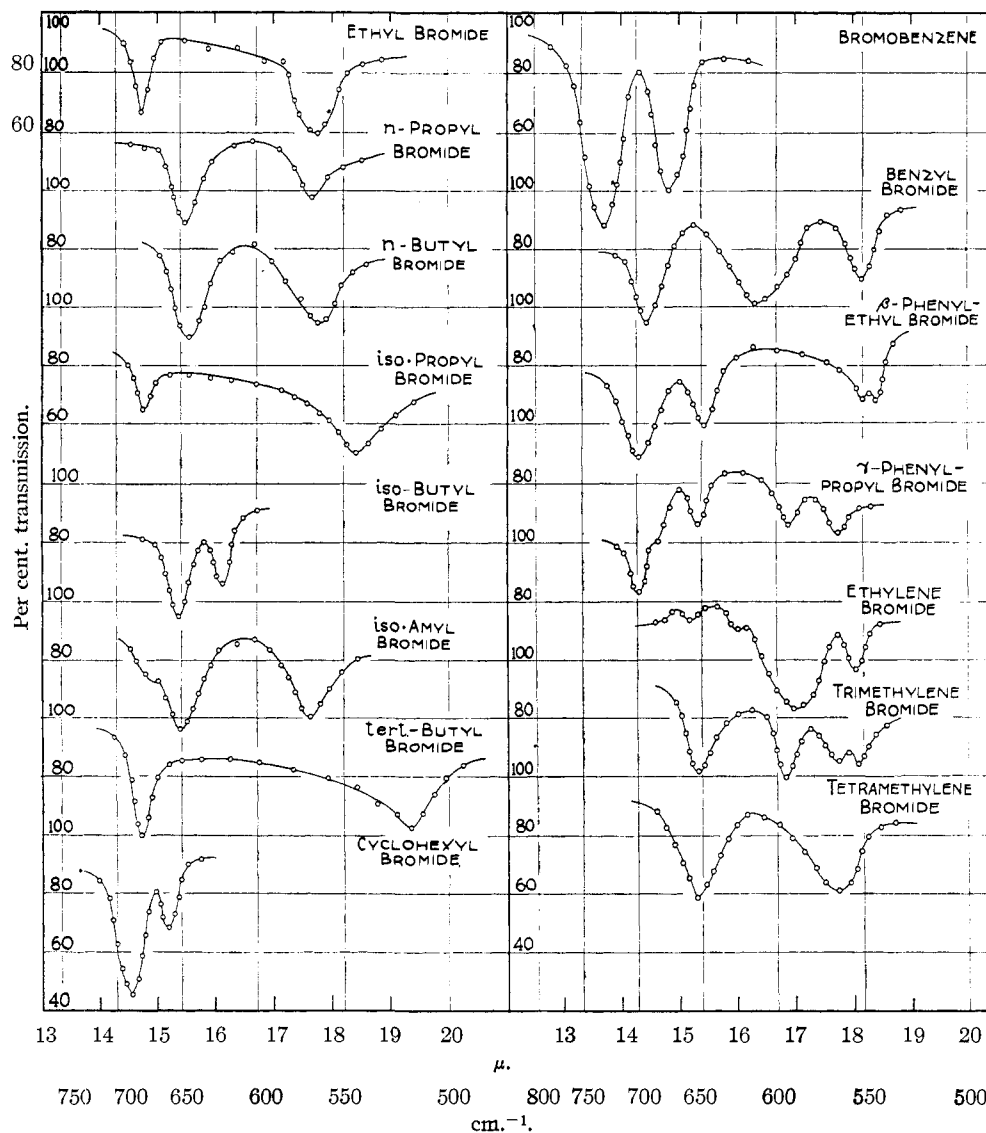


Fig. 2.—Transmission curves for fifteen bromides.

carbon dioxide at  $14.97 \mu$ . This band occurs in the region studied and was recorded as a dip in the energy distribution curve on the photographic record of every spectrum. The position of this band, shown in the right-hand portion of the upper curve in Fig. 1, served as an excellent reference point for every measurement. The accuracy of the wave lengths as recorded here is probably better than  $\pm 0.05 \mu$  which in this region of the spectrum is equivalent to about  $\pm 1.5 \text{ cm.}^{-1}$ .

No attempt was made to investigate the amount of stray energy in the region studied, but it was probably in the neighborhood of 10–20%.

#### Source and Preparation of Samples

Most of the compounds used in this investigation were obtained from Professor S. M. McEl-

vain, who had prepared them for a previous investigation.<sup>8</sup> The purity of the liquids thus obtained was very high. For this reason an additional fractionation in which the portion of the liquid boiling on a "flat," constant to  $0.1^\circ$ , was considered sufficient to give samples of high purity (probably 98%). The spectra as recorded before and after the fractionation were identical except that some of the purified liquids showed fewer irregularities than the corresponding ones obtained with the original sample. The spectra included in Fig. 2 are those recorded with the purified sample using a potassium bromide cell, having a layer of liquid approximately 0.04 mm. thick. The construction of the cell was similar to that described by Gildart and Wright.<sup>9</sup>

(8) McElvain and Semb, *THIS JOURNAL*, **53**, 690 (1931).

(9) Gildart and Wright, *Rev. Sci. Inst.*, **12**, 204 (1941).

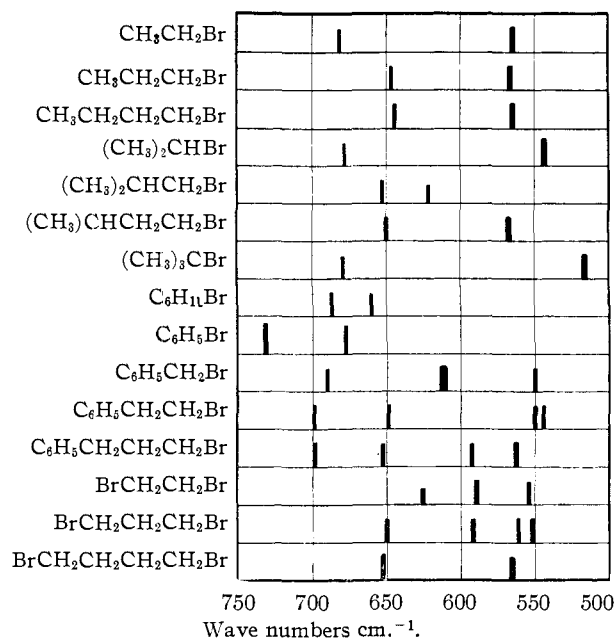


Fig. 3.—Positions of the principal absorption bands.

### Discussion

Figures 2 and 3 show respectively the curves and relative positions of the principal absorption band while Table I gives the frequencies and a possible assignment, *W*, for these bands.

A complete vibrational analysis of molecules of the complexity studied here has never been carried out. However, it is possible to gain some knowledge concerning the vibrations of the carbon-bromine skeleton of such molecules. Such a method has been used by Cross and Van Vleck<sup>10</sup> in their study of ethyl bromide and has been used by Kohlrausch<sup>11</sup> and his associates in the study of many of the molecules included in this investigation. The method consists of applying a normal coordinate treatment to the molecule considering CH<sub>3</sub>, CH<sub>2</sub>, Cl, Br, and similar groups or atoms as single mass points. Thus ethyl bromide is reduced to a three body system, etc. This procedure allows the assignment of most of the bands in this region, since most frequencies less than 1000 cm.<sup>-1</sup> are associated with vibrations of C-C bonds or C-Cl, C-Br and C-I bonds. The bending frequencies associated with the skeleton, however, usually appear at such low frequencies that they are not accessible even with a potassium bromide prism.

The primed frequencies serve to differentiate between the two vibrations resulting from Fermi resonance. Those marked (K) are notations of Kohlrausch and Ypsilanti.

In the spectra of the aliphatic bromides, it is seen that in each case there are two absorption bands in the region studied. One explanation of

the appearance of two bands of similar intensities in a region where one expects only one fundamental involving the vibration of the bromine atom with respect to the rest of the molecule has been given by Kohlrausch and associates.<sup>11</sup> He assumes that all such molecules with more than two carbon atoms can exist in two forms, designated by him as "*cis*" and "*trans*." He then assigns to each of the bands found, the carbon-bromine stretching frequency corresponding to one of the two forms. However, it seems unlikely that a rotation of the carbon-bromine bond in an aliphatic bromide can result in the splitting of the energy levels sufficiently to give rise to two infrared bands separated by 80 to 120 cm.<sup>-1</sup>. Moreover, there are two bands in the infrared spectra of all of the aliphatic monobromides studied in this work although in the Raman spectra reported by Kohlrausch, ethyl bromide, *i*-propyl bromide, and *t*-butyl bromide exhibit only one line in this region. The presence of only one band in these three compounds is predicted by the *cis-trans* theory since it is in just these molecules that there is no distinction between the "*cis*" and "*trans*" forms. However, the fact that these molecules, too, exhibit two bands in their infrared spectra makes this "*cis-trans*" explanation unsatisfactory.

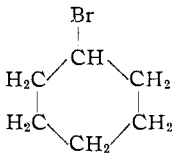
The presence of double lines may perhaps be explained on the basis of Fermi resonance. In the Raman spectrum of each of the aliphatic bromides studied here there is a low-frequency bending vibration which should give rise to a harmonic in this region of the spectrum. Further, the harmonic and fundamental are in each case of the same symmetry class, thus allowing resonance and the resulting unperturbed positions. The fact that the second band does not occur in the Raman spectra of the above-mentioned three compounds may be due to differences in intensity occurring in these more symmetrical molecules.

Again, the presence of double absorption bands corresponding to the carbon-bromine stretching vibration may be explained on the basis of a simple hypothesis suggested by a referee. If the vibration of the hydrogen atoms attached to the carbon atom is considered with respect to the vibration of the carbon-bromine atom, it would be possible to account for two frequencies—one in which the motions are in the same direction and the other in which the motion of the hydrogen atom is opposite in direction to that of the carbon atom. These in-phase and out-of-phase motions of the hydrogens with respect to the carbon of the carbon-bromine bond should give rise to two different frequencies associated with the carbon-bromine bond. The measurements recorded here give a favorable opportunity for observing such a phenomenon, because the bond due to stretching of the carbon-bromine bond is comparatively uncomplicated by overlapping bands in the infrared absorption spectra from other modes of vi-

(10) Cross and Van Vleck, *J. Chem. Phys.*, **1**, 350 (1933).

(11) Kohlrausch, "Der Smekal-Raman Effect," *Erganzungshand.*, J. Springer, 1938.

TABLE I  
 ASSIGNMENT OF FUNDAMENTAL FREQUENCIES

Bromides	Formula	Wave length, $\mu$	Frequency, $\text{cm.}^{-1}$	Assignment	Raman frequency in $\text{cm.}^{-1}$
Ethyl	$\text{CH}_3\text{CH}_2\text{Br}$	14.68	681	W' C-Br	...
		17.70	565	W C-Br	560 <sup>a</sup>
<i>n</i> -Propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	15.46	647	W' C-Br	647 <sup>b</sup>
		17.63	567	W C-Br	564
<i>n</i> -Butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	15.50	645	W' C-Br	641 <sup>c</sup>
		17.74	564	W C-Br	561
<i>i</i> -Propyl	$(\text{CH}_3)_2\text{CHBr}$	14.74	678	W' C-Br	... <sup>b</sup>
		18.42	543	W C-Br	536
<i>i</i> -Butyl	$(\text{CH}_3)_2\text{CHCH}_2\text{Br}$	15.32	653	W' C-Br	653 <sup>d</sup>
		16.08	622	W C-Br	621
<i>i</i> -Amyl	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$	15.38	650	W' C-Br	646 <sup>e</sup>
		17.62	568	W C-Br	563
<i>t</i> -Butyl	$(\text{CH}_3)_3\text{CBr}$	14.72	679	W' C-Br	... <sup>f</sup>
		19.36	517	W C-Br	515
Cyclohexyl		14.55	687	W C-Br	683 <sup>g</sup>
		15.15	660	W ring	655
Phenyl	$\text{C}_6\text{H}_5\text{Br}$	13.67	732	W ring	734 <sup>h</sup>
		14.75	678	W C-Br	673
Benzyl	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	14.47	691	W ring	690 <sup>i</sup>
		16.34	612	W ring	605
		18.18	550	W C-Br	548
$\beta$ -Phenyl ethyl	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$	14.31	699	W ring	... <sup>i</sup>
		15.42	649	W' C-Br	652
		18.18	550	W' ring	575
		18.38	544	W C-Br	548
$\gamma$ -Phenyl propyl	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	14.31	699	W ring	... <sup>i</sup>
		15.34	652	W' C-Br	649
		16.90	592	W' ring	590
		17.77	563	W C-Br	562
Ethylene	$\text{BrCH}_2\text{CH}_2\text{Br}$	16.00	625	W <sub>4</sub> (I) (K)	Inactive
		17.00	588	W <sub>4</sub> (II) (K)	583 <sup>k</sup>
		18.06	554	W <sub>2</sub> (II) (K)	552
Trimethylene	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br}$	15.38	650	W <sub>2</sub> (II) (K)	650 <sup>l</sup>
		16.90	592	W <sub>2</sub> (I) (K)	591
		17.82	561	W <sub>6</sub> (II) (K)	562
		18.13	552	W <sub>6</sub> (I) (K)	552
Tetramethylene	$\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	15.35	652	W C-Br (in-phase)	652 <sup>j</sup>
		17.70	565	W C-Br (out-of-phase)	562

<sup>a</sup> Wagner, *Z. physik. Chem.*, **B-45**, 69 (1939). <sup>b</sup> Radinger and Wittek, *ibid.*, **B-45**, 329 (1940). <sup>c</sup> Kahovec and Kohlrausch, *ibid.*, **B-48**, 7 (1940). <sup>d</sup> Ballaus and Wagner, *ibid.*, **B-45**, 272 (1940). <sup>e</sup> Dadiou, Pongratz and Kohlrausch, *Monatsh.*, **61**, 459 (1933). <sup>f</sup> Wagner, *Z. physik. Chem.*, **B-45**, 341 (1940). <sup>g</sup> Kohlrausch and Stockmair, *ibid.*, **B-31**, 382 (1936). <sup>h</sup> Kahovec and Reitz, *Monatsh.*, **69**, 363 (1936). <sup>i</sup> Reitz and Stockmair, *ibid.*, **67**, 92 (1935). <sup>j</sup> Bender and Chien, to be published. <sup>k</sup> Kohlrausch and Ypsilanti, *Z. physik. Chem.*, **B-29**, 274 (1935). <sup>l</sup> Kohlrausch and Ypsilanti, *ibid.*, **B-32**, 407 (1946).

bration. It is interesting to note that in the case of trimethyl-methyl bromide the frequencies are very widely split as would be expected from the in-phase and out-of-phase interactions of the heavier methyl groups.

The bromobenzene, benzyl bromide,  $\beta$ -phenylethyl bromide and  $\gamma$ -phenylpropyl bromide series provides an interesting study. The assign-

ment of frequencies of modes of vibration involving the carbon-bromine bond for this series is complicated by the presence of bands due to vibrations of the benzene ring. Thus, Lecomte<sup>12</sup> assigned the bands which he found in the infrared spectrum of bromobenzene as follows: the band at 732  $\text{cm.}^{-1}$  to one of the modes of vibration in-

(12) Lecomte, *J. Phys. Radium*, **8**, 489 (1937).

volving the benzene ring, the band at 677  $\text{cm.}^{-1}$  to the carbon-bromine stretching vibration, and the band at 679  $\text{cm.}^{-1}$  to another of the vibrations of the ring.

In the case of benzyl bromide,  $\beta$ -phenylethyl bromide and  $\gamma$ -phenylpropyl bromide there also seem to be two bands due to the benzene ring in this region (as noted in the assignment in Table I). If this assignment is correct, the spectrum of benzyl bromide has only one vibration due to the carbon-bromine bond and  $\beta$ -phenylethyl bromide and  $\gamma$ -phenylpropyl bromide each have two. The existence of two carbon-bromine vibrations may be due to the possibility of the "cis" and "trans" forms as suggested by Kohlrausch for the aliphatic bromides discussed above. The fact that benzyl bromide has only one vibration due to the carbon-bromine band may be explained on the basis that the benzene ring is sufficiently large for it to interact with the bromine atom. This interaction should decrease as the aliphatic side chain increases in length.

In the aliphatic dibromide series of compounds involving two or three carbon atoms the interactions between the two bromine atoms may also be sufficient to result in "cis" and "trans" forms of significantly different energies. If this is the case, the modes of vibration involving in-phase and out-of-phase vibrations of the carbon-bromine bonds would each be split, resulting in four possible infrared absorption bands. As an example, the modes of vibrations for the two forms of ethylene bromide are shown in Fig. 4. It should be noted, however, that the "cis" form is not a true "cis" compound since it is obtained by rotating one bromine atom in the "trans" form by  $120^\circ$  (not  $180^\circ$ ) about the carbon-carbon band.

Due to the symmetry of ethylene bromide, the

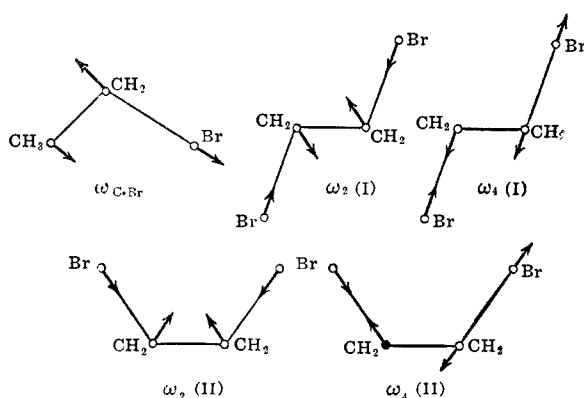


Fig. 4.--The C-Br vibrations for ethyl bromide and ethylene bromide.

in-phase vibration of the "trans" form,  $W_2(\text{I})$ , is infrared inactive. The other vibrations are infrared active and have been observed (see Table I). The notations used in the table are those of Kohlrausch and Ypsilanti<sup>13</sup> who discussed the problem from the standpoint of free rotation around the carbon-carbon bond. In their notation,  $W_2$  refers to the in-phase vibration,  $W_6$  to the out-of-phase vibration, (I) to the "trans" form and (II) to the "cis" form. Apparently the out-of-phase carbon-bromine vibration of the "trans" form was not observed by Cheng and Lecomte<sup>14</sup> in their investigation of the infrared spectrum of this compound. The band at 625  $\text{cm.}^{-1}$  observed here is probably due to this mode of vibration. Since this frequency is Raman inactive, it cannot be checked in this way.

The case of trimethylene bromide is similar to that of ethylene bromide, except that all four of the possible carbon-bromine vibrations are infrared active and are observed. The assignment, following the notation of Kohlrausch and Ypsilanti given above, appears in Table I.

The spectrum of tetramethylene bromide shows only two bands in this region. This is undoubtedly due to the fact that the two bromine atoms are sufficiently removed from one another in this molecule that the interactions causing the "cis" and "trans" forms is no longer present. Thus only the two fundamental modes of vibration remain—the in-phase and out-of-phase vibrations of the carbon-bromine bond. This interpretation is borne out by the Raman spectra of tetramethylene bromide and pentamethylene bromide recently measured by Bender and Chien.<sup>15</sup> Both molecules show only the two lines in this region corresponding to those reported here for tetramethylene bromide.

### Summary

Fifteen organic bromides have been studied in the liquid form in the region of the C-Br band from 14.5 to 19.5  $\mu$ . They include ethyl bromide, *n*-propyl bromide, *n*-butyl bromide, *i*-propyl bromide, *i*-butyl bromide, *i*-amyl bromide, *t*-butyl bromide, cyclohexyl bromide, bromobenzene, benzyl bromide,  $\beta$ -phenyl ethyl bromide,  $\gamma$ -phenyl propyl bromide, ethylene bromide, trimethylene bromide, and tetramethylene bromide. The main absorption bands are identified with fundamental vibrations.

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(13) Reference <sup>k</sup> in Table I.

(14) Cheng and Lecomte, *J. Phys. Radium*, **6**, 477 (1935).

(15) Reference <sup>j</sup> in Table I.

(16) Original manuscript received August 2, 1943.