The C-H Stretching Spectra and Intensities of Dihalogenomethanes and Intermolecular Interaction

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Many experiments and theoretical considerations concerning the vibrational spectra of dihalogenomethanes have been carried out.1-7) Regarding the C-H stretching bands of each compound in the condensed phase, a band existing between 2970 and 3000 cm^{-1} was assigned to ν_1 (a symmetric stretching vibration) and another between 3040 and 3070 cm^{-1}, to ν_6 (an antisymmetric stretching vibration).

In the C-H stretching region of the infrared spectrum of dichloromethane vapor, there is found only a doublet centered at 2995 cm^{-1}. In the dilute solution state, a band of weak intensity appears on the high frequency side (3048 cm^{-1} in the case of the carbon tetrachloride solution), whereas none is observed in the vapor state. As the concentration of the solute increases, the absorptivity* of this band also increases, while that of the band of low frequencies (2983 cm^{-1} in the carbon tetrachloride solution) decreases. In the pure liquid, the former is much stronger than the latter, as Josien et al.8) have indicated.

In ordinary cases, where the existence of intermolecular interaction, rotational isomerism, etc. can be ignored, neither the frequency nor the absorptivity of an infrared band changes appreciably as a function of the concentration in a non-polar solvent. Considering this well-known fact, it is very interesting to find such experimental results as have been presented above.

Experimental

The commercial products of dichloromethane, chlorobromomethane, dibromomethane, and diiodomethane were purified by distillation. Dimethoxymethane-d_6 was prepared at the author's laboratory.9) The purity of these compounds was checked by means of gas chromatography.

The infrared spectra in the C-H stretching region were obtained by means of a Perkin-Elmer model 12 C spectrophotometer equipped with a lithium fluoride prism. The recording of spectra in the vapor state was made in cells with path lengths of 10 cm. and 100 cm. on dichloromethane and chlorobromomethane, 100 cm. on dibromomethane, and 10 cm. on dimethoxymethane-d_6, all at a total pressure of 1 atm. The recording of spectra in solution was made with carbon tetrachloride and carbon disulfide as the solvents, and at the following volume percentage concentrations: dichloromethane-50% (cell thickness, 0.10 mm.), 10% (0.2 and 0.5 mm.) and 1.0% (0.5 and 1.0 mm.); chlorobromomethane—50% (0.05 and 0.1 mm.), 10% (0.2 and 0.5 mm.) and 2% (0.5 and 1.0 mm.); dibromomethane—50% (0.01, 0.03 and 0.05 mm.), 10% (0.2 mm.) and 2% (1.0 mm.); diiodomethane—50% (0.03 and 0.05 mm.), 10% (0.2, 0.5 and 1.0 mm.), 5% (1.0 mm.) and 2% (1.0 and 5.0 mm.); and dimethoxymethane-d_6 (in carbon tetrachloride solution only)—25% (0.15 mm.). In the pure liquids spectral, measurements were made in cells 0.05 and 0.03 mm. thick for dichloromethane and chlorobromomethane, 0.03 and 0.014 mm. thick for dibromomethane and diiodomethane, and 0.014 mm. thick for dimethoxymethane-d_6.

Spectra were also obtained with a Perkin-Elmer model 21 spectrophotometer equipped with a sodium chloride prism on the compounds in the vapor state, in solution (solvent: carbon tetrachloride and carbon disulfide) and as pure liquids. Especially on dichloromethane, the variation in intensity and frequency with concentration was observed minutely with varied concentrations—the CH_2 bending vibration* (1425 cm^{-1}) and the CH_2 rocking vibration (895 cm^{-1}) in carbon tetrachloride solution, and the CH_2 wagging vibration (1154 cm^{-1}) and the C-Cl stretching vibrations (740 and 707 cm^{-1}) in carbon disulfide solution.

As for the Raman spectra, observation was made by means of a Cary model 81 spectrophotometer on dichloromethane, chlorobromomethane and dibromomethane in pure liquid and in carbon tetrachloride solution (50, 20 and 10% by volume). On the compounds in pure liquid, the qualitative degrees of depolarization were measured by alternately wrapping the Raman tube with two types of polarizing cylinders.

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1) J. W. Straley, *J. Chem. Phys.*, **23**, 2183 (1955).

2) J. Wagner, *Z. physik. Chem.*, **45**, 69 (1940).

3) Ta-You Wu, *J. Chem. Phys.*, **10**, 116 (1942).

4) J. C. Decius, ibid., **16**, 214 (1948).

5) T. Shimanouchi, ibid., **17**, 848 (1949).

6) E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

7) I. Suzuki and T. Shimanouchi, *J. Mol. Spectroscopy*, **6**, 277 (1961).

8) M.-L. Josien, N. Fuson and A. Lafaix, *Compt. rend.*, **249**, 256 (1959).

* $\frac{1}{cl}\log_{10}\frac{I_0}{I}$

9) K. Nukada, *Spectrochimica Acta*, **18**, 745 (1962). *Reports Gov. Chem. Ind. Research Inst. Tokyo* (to be published).

* In pure liquid, dichloromethane has a band at 1425 cm^{-1} and a very weak shoulder at 1445 cm^{-1}. When it is diluted with carbon tetrachloride, the intensity at 1445 cm^{-1} becomes larger, but that at 1425 cm^{-1} becomes a bit smaller.

Results

Variation of the Relative Intensities.—*Infrared Spectra.*—The ratio of the absorbance of ν_6 to that of ν_1 (D_6/D_1) was computed from the observed spectra of the dihalogenomethanes and dimethoxymethane-d$_6$ by means of the base-line method.* In the cases of carbon tetrachloride and carbon disulfide solutions, plots of the observed values of D_6/D_1 against the concentration yield straight lines (see Figs. 2 and 3). If these straight lines are extended to zero concentration, the values of D_6/D_1 at

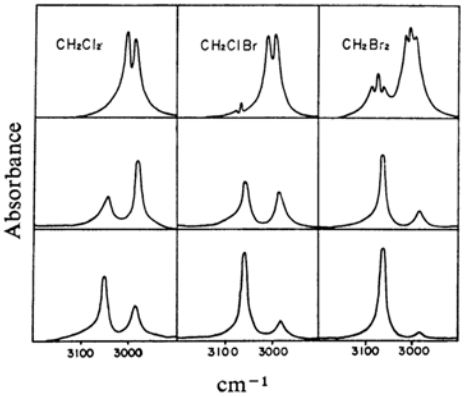

Fig. 1. C–H stretching spectra of CH_2Cl_2, CH_2ClBr, and CH_2Br_2 in vapor, carbon tetrachloride solution and in pure liquid.**
Upper row: Vapor
Middle row: Solution in carbon tetrachloride 10% by volume
Bottom row: Pure liquid

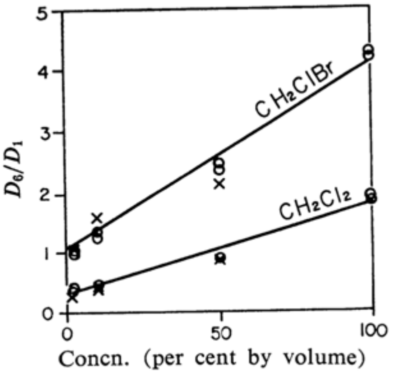

Fig. 2. Plot of D_6/D_1 vs. concentration in CCl_4 and CS_2 solutions for CH_2Cl_2 and CH_2ClBr.
○ CCl_4 solution and pure liquid
× CS_2 solution

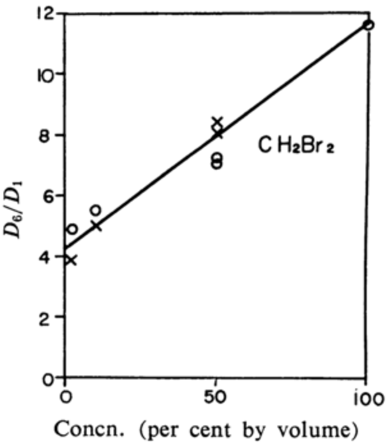

Fig. 3. Plot of D_6/D_1 vs. concentration in CCl_4 and CS_2 solutions for CH_2Br_2.
○ CCl_4 solution and pure liquid
× CS_2 solution

TABLE I. C–H STRETCHING FREQUENCIES OF DICHLOROMETHANE, CHLOROBROMOMETHANE, DIBROMOMETHANE AND DIIODOMETHANE IN cm^{-1}

	Infrared		Raman	
	ν_1	ν_6	ν_1	ν_6
Dichloromethane				
Vapor	3002 2988	—	(3002)[a]	
Solution (CCl_4)[b]	2983	3048	2984	3044
Solution (CS_2)[b]	2974	3039		
Liquid	2987	3054	2986	3051
Solid	2983	3054		
Chlorobromomethane				
Vapor	3008 2993	3078 3065 —		
Solution (CCl_4)[b]	2987	3058	2986	3055
Solution (CS_2)[b]	2980	3049		
Liquid	2985	3059	2986	3055
Dibromomethane				
Vapor	3017 3005 2996	3087 3077 3065		
Solution (CCl_4)[b]	2986	3066	2993	3065
Solution (CS_2)[b]	2979	3059		
Liquid	2988	3064	2986	3060
Diiodomethane				
Vapor				
Solution (CCl_4)[b]	2981	3061		
Solution (CS_2)[b]	2975	3053		
Liquid	2968	3046		

a) J. Rud Nielsen and N. E. Ward, *J. Chem. Phys.*, **10**, 81 (1942).
b) Frequencies obtained by extrapolating to zero concentration are shown.

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* Since spectra were obtained with a single-beam spectrophotometer, the reproducibility of the observed values of absorbances was not very good. For this reason, ratios of absorbances were calculated.

** The absorptivities of C-H stretching bands vary with the kind of compound as well as with phase. So the absorbance is plotted on the ordinate axis.

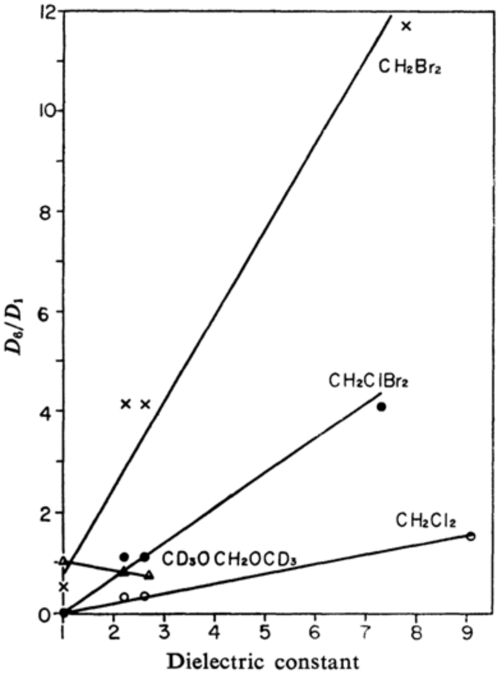

Fig. 4. Plot of D_6/D_1 vs. the dielectric constant of the medium for CH_2Cl_2 (○), CH_2ClBr (●), CH_2Br_2 (×) and $CD_3OCH_2OCD_3$ (△).

infinite dilution in carbon tetrachloride and carbon disulfide solutions are obtained. Then, in the cases of chlorobromomethane, dibromomethane and dimethoxymethane-d$_6$, if the values of D_6/D_1 are plotted against the dielectric constants of the media (vapor, carbon tetrachloride, carbon disulfide and pure liquid), they fall on a straight line. (Fig. 4) Moreover, in the case of dichloromethane, if the values of D_6/D_1 in pure liquid and in carbon tetrachloride and carbon disulfide solutions are plotted against the dielectric constants of the media, the value of D_6/D_1 obtained by setting the dielectric constants at one (vapor) by extrapolation is nearly zero. This agrees well with the author's interpretation that, in vapor, the intensity of ν_6 is extremely weak. Details of this interpretation are given below.

As Fig. 4 shows, the value of D_6/D_1 increases with the dielectric constant in the cases of dichloromethane, chlorobromomethane and dibromomethane, but decreases in the case of dimethoxymethane-d$_6$.

In the case of dichloromethane, the variations in the band intensities with the concentration in the sodium chloride prism region, were observed to be smaller than those in the C–H stretching region.

Raman Spectra.—The relative intensity of ν_1 and ν_6 were estimated in the cases of dichloromethane, chlorobromomethane and dibromomethane in the pure liquid and in carbon tetrachloride solutions of various concentrations. The ratio of the peak intensity of ν_6 to that of ν_1 (h_6/h_1) shows no variation beyond the range of experimental errors. The values of h_6/h_1 are 0.16∼0.18 for dichloromethane, 0.17∼0.18 for chlorobromomethane, and 0.28∼0.29 for dibromomethane.

Frequency Shifts.—When the compound is in a solution, the frequency shifts of ν_1 and ν_6 are linear functions of the concentration in both the infrared and Raman spectra. The slope varies with the kind of compound as well as with the kind of band and solvent. The frequencies shown in Table I for carbon tetrachloride and carbon disulfide solutions were obtained by extrapolation to zero concentration. When the compound is in a vapor, carbon tetrachloride solution or carbon disulfide solution, the relation between $(\nu_{\text{vapor}}-\nu_{\text{solution}})/\nu_{\text{vapor}}$ and $(\varepsilon-1)/(2\varepsilon+1)$ is approximately linear. However, the value in the case of a pure liquid is not on the same line.

Discussion

Assignment of C–H Stretching Vibrations of the Dichloromethane Molecule in Vapor. — In the infrared spectra of dichloromethane in the condensed phases, single bands are observed at about 2980 and 3050 cm^{-1}. However, in the vapor, only a doublet centered at 2995 cm^{-1} is found, and no band is observed in the vicinity of 3050 cm^{-1}. Straley[1)] has reported the doublet as being due to a partial overlapping of ν_1 and ν_6. However, the present author has concluded, on the basis of the following considerations, that the doublet at 2995 cm^{-1} corresponds to ν_1, showing P and R branches, and that ν_6, which may exist in a higher frequency region, is not observed because of its very weak intensity (see Fig. 1). This result is in good agreement with Kagarise's.[10)]

(1) In the infrared spectrum of chlorobromomethane vapor, a band of weak intensity is observed at 3065 cm^{-1} in addition to the doublet centered at 3000 cm^{-1}. These two bands, which are also observed in the condensed phase, can reasonably be assigned to ν_6* and ν_1 respectively. In the case of dibromomethane, the bands at 3005 and 3077 cm^{-1} in the vapor are also observed in the condensed phase and can be reasonably assigned to ν_1 and ν_6 respectively. In both cases, the difference in frequency between ν_1 and ν_6 is 60∼80 cm^{-1} irrespective of the phase. Assuming that

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10) R. E. Kagarise, *Spectrochim. Acta* (in press).

* The asymmetric C–H stretching vibration in the cases of chlorobromomethane and dimethoxymethane-d$_6$ molecules is also represented by ν_6.

Straley's assignment is correct in the case of dichloromethane, the difference in frequency in the vapor is 14 cm^{-1}, while that in the condensed phase is 60$\sim$70 cm^{-1}. This frequency difference of 14 cm^{-1} in the vapor is abnormally small when compared with the other dihalogenomethanes.

When the compounds are in vapor, the intensity of ν_6 is much weaker than that of ν_1 in the case of chlorobromomethane but not very different in the case of dibromomethane. When the compounds are in the condensed phase, the intensity of ν_6 compared with that of ν_1 increases in the order of: dichloromethane → chlorobromomethane → dibromomethane. If the same tendency exists in vapor, it must be expected that the intensity ratio of ν_6 to ν_1 is smaller in the case of dichloromethane than in the case of chlorobromomethane.

(2) The dichloromethane molecule is a nearly prolate symmetric top* and ν_1 is a type-B band, while ν_6 is a type-C band. It is inferred from the band contours of the other fundamental bands, overtones and combination bands[11] of dichloromethane that the type-B bands lack a Q branch, while the type-C bands have a relatively strong Q branch. The doublet of dichloromethane centered at 2995 cm^{-1} does not exhibit a prominent Q branch; therefore, it is reasonably regarded as a type-B band.

In the case of a nearly prolate symmetric top, the approximate value of the separation of the maxima of P and R branches is given as follows;

$$\Delta\nu=\sqrt{\frac{8kT}{hc}\cdot\frac{B+C}{2}}$$

As estimated by this formula, $\Delta\nu$ is 13 cm^{-1} in the case of dichloromethane, a value which is in good accordance with the observed separation of 14 cm^{-1}, between the maxima of the doublet at 2995 cm^{-1}.

Variation of the Infrared Intensities of the C–H Stretching Bands and Intermolecular Interaction.—The intensities of the C–H stretching bands of dihalogenomethanes vary extraordinarily with the dielectric constant of the medium, as is shown in Fig. 4, but the frequency shifts are comparatively small, as Table I shows. According to Josien et al.,[8] in the case of dichloromethane the ratios between the integrated intensities in a dilute carbon tetrachloride solution (0.15 mol./l.) and in pure liquid are 1 : 0.6 for ν_1 and 1 : 2.4 for ν_6.

According to Polo et al.,[12] the ratio of the infrared intensity in the condensed phase to that in vapor hinges solely on the refractive indices of the media as estimated by the Debye model. In other words, the ratio between the intensities in vapor is identical with the ratio in the condensed phase.

If Polo's theory were valid, the intensity of any band in the carbon tetrachloride solution would be nearly equal to that in pure liquid, since the refractive index of dichloromethane (1.42) is nearly equal to that of carbon tetrachloride (1.46). Nevertheless, it is observed that the absorptivities of ν_1 and ν_6 vary markedly with the concentration of both in carbon tetrachloride and carbon disulfide solutions. Such variation cannot be explained by the simple model mentioned above, rather, it suggests the existence of some intermolecular interaction, as Polo indicated. Caldow et al.[13,14] have made an experimental study of the effect of solvents on the absorption bands of hydrogen cyanide. They have concluded that the observed solvent effects in the case of hydrogen cyanide result from the superposed contributions of both bulk dielectric effects and intermolecular interaction between a solute molecule and a solvent molecule. It is considered reasonable, therefore, that the remarkable concentration effect on the infrared intensities of ν_1 and ν_6 in the case of dichloromethane result from intermolecular interaction. In this case the interaction between solute molecules (dichloromethane) is more predominant than the interaction between a solute molecule and a solvent molecule (carbon tetrachloride or carbon disulfide); it is observed that the intensity ratio between ν_1 and ν_6 in solution approaches the ratio in vapor as the solution is diluted (see Fig. 4). Kagarise concluded also that dichloromethane forms a complex with aceton.[10]

Hydrogen bonding generally causes not only a large variation in the intensity of the stretching band, but also a remarkable lowering of its frequency. In such cases, the effect of intermolecular interaction has more influence on the intensity than on the frequency. Therefore, to presuppose the existence of intermolecular interaction in the case of dichloromethane seems not to contradict the experimental finding that the frequency shift is comparatively small. In chlorobromomethane and dibromomethane, a similar variation is also observed; therefore, a similar interaction

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* $I_A=2.6\times10^{-39}$, $I_B=25.6\times10^{-39}$ and $I_C=27.7\times10^{-39}$ g.cm^2

[11] E. K. Plyler and W. S. Benedict, *J. Res. Nat. Bur. Stand.*, **49**, 1 (1952).

[12] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).

[13] G. L. Caldow and H. W. Thompson, *Proc. Roy. Soc. (London)*, **A254**, 1 (1960).

[14] G. L. Caldow and H. W. Thompson, ibid., **A254**, 17 (1960).

is presupposed. Again, in the case of dimethoxymethane-d$_6$, where such an interaction seems negligible, the variation in the ratio of intensities (D_6/D_1) is smaller than in the cases of dihalogenomethanes, and its slope against the dielectric constants of media is opposite to the slope in dihalogenomethanes (see Fig. 4).

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