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Infrared Spectra of Polychlorobenzenes

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The infrared spectra of 12 chlorinated benzenes have been measured from 2 to 38 microns. In addition, the spectra of benzene, monofluorobenzene, monobromobenzene, and monoiodobenzene have been included. An assignment of the fundamental bands of the monosubstituted benzenes has been made. Some of the frequencies of the other compounds have also been assigned.

The spectrum of each compound is shown in the figures, and a table containing all the observed bands is included.

1. Introduction

There is now available the complete group of substituted chlorobenzenes, from monochlorobenzene to hexachlorobenzene. These have been purified by the Hooker Electrochemical Co. and have been made available through R. H. Kimball. A measurement of the infrared spectra of these chlorinated benzenes will serve two purposes. First, it will serve as a catalog of the spectra of these compounds, which will be useful for identification and for intercomparison with other substituted benzenes. Second, some of the typical vibrations can be traced from one substituted molecule to another, thus showing the effect of position of the chlorine atoms in the molecules on the vibrational frequencies.

It would be a gigantic task to try to assign all the observed bands for 12 chlorinated benzenes. This has not been undertaken, but a study of some of the types of vibrations has been made and the classifications listed.

In addition to the spectra of the chlorobenzenes, there have been included the spectra of monofluorobenzene, monobromobenzene, and monoiodobenzene. These vibrational bands of monosubstituted benzenes have been classified and the wave numbers compared with those of monofluorobenzene.

2. Experimental Methods and Results

The spectra were measured on a prism spectrometer. Prisms of NaCl, KBr, and KRS-5 were used for the measurements from 2 to 38 μ. Cell thicknesses from 0.05 to 1.6 mm were used in different parts of the spectrum. The cell thickness was varied in regions of strong absorption so that the position of band center could be adequately determined. Where a thinner cell was used, the results are placed on the graphs as an insert curve. Several of the chlorinated benzenes are normally solids and have been measured in solution. Carbon tetrachloride was used for the solvent from 2 to 8 μ, carbon disulfide from 8 to 22 μ, and benzene or methylcyclohexane from 22 to 38 μ. In some regions the absorption of several of the liquids was so intense that the spectrum was determined in solution. The bands measured under these conditions are designated on the figures. Carbon tetrachloride has an absorption band of medium intensity in the region of 6.4 μ, and bands of the solutes in this region could be determined only approximately. The absorption spectrum of the compounds in the CCl_4 solution show the CCl_4 band at 6.4 μ plus any absorption of the solute.

The observed spectra of the chlorinated benzenes are shown in nine figures. The absorption spectra of benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene are shown from 2 to 38 μ in figures 1 and 2. Figures 3 and 4 include the spectra of *o*-dichlorobenzene, *m*-dichlorobenzene, and *p*-dichlorobenzene. The *p*-dichlorobenzene was measured in solution. The spectra of the three trichlorobenzenes are shown in figures 5 and 6, and the spectra of the tetrachlorobenzenes are included in figures 8 and 9. The spectra of pentachlorobenzene and hexachlorobenzene from 2 to 15 μ are shown in figure 7 and from 15 to 38 μ in figure 9.

In the region from 23 to 38 μ the spectrum of hexachlorobenzene is represented by a broken line. In this case, and other spectral regions of the compounds, the broken line indicates that the spectrum is less accurately determined than for the regions of the solid line. The uncertainty arises either from atmospheric absorption or some absorption present in the solvent. Bands of low intensity in the regions of solvent absorption are probably not observed.

Table 1 is a list of the observed bands of all the compounds. The wavelength, wave number, and intensity are listed for the bands of each substance. Bands of low intensity are not included. The intensity is given in terms of percentage of transmission, and is included primarily for identification purposes. No correction has been applied for radiation loss at the cell windows, nor has the percentage of transmission been reduced to a uniform cell thickness, but sufficient data are given so that a quantitative comparison of intensities can be made. It is estimated that the wavelengths are correct to ± 0.03 μ in the region from 2 to 15 μ and to ± 0.06 μ from 15 to 38 μ.

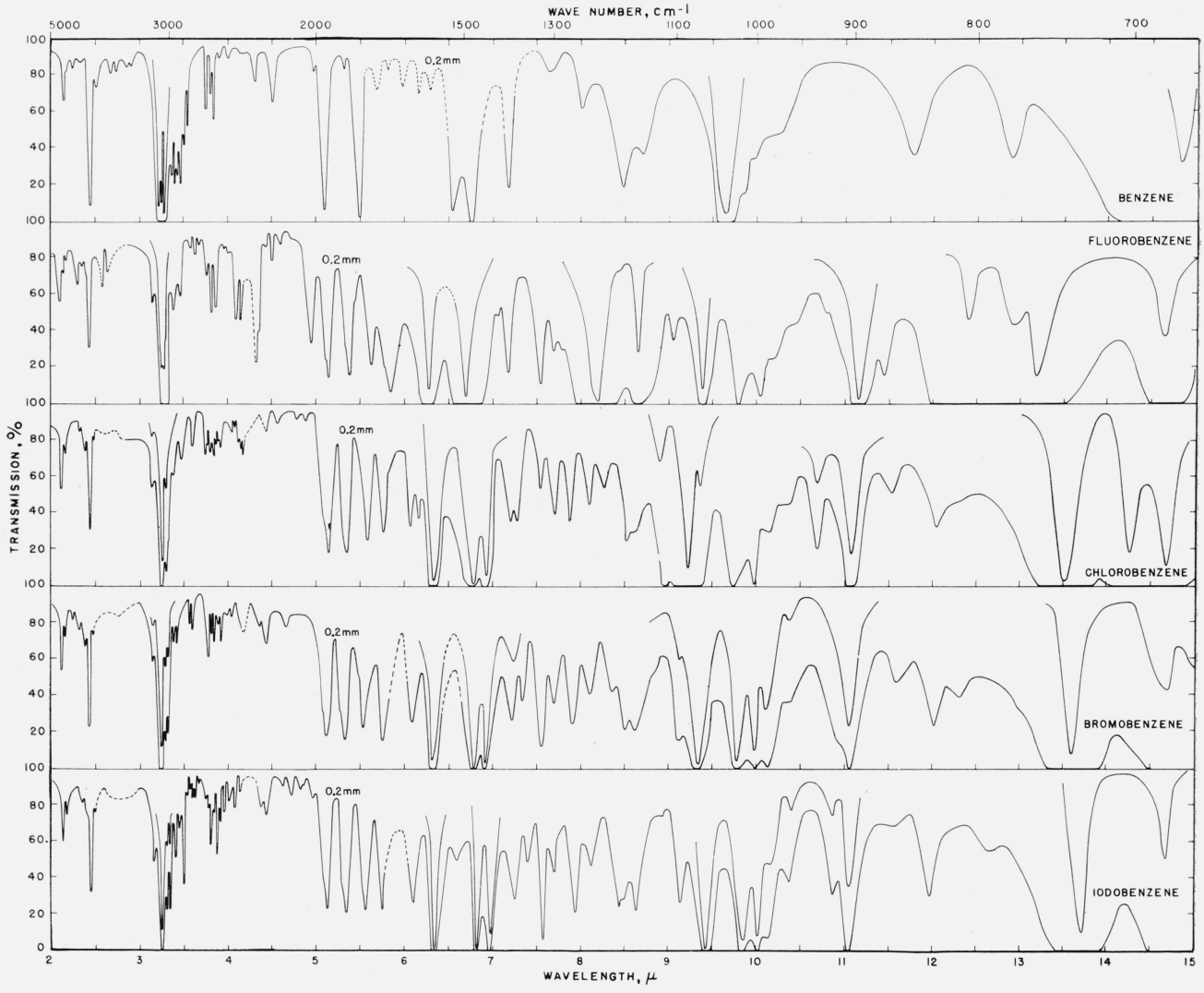

FIGURE 1. *Infrared absorption spectra of benzene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene from 2 to 15 microns.*

Dotted sections represent regions of atmospheric interference.

3. Discussion of Results

Any complete assignment of the vibrational frequencies as determined from liquids or solutions is very difficult because the distinctive band shapes arising from the rotational fine structure are washed out. In the present case the difficulty is aggravated because the spectra beyond 38 μ were not obtained. Thus many of the important low-lying fundamentals were not observed. However, with the help of the excellent work of Randle and Whiffen,[1] some of the bands have been assigned. Some help was also obtained from the calculations of Garg.[2]

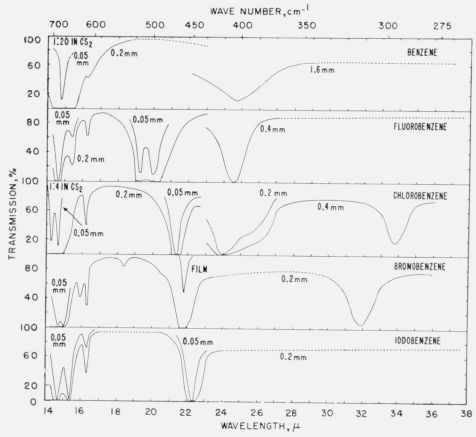

FIGURE 2. *Continuation of the spectra of the compounds of figure 1 in the region from 14 to 38 microns.*

[1] R. R. Randle and D. H. Whiffen, Molecular Spectroscopy Rept. of Conf. Hydrocarbon Research Group, Inst. Petroleum (Oct. 1954).

[2] S. N. Garg, Current Sci. **22,** 298 (1953).

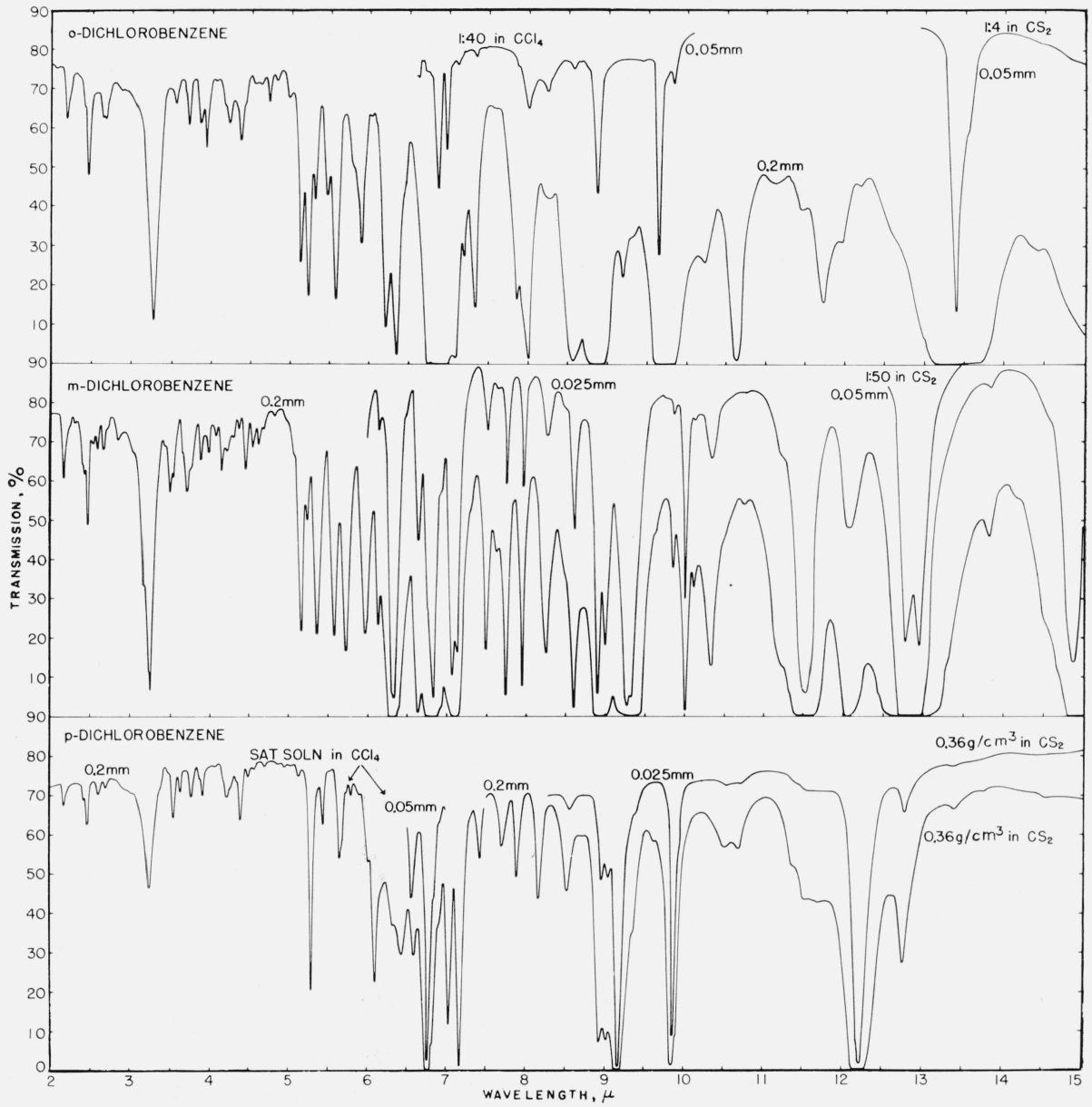

FIGURE 3. *Infrared spectra of orthodichlorobenzene, metadichlorobenzene, and paradichlorobenzene from 2 to 15 microns.*

The insert curves are for thinner cells or solutions in CCl_4 or CS_2.

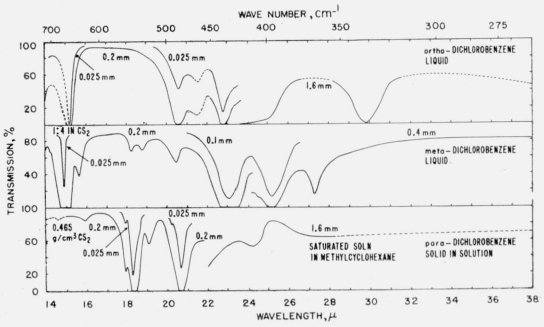

FIGURE 4. *Continuation of the spectra of figure 3 in the region from 14 to 38 microns.*

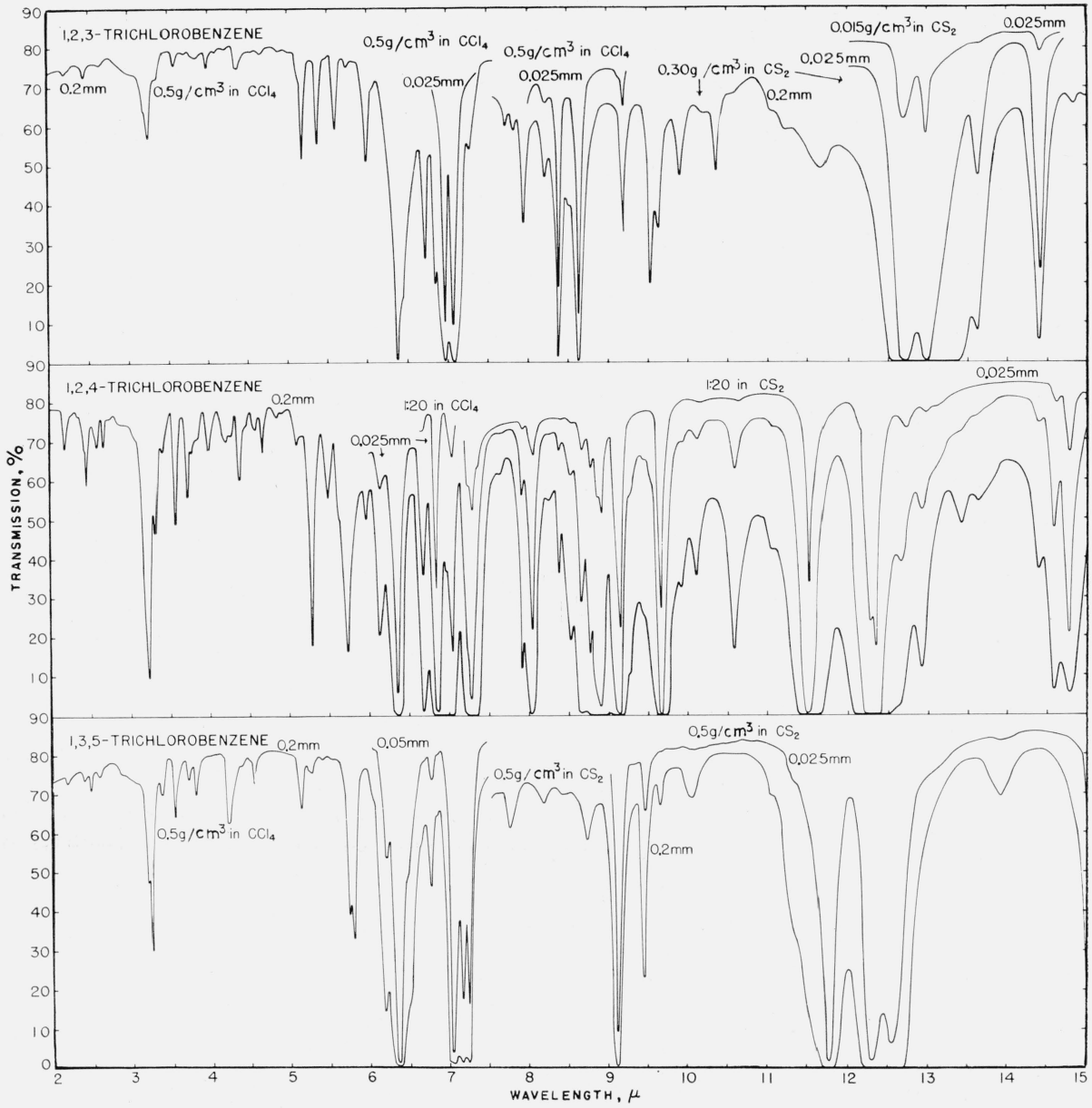

FIGURE 5. *Infrared spectra of 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5-trichlorobenzene from 2 to 15 microns.*

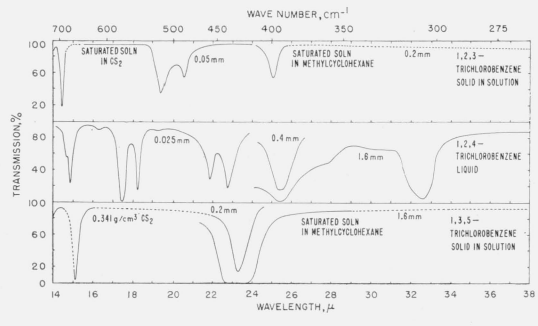

FIGURE 6. *Continuation of the spectra of the trichlorobenzenes from 14 to 38 microns.*

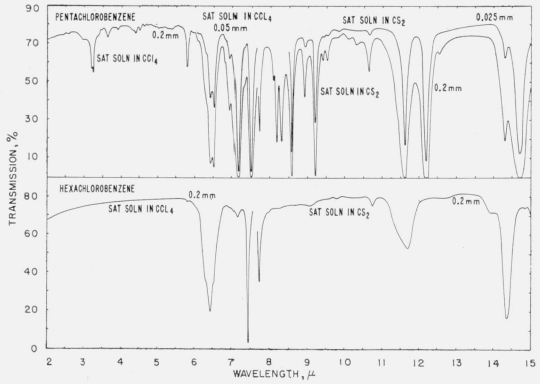

FIGURE 7. *Infrared spectra of pentachlorobenzene and hexachlorobenzene from 2 to 15 microns.*

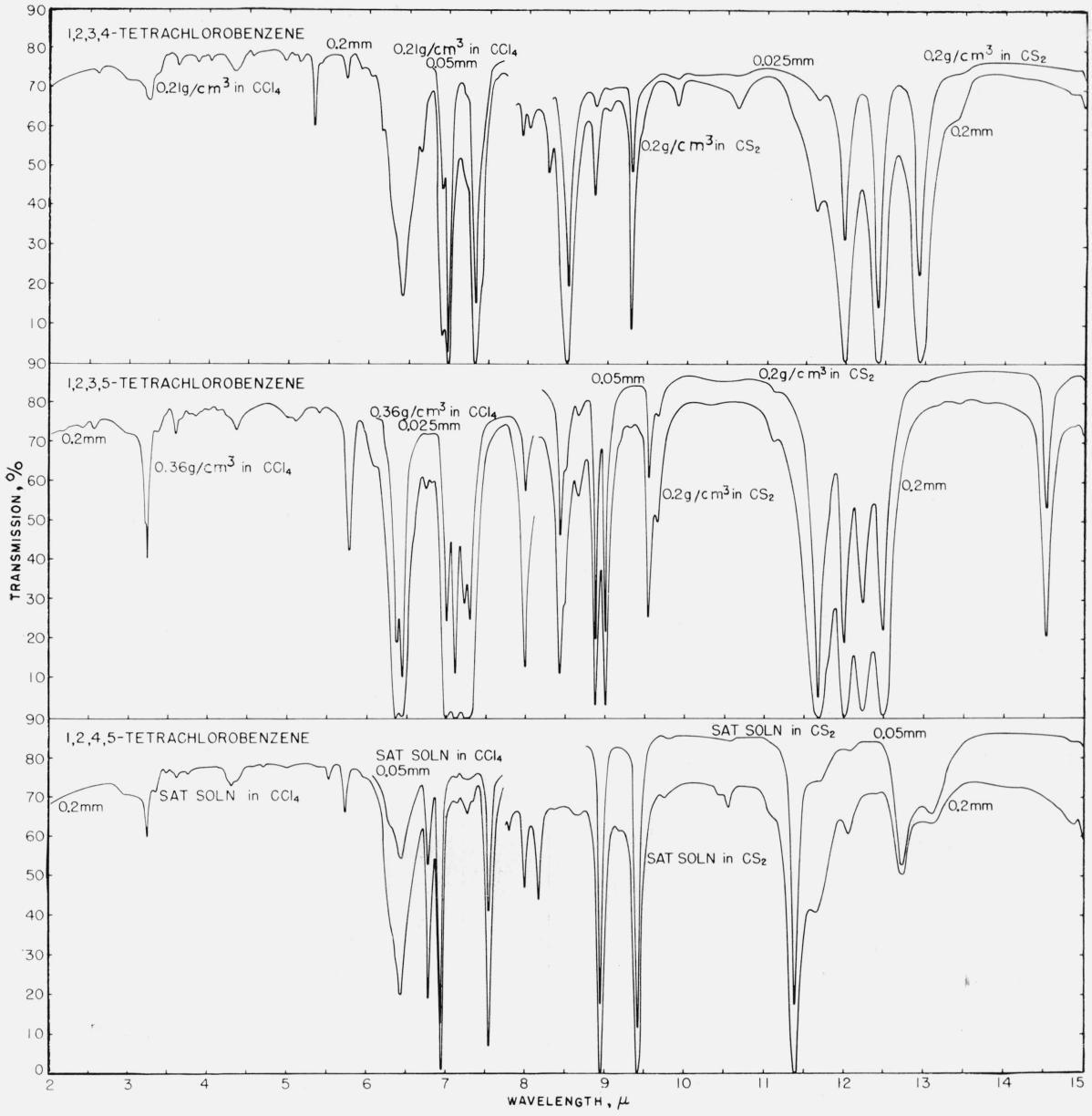

FIGURE 8. *Spectra of 1,2,3,4-tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, and 1,2,4,5-tetrachlorobenzene from 2 to 15 microns.*

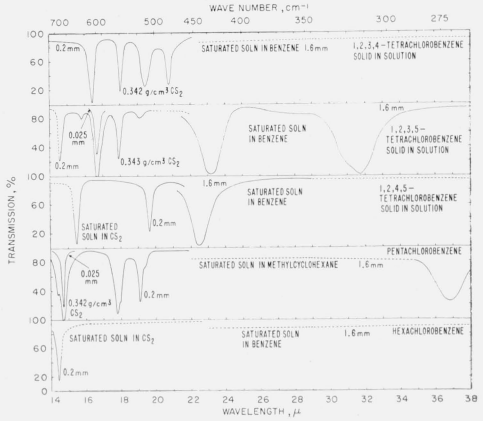

FIGURE 9. *Infrared spectra of the tetachlorobenzenes, pentachlorobenzene, and hexachlorobenzene from 14 to 38 microns.*

The dotted lines indicate that no bands of medium or strong intensity are present in that part of the spectrum.

TABLE 1. *Observed bands*

Observed wavelength	Wave number	Intensity [a]	Observed wavelength	Wave number	Intensity [a]
Benzene					
μ	cm^{-1}	%	μ	cm^{-1}	%
2.12	4,716	35	4.98	2,008	20
2.15	4,651	20	5.11	1,957	94
2.22	4,505	20	5.33	1,876	20
2.31	4,329	15	5.50	1,818	96
2.42	4,132	90	5.70	1,754	35
2.48	4,032	30	5.83	1,715	20
2.65	3,774	20	5.99	1,669	30
2.71	3,690	20	6.17	1,621	35
2.83	3,534	15	6.29	1,590	35
2.88	3,472	15	6.55	1,527	95
3.21	3,115	[b] 92	6.77	1,477	100
3.23	3,096	[b] 90	7.18	1,393	80
3.26	3,067	[b] 95	7.64	1,309	20
3.36	2,976	75	8.01	1,248	40
3.39	2,950	80	8.48	1,179	80
3.42	2,924	75	8.71	1,148	65
3.45	2,899	80	9.65	1,036	[b] 95
3.49	2,865	60	9.86	1,014	85
3.52	2,841	50	9.97	1,003	65
3.74	2,674	40	10.27	974	55
3.79	2,639	30	11.77	850	65
3.82	2,618	45	12.88	776	65
3.89	2,571	10	14.81	675	100
4.01	2,494	10	16.26	615	60
4.31	2,320	25	24.79	403	[d] 90
4.52	2,212	35			
Fluorobenzene					
2.08	4,808	45	5.39	1,855	85
2.10	4,762	30	5.44	1,838	45
2.15	4,651	20	5.63	1,776	80
2.27	4,405	35	5.78	1,730	80
2.32	4,310	25	5.85	1,709	90
2.40	4,167	70	6.28	1,592	[b] 90
2.56	3,906	35	6.69	1,495	[b] 95
2.62	3,817	30	7.07	1,414	50
3.14	3,185	45	7.18	1,393	80
3.22	3,106	[b] 75	7.54	1,326	90
3.24	3,086	[b] 80	7.70	1,299	70
3.26	3,067	[b] 80	7.79	1,284	70
3.27	3,058	[b] 70	8.15	1,227	[b] 95
3.37	2,967	50	8.20	1,220	[b] 100
3.45	2,899	45	8.66	1,155	[b] 70
3.55	2,817	15	9.07	1,103	65
3.57	2,801	15	9.46	1,064	[b] 90
3.62	2,762	20	9.81	1,019	100
3.66	2,732	15	10.06	994	80
3.75	2,667	30	10.11	989	75
3.80	2,632	50	------	------	------
3.85	2,597	45	------	------	------
3.95	2,532	15	------	------	------
4.60	2,500	15	11.16	896	[b] 95
4.09	2,445	55	11.46	873	80
4.11	2,433	55	12.39	807	[b] 55
4.16	2,404	55	12.45	803	[b] 40
4.33	2,309	80	12.93	773	[b] 55
4.35	2,299	60	13.18	759	[b] 85
4.44	2,252	15	14.64	683	[b] 95
4.52	2,212	25	15.53	644	[b] 40
4.61	2,169	15	16.28	614	40
4.95	2,020	65	19.26	519	[b] 90
5.11	1,957	75	20.00	500	[b] 90
5.15	1,942	85	24.56	407	[c] 100
5.34	1,873	70			
Chlorobenzene					
2.08	4,808	50	4.11	2,433	25
2.13	4,695	30	4.14	2,416	30
2.28	4,386	15	4.17	2,398	30
2.35	4,255	25	4.44	2,252	20
2.41	4,149	70	4.56	2,193	15
2.45	4,082	20	4.78	2,092	10
3.12	3,205	45	4.89	2,045	10
3.24	3,086	100	5.14	1,946	80
3.28	3,049	95	5.35	1,869	80
3.36	2,976	40	5.59	1,789	75
3.45	2,899	30	5.76	1,736	70
3.58	2,793	25	6.07	1,647	70
3.72	2,688	30	6.16	1,623	65
3.75	2,667	25	6.33	1,580	[b] 95
3.78	2,646	30	6.78	1,475	[b] 95
3.82	2,618	30	6.92	1,445	[b] 90
3.85	2,597	25	7.20	1,389	60
3.87	2,584	25	7.27	1,376	60
3.90	2,564	25	7.54	1,326	45
4.05	2,469	15	7.70	1,299	60
4.08	2,451	15	7.87	1,271	65

See footnotes at end of table.

TABLE 1. *Observed bands*—Continued

Observed wavelength	Wave number	Intensity [a]	Observed wavelength	Wave number	Intensity [a]
Chlorobenzene—Continued					
μ	cm^{-1}	%	μ	cm^{-1}	%
8.10	1,235	55	11.08	903	[b] 80
8.26	1,211	45	11.54	867	50
8.51	1,175	75	12.05	830	65
8.90	1,124	100	13.52	740	[b] 95
9.22	1,085	[b] 90	14.25	702	[b] 85
9.36	1,068	[b] 40	14.66	682	[b] 90
9.74	1,027	100	16.22	617	60
9.98	1,002	100	21.32	469	[b] 100
10.16	984	65	23.94	418	100
------	------	------	25.44	393	70
10.69	935	80	33.78	296	80
Bromobenzene					
2.09	4,785	50	6.09	1,642	70
2.13	4,695	30	6.30	1,585	[b] 95
2.21	4,525	20	6.78	1,475	[b] 100
2.29	4,367	25	6.91	1,447	[b] 95
2.35	4,255	35	7.21	1,387	75
2.40	4,167	80	7.33	1,364	60
2.44	4,098	25	7.55	1,324	85
2.73	3,663	15	7.69	1,300	60
3.13	3,195	45	7.91	1,264	75
3.22	3,106	100	8.10	1,235	60
3.27	3,058	85	8.36	1,196	60
3.31	3,021	80	8.50	1,176	80
3.36	2,976	30	8.62	1,160	80
3.40	2,941	30	9.12	1,097	85
3.54	2,825	20	9.34	1,071	[b] 95
3.57	2,801	25	9.78	1,023	[b] 95
3.76	2,660	40	9.98	1,002	[b] 90
3.79	2,639	30	10.11	989	[b] 65
3.82	2,618	35	10.37	964	60
3.87	2,584	20	11.05	905	100
3.90	2,564	35	11.59	863	50
3.97	2,519	15	12.02	832	80
4.04	2,475	15	12.31	812	60
4.18	2,392	25	13.60	735	[b] 90
4.36	2,293	25	14.68	681	[b] 95
4.44	2,252	35	15.00	667	[b] 95
4.67	2,141	25	15.94	627	60
5.08	1,969	70	16.30	614	70
5.12	1,953	80	18.36	545	15
5.28	1,894	70	20.60	485	30
5.33	1,876	80	21.81	459	100
5.48	1,824	50	22.15	452	90
5.54	1,805	75	31.87	314	90
5.76	1,736	85			
Iodobenzene					
2.11	4,739	40	5.34	1,873	80
2.15	4,651	25	5.56	1,799	80
2.32	4,310	20	5.75	1,739	80
2.42	4,132	70	6.10	1,639	75
2.46	4,065	25	6.34	1,577	[b] 100
3.14	3,185	50	6.60	1,515	45
3.23	3,096	[b] 90	6.81	1,468	[b] 100
3.29	3,040	80	6.97	1,435	[b] 90
3.32	3,012	80	7.25	1,379	70
3.38	2,959	50	7.40	1,351	50
3.42	2,924	30	7.57	1,321	90
3.48	2,874	65	7.70	1,299	55
3.52	2,841	15	7.94	1,259	80
3.55	2,817	10	8.12	1,232	50
3.57	2,801	15	8.44	1,185	70
3.61	2,770	15	8.51	1,175	65
3.65	2,740	10	8.63	1,159	70
3.72	2,688	20	8.95	1,117	25
3.75	2,667	25	9.14	1,094	65
3.78	2,646	45	9.43	1,060	[b] 100
3.82	2,618	30	9.85	1,015	[b] 90
3.85	2,597	50	10.03	997	[b] 90
3.89	2,571	30	10.16	984	90
3.93	2,545	25	10.38	963	55
4.01	2,494	15	10.87	920	60
4.07	2,457	20	11.06	904	[b] 55
4.14	2,415	10	11.57	864	25
4.37	2,288	20	11.97	835	65
4.43	2,257	25	12.66	790	40
4.63	2,160	10	13.71	729	[b] 85
4.72	2,119	15	14.17	707	90
4.83	2,070	10	14.68	681	[b] 95
4.86	2,058	10	15.31	653	[b] 95
4.96	2,016	20	16.32	613	65
5.13	1,949	80	22.32	448	[b] 100

TABLE 1. *Observed bands*—Continued

Observed wavelength	Wave number	Intensity [a]	Observed wavelength	Wave number	Intensity [a]
Orthodichlorobenzene					
μ	cm^{-1}	%	μ	cm^{-1}	%
2.17	4,608	35	5.90	1,695	70
2.41	4,149	35	6.02	1,661	40
2.44	4,098	50	6.21	1,610	90
2.62	3,817	35	[e] 6.34	1,577	95
2.65	3,775	35	6.74	1,484	[b] 25
3.25	3,077	90	6.86	1,458	[b] 55
3.53	2,833	35	6.97	1,435	[b] 45
3.69	2,710	40	7.11	1,406	95
3.85	2,597	40	7.19	1,391	75
3.91	2,558	45	7.33	1,364	85
4.17	2,398	35	7.47	1,339	40
4.23	2,364	40	[e] 7.86	1,272	85
[e] 4.38	2,283	45	[e] 7.99	1,252	100
4.41	2,268	35	8.57	1,167	100
4.55	2,198	30	8.86	1,129	[b] 55
4.62	2,164	30	9.64	1,037	[b] 70
4.73	2,114	35	[e] 9.82	1,018	[b] 30
4.84	2,066	30	10.63	941	100
4.98	2,008	35	13.38	747	[b] 85
5.13	1,949	75	13.52	739	[b] 40
5.24	1,908	85	15.18	659	[b] 100
5.31	1,883	60	20.60	485	100
5.47	1,828	60	21.56	464	90
5.58	1,792	85	22.82	438	100
5.79	1,727	50	30.85	324	100
Metadichlorobenzene					
2.15	4,651	40	[e] 6.33	1,580	100
2.29	4,367	25	[e] 6.64	1,506	95
2.39	4,184	35	6.82	1,466	100
2.40	4,167	35	6.90	1,449	95
2.45	4,082	50	7.07	1,414	100
2.51	3,984	30	7.18	1,393	100
2.57	3,891	30	7.49	1,335	85
2.64	3,788	30	7.63	1,311	60
2.83	3,534	25	7.73	1,295	95
3.02	3,311	30	7.94	1,259	90
3.17	3,155	70	[f] 8.25	1,212	85
3.22	3,106	90	8.48	1,179	60
3.24	3,086	95	8.59	1,164	95
[e] 3.48	2,874	45	8.88	1,126	100
[e] 3.51	2,849	40	8.98	1,114	100
3.64	2,747	35	9.23	1,083	100
3.70	2,703	45	9.25	1,081	100
3.74	2,674	40	9.31	1,074	100
3.86	2,591	35	[f] 9.62	1,040	55
3.96	2,525	35	9.83	1,017	60
4.08	2,451	30	10.00	1,000	100
4.16	2,404	40	10.11	989	65
4.22	2,370	35	10.32	969	85
4.30	2,326	30	10.48	954	55
4.46	2,242	30	10.74	931	45
4.55	2,198	40	[f] 11.20	893	85
4.62	2,164	30	11.51	869	100
4.68	2,137	30	12.06	829	100
4.82	2,075	25	12.77	783	100
5.08	1,968	35	12.92	774	100
5.17	1,934	80	14.86	673	100
5.23	1,912	50	15.64	639	60
5.37	1,862	80	18.25	548	30
5.58	1,792	80	18.79	532	30
[e] 5.73	1,745	85	20.46	489	45
5.97	1,675	80	23.09	433	100
5.99	1,669	75	25.19	397	100
6.13	1,631	75	27.29	366	80
Paradichlorobenzene					
2.15	4,651	35	4.22	2,370	30
2.40	4,167	30	4.26	2,347	30
2.45	4,082	35	4.34	2,304	25
2.59	3,861	30	[e] 4.39	2,278	35
2.68	3,731	30	4.50	2,222	20
3.22	3,106	55	4.57	2,188	20
[e] 3.52	2,841	35	4.70	2,128	20
3.61	2,770	30	4.95	2,020	20
3.75	2,667	30	5.12	1,953	25
3.85	2,597	25	5.28	1,894	80
3.90	2,564	30	5.43	1,842	35
4.19	2,387	30	5.65	1,770	45

See footnotes at end of table.

TABLE 1. *Observed bands*—Continued

Observed wavelength	Wave number	Intensity [a]	Observed wavelength	Wave number	Intensity [a]
Paradichlorobenzene—Continued					
μ	cm^{-1}	%	μ	cm^{-1}	%
5.68	1,760	45	9.18	1,089	100
[e] 5.72	1,748	30	9.36	1,068	65
5.90	1,695	30	9.85	1,015	100
6.01	1,664	50	9.90	1,010	90
6.08	1,645	80	10.52	951	40
[e] 6.32	1,582	70	10.69	935	40
6.77	1,477	70	12.21	819	100
6.82	1,466	100	12.75	784	70
6.89	1,451	95	13.40	746	25
7.02	1,424	85	14.59	685	20
7.16	1,397	100	15.91	628	20
7.43	1,346	45	17.92	558	80
7.77	1,287	40	18.28	547	100
7.91	1,264	50	19.08	524	45
8.18	1,222	55	20.21	495	100
8.53	1,172	55	20.67	484	45
8.94	1,118	90	24.18	414	45
9.03	1,107	90			
1,2,3-Trichlorobenzene					
2.17	4,608	25	7.83	1,277	40
2.42	4,132	25	7.90	1,266	65
2.61	3,831	25	[f] 8.22	1,216	50
3.20	3,125	40	8.38	1,193	100
3.24	3,086	45	8.52	1,174	65
3.34	2,994	25	8.63	1,159	100
3.55	2,817	20	9.19	1,088	65
3.96	2,525	25	9.53	1,049	80
4.67	2,141	20	[f] 9.63	1,038	65
5.18	1,930	50	9.91	1,009	50
5.38	1,859	45	10.21	979	40
5.60	1,786	40	10.37	964	50
5.99	1,669	50	[f] 12.70	787	100
6.72	1,488	75	12.98	770	100
6.85	1,460	80	13.63	733	90
6.97	1,435	100	14.39	695	95
7.07	1,414	100	19.42	515	65
[e] 7.27	1,376	45	20.57	486	45
7.73	1,294	40	25.06	399	45
1,2,4-Trichlorobenzene					
2.15	4,651	35	8.03	1,245	100
2.40	4,167	35	8.37	1,195	65
2.44	4,098	40	8.52	1,173	80
2.54	3,937	30	8.65	1,156	95
2.64	3,788	30	8.76	1,142	100
3.21	3,115	90	8.86	1,129	100
3.31	3,021	55	8.91	1,122	100
3.56	2,809	50	[f] 9.14	1,094	100
3.71	2,695	45	9.25	1,081	90
3.76	2,660	35	[f] 9.65	1,036	100
3.82	2,618	30	9.90	1,010	70
3.97	2,519	35	10.09	991	65
4.21	2,375	30	10.58	945	85
4.28	2,336	30	11.05	905	60
4.58	2,183	40	[f] 11.52	868	100
4.67	2,141	25	12.27	815	100
4.86	2,058	35	12.33	811	100
5.11	1,957	30	12.65	790	95
5.29	1,890	85	12.92	774	85
5.50	1,818	45	13.41	746	50
5.65	1,770	50	13.62	734	45
[e] 5.73	1,745	85	14.39	695	65
5.97	1,675	50	14.58	686	95
6.14	1,629	80	14.77	677	95
[e] 6.37	1,570	100	16.30	613	40
6.68	1,497	95	17.40	575	100
6.84	1,462	100	18.16	551	100
7.04	1,420	100	19.20	521	40
7.23	1,383	100	21.80	459	100
7.28	1,374	100	22.76	439	100
7.35	1,360	100	25.44	393	[d] 95
7.63	1,311	49	32.57	307	[d] 90
7.91	1,264	85			

TABLE 1. *Observed bands*—Continued

Observed wavelength	Wave number	Intensity [a]	Observed wavelength	Wave number	Intensity [a]
		1,3,5-Trichlorobenzene			
μ	cm^{-1}	%	μ	cm^{-1}	%
2.16	4,630	25	6.77	1,477	55
2.38	4,202	25	7.04	1,420	[b] 95
2.45	4,082	25	7.16	1,397	[b] 80
2.56	3,906	25	7.24	1,381	[b] 80
3.19	3,135	55	7.77	1,287	35
3.23	3,096	70	8.19	1,221	30
3.52	2,841	35	8.43	1,180	30
3.70	2,703	25	8.74	1,144	40
3.79	2,639	30	9.13	1,095	100
4.23	2,364	40	9.46	1,057	80
4.55	2,198	30	[f] 9.66	1,035	35
5.13	1,949	40	10.05	995	30
5.27	1,898	25	11.05	905	30
5.42	1,845	20	[f] 11.77	850	100
[e] 5.74	1,742	60	12.31	812	100
[e] 5.79	1,727	65	12.55	797	100
[e] 6.21	1,610	85	13.93	718	30
[e] 6.37	1,570	[b] 100	15.10	662	95
[e] 6.46	1,548	85	23.29	429	80
		1,2,3,4-Tetrachlorobenzene			
2.59	3,861	25	7.93	1,261	40
3.23	3,096	35	8.03	1,245	40
3.61	2,770	25	8.27	1,209	50
3.86	2,591	25	8.52	1,174	100
4.03	2,481	25	8.84	1,131	55
[e] 4.33	2,309	25	9.03	1,107	35
[e] 4.56	2,193	25	9.31	1,074	90
[e] 4.97	2,012	25	9.40	1,064	40
5.15	1,942	25	9.88	1,012	35
5.33	1,876	40	10.64	940	35
5.42	1,845	25	[f] 11.98	835	100
[e] 5.73	1,745	30	12.42	805	100
5.92	1,689	25	12.92	774	100
6.05	1,653	30	13.39	746	40
6.17	1,620	40	16.44	608	95
6.66	1,502	45	18.05	554	80
6.93	1,443	95	19.43	515	70
6.99	1,430	160	20.80	481	70
7.33	1,364	100			
		1,2,3,5-Tetrachlorobenzene			
2.40	4,167	25	8.42	1,188	20
2.54	3,937	25	8.48	1,179	70
3.20	3,125	50	8.66	1,155	45
3.22	3,106	60	8.87	1,127	95
[e] 3.35	2,985	25	8.99	1,112	95
3.58	2,793	25	[f] 9.53	1,049	75
3.63	2,755	25	9.65	1,036	50
5.41	1,848	25	[f] 11.67	857	100
[e] 5.77	1,734	55	[f] 12.00	833	100
6.10	1,639	35	12.23	818	100
[e] 6.37	1,570	100	12.48	801	100
[e] 6.44	1,553	100	14.54	688	80
6.74	1,484	45	15.79	633	20
7.00	1,428	100	16.70	599	100
7.10	1,408	100	17.93	558	75
7.22	1,385	100	19.10	523	20
7.29	1,372	100	23.10	431	[d] 95
8.00	1,250	90	31.74	315	[d] 95
		1,2,4,5-Tetrachlorobenzene			
3.23	3,096	40	9.42	1,062	100
[e] 4.32	2,288	25	10.45	957	30
5.54	1,805	25	10.56	947	35
[e] 5.74	1,742	35	[f] 11.40	877	100
6.79	1,473	80	12.08	828	40
6.95	1,439	100	[f] 12.74	785	50
7.54	1,326	90	13.13	762	35
7.81	1,280	40	15.49	646	95
8.00	1,250	55	19.63	509	80
8.13	1,230	55	22.52	444	[d] 100
8.97	1,115	100			

TABLE 1. *Observed bands*—Continued

Observed wavelength	Wave number	Intensity [a]	Observed wavelength	Wave number	Intensity [a]
		Pentachlorobenzene			
μ	cm^{-1}	%	μ	cm^{-1}	%
3.21	3,115	45	8.92	1,121	60
3.25	3,077	45	9.22	1,084	100
3.63	2,755	25	9.40	1,064	40
3.90	2,564	25	9.52	1,050	40
[e] 5.79	1,727	45	10.11	989	25
6.09	1,642	30	10.31	970	30
[e] 6.32	1,582	60	10.64	940	45
[e] 6.42	1,558	95	[f] 11.60	862	100
[e] 6.53	1,531	95	12.17	822	100
6.94	1,441	65	12.54	797	35
7.15	1,399	100	14.29	700	80
7.49	1,335	100	14.70	680	100
7.70	1,299	75	17.79	562	90
8.08	1,238	50	17.92	558	80
8.17	1,224	80	19.09	524	80
8.30	1,204	80	19.36	516	25
8.57	1,167	100	36.80	272	[d] 75
		Hexachlorobenzene			
[e] 7.14	1,400	30	[f] 10.75	930	25
7.42	1,347	95	13.92	718	30
7.71	1,297	65	14.37	696	85

[a] Intensities not corrected for background.
[b] 0.05-mm cell.
[c] 0.40-mm cell.
[d] 1.6-mm cell.
[e] Solid in solution of CCl_4 and band partially contributed by CCl_4.
[f] Solid in solution of CS_2 and band partially contributed by CS_2.

TABLE 2. *Fundamental vibrations of monohalobenzenes in* cm^{-1}

D_{6h}		Benzene [a]	Band types	Fluorobenzene	Chlorobenzene	Bromobenzene	Iodobenzene
ν_1	A_{1g}	3,062	A_1	------	------	------	------
ν_2	A_{1g}	992	A_1	1,019	1,002	1,002	997
ν_3	A_{2g}	[b] 1,340	B_1	[c]	[c]	[c]	[c]
ν_4	A_{2u}	671	B_2				
ν_5	B_{1u}	3,071	A_1	------	------	------	------
ν_6	B_{1u}	[b] 1,008	A_1	807	701	668	653
ν_7	B_{2g}	995	B_2	759	740	735	729
ν_8	B_{2g}	703	B_2	684	682	681	681
ν_9	B_{2u}	[b] 1,150	B_1	------	------	------	------
ν_{10}	B_{2u}	[b] 1,310	B_1	1,155	1,175	1,160	1,159
ν_{11}	E_{1g}	849	A_2	------	------	------	------
			B_2	[c]	[c]	[c]	[c]
ν_{12}	E_{1u}	3,063	A_1	3,086	------	------	------
			B_1	3,068	------	------	------
ν_{13}	E_{1u}	1,485	A_1	1,495	1,475	1,475	1,468
			B_1	1,326	1,326	1,324	1,321
ν_{14}	E_{1u}	1,037	A_1	1,019	1,027	1,022	1,015
			B_1	------	------	------	------
ν_{15}	E_{2g}	3,047	A_1	1,220	1,085	1,071	1,060
			B_1	3,040	3,030	3,040	3,030
ν_{16}	E_{2g}	1,585	A_1	1,592	1,580	1,585	1,577
			B_1	1,495	1,475	1,475	------
ν_{17}	E_{2g}	1,178	A_1	1,155	------	1,160	1,159
			B_1	1,064	1,068	1,071	1,060
ν_{18}	E_{2g}	606	A_1	519	418	314	------
			B_1	614	617	614	613
ν_{19}	E_{2u}	[b] 975	A_2	------	------	------	------
			B_2	989	984	964	984
ν_{20}	E_{2u}	404	A_2	407	393	------	------
			B_2	500	469	458	448

[a] Benzene assignments and wave numbers from R. D. Mair and D. F. Hornig, J. Chem. Phys. **17**, 1236 (1949).
[b] Partially contributed by solvent.
[c] Band lies below the range of observations.

TABLE 3. *Assignments of some of the bands of polychlorobenzene*

Orthodichlorobenzene			Metadichlorobenzene			Paradichlorobenzene			1,2,3-Trichlorobenzene			1,2,4-Trichlorobenzene		
Wave number	Identification	Intensity	Wave number	Identification	Intensity	Wave number	Identification	Intensity	Wave number	Identification	Intensity	Wave number	Identification	Intensity
cm^{-1}		%	cm^{-1}		%	cm^{-1}		%	cm^{-1}		%	cm^{-1}		%
1,610	A_1 C—C	90	1,631	B_1 C—C	75	1,645	A_g C—C	75				1,629	A^1 C—C	80
[a] 1,577	B_1 C—C	95	[a] 1,580	A_1 C—C	100	[a] 1,582	B_{1g} C—C	65	1,488	A_1 C—C	75	1,570	A^1 C—C	100
1,484	B_1 C—C	100	[a] 1,506	B_1 C—C	95							1,497	A^1 C—C	95
1,458	A_1 C—C	[b] 55	1,449	A_1 C—C	95	1,451	B_{3u} C—C	90				1,462	A^1 C—C	100
1,167	A_1 C—H	95	1,164	B_1 C—H	65	1,172	A_g C—H	55				1,156	A^1 C—H	100
						1,118	B_{3u} C—H	90						
1,129	B_1 C—H	[b] 55							1,159	B_1 C—H	100			
			1,081	A_1 C—H	100				1,088	A_1 C—H	70			
1,037	A_1 C—H	[b] 75	[a] 1,040	B_1 C—H	50									
			1,000	A_1 ring	95	1,015	B_{2u} C—H	95	979	A_1 ring	35	1,010	A^1 ring	70
			969	B_2 C—H	85				964	B_2 C—H	50			
941	B_2 C—H	100	[a] 869	B_2 C—H	[b] 90	935	[c] A_u C—H	45				868	A^{11} C—H	100
			[a] 893	A_2 C—H	85							815	A^{11} C—H	100
747	B_2 C—H	[b] 85	783	B_2 C—H	[b]100	819	B_{1u} C—H	100						
			673	B_2 C—C	[b] 85	685	B_{3g} C—C—C	10	770	B_2 C—C	100			
						628	B_{1g} C—C—C	10	733	B_2 C—C	90			
						414	A_u C—C	[d] 50						

1,3,5-Trichlorobenzene			1,2,3,4-Tetrachlorobenzene			1,2,3,5-Tetrachlorobenzene			1,2,4,5-Tetrachlorobenzene			Pentachlorobenzene		
Wave number	Identification	Intensity	Wave number	Identification	Intensity	Wave number	Identification	Intensity	Wave number	Identification	Intensity	Wave number	Identification	Intensity
cm^{-1}		%	cm^{-1}		%	cm^{-1}		%	cm^{-1}		%	cm^{-1}		%
1,610	E^1 C—C	85	1,620	C—C	40	1,639	C—C	60				1,642	C—C	30
			1,502	C—C	45	1,570	C—C	100				1,558	C—C	90
1,477	E^1 C—C	50				1,484	C—C	45						
1,186	E^1 C—H	30	1,174	C—H	100				1,062	C—H	100			
995	A^1 ring	35												
850	A_2^{11} C—H	100							[a] 877	C—H	100	[a] 862	C—H	100
662	A_2^{11} C—C	95	805	C—H	100	[a] 833	C—H	100						

[a] Partially contributed by solvent. [b] 0.05-mm cell. [c] A_u or B_{3g}. [d] 1.6-mm cell.

The most success was possible in the case of the monohalogenated benzenes. Benzene has the symmetry D_{6h}, and thus 20 distinct vibrational frequencies are present, 10 of which are doubly degenerate. In the monohalogenated benzenes, the symmetry is reduced to C_{2v}. As a result, there are no degenerate frequencies remaining, and there are 36 distinct frequencies, although the A_2 species will be infrared inactive. A correlation between the benzene frequencies and some of the monohalogenated benzene frequencies is given in table 2. For fluorobenzene the published assignments[3] for the gas were used as a guide.

[3] D. C. Smith, E. E. Ferguson, R. L. Hudson, and J. Rud Nielsen, J. Chem. Phys. **21**, 1475 (1953).

For the more highly substituted chlorobenzenes more of the frequencies were inaccessible, and in each case only the C—C, C—H, and ring frequencies, which are more or less constant from molecule to molecule, have been designated in table 3. These assignments should be regarded as tentative, although they were made according to the procedure suggested in the paper by Randle and Whiffen.

WASHINGTON, December 4, 1956.