

INTERMOLECULAR INTERACTIONS AND VIBRATIONAL SPECTRA OF MOLECULES. I. INFLUENCE OF SOLVENT AND TEMPERATURE ON SOME INFRARED AND RAMAN BANDS OF CHLOROBENZENE AND CHLOROFORM

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On the basis of the intensity of some chlorobenzene and chloroform bands in the Raman and infrared spectra for pure liquids and their equimolar solutions it is concluded that chlorobenzene forms specific autocomplexes and with chloroform mixed complexes. The raising of temperature by 50°C does not influence these complexes. Measurements of widths and contour shapes of the bands suggest that the autocomplexes of chlorobenzene are formed by π ring electrons, whereas the mixed complexes by $H_5C_6-Cl...H-CCl_3$ bonds. The difference in variation of Raman and infrared band parameters for the same experimental conditions was examined and discussed.

In the discussion all intermolecular interactions are considered as the result of complex formation. No essential difference exists between the specific and universal interactions. The mean life time of the complex is proposed as a criterion of their spectroscopic discrimination. For the two types of complexes the names of spectroscopic and statistical complexes are proposed.

Introduction

The influence of intermolecular interactions on vibrational band parameters is one of the most important problems in modern molecular spectroscopy. Spectroscopists specify two types of interactions: the specific and universal interactions. The variation of frequency and/or intensity when universal interactions are changed is described by several formulae based on the theory of continuous dielectric medium (the so called internal field effect). The disagreement of the observed variations with these formulae is considered as a proof that the specific interactions occur (Bakhshev 1963, 1964, 1966; Josien 1954, 1955, 1958, 1959, 1962; Hallam 1963; Fini, Mirone, Patella 1968).

The intermolecular interactions can be changed in a liquid when the solvent and/or temperature are varied. In this work both methods are used to study the structure of liquid

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chlorobenzene and its solution in chloroform by comparison of Raman and infrared band parameters. In a previous publication (Mierzecki 1964) it was shown that the C—Cl stretching infrared bands of chlorobenzenes and chlorotoluenes became sharper and more intense at maximum at elevated temperature in contrast to other bands studied. These bands are unfortunately very weak in Raman spectra. The change of intensity and width of other Raman bands of *o*-dichlorobenzene when temperature is varied scarcely exceeds experi-

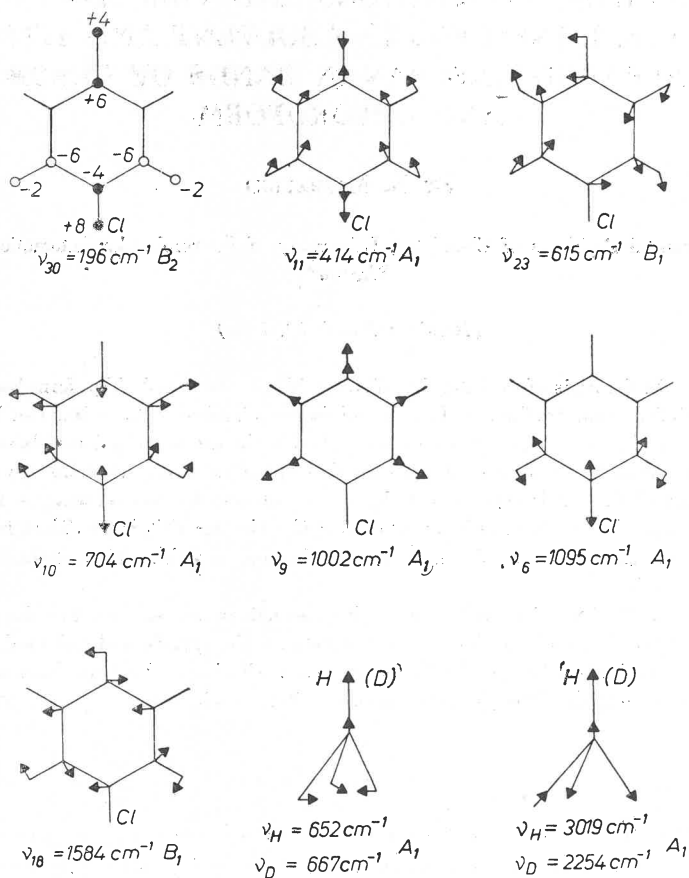


Fig. 1

mental errors. In accord with results of Sokolovskaya (1964) the Raman band parameters of smaller molecules are more sensitive to temperature variation than those of larger ones. Thus, simple chlorobenzene was the main object of the present studies. Five bands corresponding to different vibration symmetry (Schmidt, Brandmüller 1960) were chosen for Raman study: 196 (B_2), 414 (A_1), 615 (B_1), 704 (A_1), 1095 (A_1), 1584 (B_1) cm^{-1} (Fig. 1). Three bands: 414, 1002 (A_1) and 1584 cm^{-1} were investigated in the infrared. The number of solvents was limited to two: polar chloroform and nonpolar *n*-heptane. The spectra were compared at two temperatures.

It is known that the intensity of the C—H (3019 cm^{-1}) or C—D (2254 cm^{-1}) stretching and $\text{C}\equiv\text{Cl}_3$ (667 cm^{-1}) deformation bands of chloroform are very sensitive to the solvent effect (Laşcombe 1964, Rea 1960, Ratajczak 1965, Szczepaniak 1963, Brahms 1959). In this work the parameters of the above bands in the Raman and those of the C—D stretching band in the infrared were compared in pure liquid and in solution in chlorobenzene. The d-chloroform was used to avoid the overlapping of the C—H bands of chlorobenzene and chloroform.

Experimental part

The Raman spectra were recorded by means of a Hilger Raman Recording Spectrograph E. 612. The slit width was chosen to meet the optimal recording conditions (Schubert 1958), taking also into account the width of each band. For measurements at elevated temperature the water stream in the waterjacket in the Raman source unit was heated in the thermostat.

For measurements of infrared spectra a Zeiss UR 10 Infrared Spectrometer was used. Different temperatures were obtained in a specially constructed chamber into which a normal cell could be inserted. The chamber consisted of a frame through which either a stream of heated glycerine or cold evaporated nitrogen is maintained. For low temperature measurements an additional pair of windows is mounted into the chamber and the space between these windows and the cell is dehydrated by means of silica gel.

For each Raman band the integral intensity I_∞ , the apparent intensity at maximum I_0 and the halfwidth $\Delta\nu_{1/2}$ were measured. For the infrared bands similar parameters were considered *i.e.* the apparent integral extinction coefficient B_∞ , the apparent extinction at maximum B_0 and the halfwidth $\Delta\nu_{1/2}$ at the half extinction value. From these data the apparent band shape factor (Sushchinskij 1960) was calculated $r = \frac{\pi}{2} \frac{I_0 \Delta\nu_{1/2}}{I_\infty}$ for Raman and $r = \frac{\pi}{2} \frac{B_0 \Delta\nu_{1/2}}{B_\infty}$ for infrared. The shape factor indicates the deviation of the band contour from the Lorentzian contour. It equals 1.00 for the Lorentzian shape and 1.47 for the Gaussian shape. Each Raman band was recorded 8–50 times and the mean values and standard deviations for I_∞ , I_0 and $\Delta\nu_{1/2}$ were calculated. The infrared bands were scanned four times and the path length was controlled before and after recording.

To compare the molar integral intensities for a particular Raman band at two temperatures t_1 and t_2 the measured area for the band at the temperature t_2 was multiplied by $n_2^2 d_1 / n_1^2 d_2$ where n and d are the refractive index and the density of the liquid or solution and subscripts 1 and 2 concern the temperatures t_1 and t_2 , respectively. Thus the change in geometrical factor and density was eliminated. To compare the molar intensities of the same band in equimolar solution and in the pure liquid, beside the geometrical factor the number of molecules of the solute per unit volume and also the change of instrumental amplifying factor A were taken into account. Thus for solutions the area was multiplied by $n_s^2 M_s d_s A_s / n_l^2 M_l d_l A_l$, where the subscripts s and l denote the equimolar solution and the liquid respectively, M_l being the molecular weight of the solute and M_s — the sum of molecular weights of solute and solvent. The ratio A_l/A_s of instrumental amplifying factors

was determined experimentally by measuring the intensity of the light of a chosen frequency scattered by the same solution with the two amplifier parameters.

To compare the extinction coefficient the area under the extinction profile was divided by lc , where c was molar concentration in mol/liter and l the path length in centimeters. The change of molar concentration when the temperature was varied was also taken into account by multiplying the concentration at elevated temperature by the ratio of densities for the two temperatures.

To calculate the discussed correction coefficients the refractive index of the studied solutions and liquids was measured by means of Abbé refractometer at various temperatures. At the same time the density was determined with a dilatometer calibrated with toluene. (The data for toluene taken from Rossini 1953.) The results of these measurements are gathered in Table I.

TABLE I

t °C	C_6H_5Cl		$CHCl_3$		$CDCl_3$		$C_6H_5Cl +$ $+n-C_7H_{16}$		$C_6H_5Cl +$ $+CHCl_3$		$C_6H_5Cl +$ $+CDCl_3$	
	n	d^* g/cm ³	n	d g/cm ³	n	d g/cm ³	n	d g/cm ³	n	d g/cm ³	n	d g/cm ³
-20						1.573						1.331
0						1.537						1.306
+20	1.5247	1.106	1.4461	1.493	1.4450	1.501	1.4460	0.860	1.4917	1.272	1.4917	1.281
28			1.4410	1.480	1.4402	1.487						
30	1.5193	1.095	1.4399	1.476	1.4392	1.483	1.4418	0.852	1.4860	1.259	1.4870	1.268
40			1.4339	1.458	1.4332	1.465	1.4379	0.843			1.4808	1.254
50	1.5086	1.074	1.4279	1.440	1.4269	1.447	1.4330	0.834	1.4749	1.233		
52.5			1.4262	1.436	1.4257	1.443					1.4741	1.238
57.5			1.4230	1.426								
60							1.4270	0.825				
65									1.4662	1.213	1.4680	1.221
70	1.4972	1.053					1.4210	0.816				
74											1.4628	1.209
75	1.4946	1.047							1.4602	1.199		
80							1.4155	0.806				
90							1.4105	0.795				

* after Timmerman (1950).

No slit or apparatus correction were taken into account, as all methods known for Raman and infrared bands alike give satisfactory results for bands of Lorentzian shape only (Bernstein, Allen 1955; Ramsay 1952; Kahiati 1967). Almost all studied bands were neither Lorentzian nor Gaussian, so these corrections could enhance the error when applied to all studied bands. For the infrared the extrapolation method could not be used for extinction measurements, as one of assumptions of this work was the supposition that the extinction coefficients depend on concentration. Thus, only the path length could be varied. To test this method the 414 cm^{-1} infrared band of chlorobenzene was recorded with three path lengths: 67.5, 38.9 and 29.8 microns and the integral extinction, the extinction at maximum

and the halfwidth were extrapolated to zero path length. A slight decrease of the shape factor value from $r_{67.5} = 1.39$ to $r_0 = 1.26$ was observed. The corrections of the Bernstein-Allen (1955) method applied to Raman band parameters also diminished the r value.

The position of almost all studied bands was altered neither by solvent nor by temperature. Only the 196 cm^{-1} B_2 chlorobenzene band was shifted towards lower frequency by 2 cm^{-1} at elevated temperature in accord with the results of Sechkarev (1965). The frequency of the chloroform C-D stretching band 2254 cm^{-1} in both Raman and infrared spectra was lowered by 1 to 2 cm^{-1} in solution of chloroform in chlorobenzene. (The error in frequency measurements was about 0.5 cm^{-1} .)

Other results are gathered in Tables II-IV. Table II represents the influence of the solvent on band intensities. The ratio of the molar integral intensities as measured in equimolar solutions to that measured in pure solutes are given for Raman band (column 4) and for infrared bands (column 5). The error limits of the ratio of Raman band intensities were calculated from intensity standard deviations Δ by means of the formula

$$\frac{a + \Delta a}{b - \Delta b} - \frac{a}{b} = \frac{\Delta a + \frac{a}{b} \Delta b}{b - \Delta b}$$

The error limits for the ratio of the infrared band intensities are about 10%.

Solvent influence on band intensities

TABLE II

Band cm^{-1}	solute	solvent	$\frac{(I_{\infty})_2}{(I_{\infty})_1}$	$\frac{(B)_2}{(B)_1}$	$\frac{n_1}{n_2} \left(\frac{n_2^2 + 2}{n_1 + 2} \right)^2$	$\frac{n_2}{n_1} \left(\frac{n_1^2 + 2}{n_2 + 2} \right)^4$
1	2	3	4	5	6	7
196	$\text{C}_6\text{H}_5\text{Cl}$	$n\text{-C}_7\text{H}_{16}$	0.92 ± 0.06		0.952	0.912
	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3	0.82 ± 0.11		0.993	0.967
414	$\text{C}_6\text{H}_5\text{Cl}$	$n\text{-C}_7\text{H}_{16}$	0.68 ± 0.08	1.05	0.952	0.912
	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3	0.63 ± 0.08	1.06	0.993	0.967
615	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3	0.86 ± 0.09		0.993	0.967
704	$\text{C}_6\text{H}_5\text{Cl}$	$n\text{-C}_7\text{H}_{16}$	0.91 ± 0.14		0.952	0.912
	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3	0.68 ± 0.11		0.993	0.967
1002	$\text{C}_6\text{H}_5\text{Cl}$	$n\text{-C}_7\text{H}_{16}$		0.91	0.952	0.912
	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3		1.08	0.993	0.967
1095	$\text{C}_6\text{H}_5\text{Cl}$	$n\text{-C}_7\text{H}_{16}$	0.81 ± 0.12		0.952	0.912
	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3	0.73 ± 0.12		0.993	0.967
1584	$\text{C}_6\text{H}_5\text{Cl}$	$n\text{-C}_7\text{H}_{16}$	0.80 ± 0.06	1.20	0.952	0.912
	$\text{C}_6\text{H}_5\text{Cl}$	CHCl_3	0.74 ± 0.12	1.22	0.993	0.967
652	CDCl_3	$\text{C}_6\text{H}_5\text{Cl}$	1.38 ± 0.07		1.009	1.005
2254	CDCl_3	$\text{C}_6\text{H}_5\text{Cl}$	1.46 ± 0.40	1.48	1.009	1.005

1 — solute 2 — solution.

Table III represents the influence of the temperature on the band intensities for pure substances and equimolar solutions. The ratios of molar integral intensities at higher temperature to that at lower temperature are given for Raman bands (column 3) and for infrared bands (column 4).

TABLE III

Temperature dependence of band intensities

Band cm ⁻¹	Solution	$\frac{I_2}{I_1}$ Raman	$\frac{B_2}{B_1}$ IR	$L = \frac{n_1}{n_2} \left(\frac{n_2^2 + 2}{n_1^2 + 2} \right)^2$	$M = \frac{n_1}{n_2} \left(\frac{n_2^2 + 2}{n_1^2 + 2} \right)^4$	$\frac{I'_2}{I'_1}$	$L \times \frac{I'_2}{I'_1}$	$M \times \frac{I'_2}{I'_1}$
1	2	3	4	5	6	7	8	9
196	C ₆ H ₅ Cl	1.16 ± 0.08 ^a		0.981	0.947	1.102	1.082	1.044
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	1.10 ± 0.10 ^a		0.946	0.879	1.102	1.042	0.968
	C ₆ H ₅ Cl+CHCl ₃	1.01 ± 0.16 ^b		0.953	0.894	1.102	1.050	0.986
414	C ₆ H ₅ Cl	0.95 ± 0.10 ^a	0.94 ^a	0.981	0.947	1.055	1.035	1.000
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	0.83 ± 0.10 ^a	0.87 ^a	0.946	0.879	1.055	0.998	0.927
	C ₆ H ₅ Cl+CHCl ₃	0.85 ± 0.09 ^b	0.96 ^a	0.953	0.894	1.055	1.006	0.943
615	C ₆ H ₅ Cl	0.91 ± 0.09 ^a		0.981	0.947	1.030	1.011	0.976
	C ₆ H ₅ Cl+CHCl ₃	0.80 ± 0.17 ^b		0.953	0.894	1.030	0.981	0.921
704	C ₆ H ₅ Cl	0.91 ± 0.10 ^a		0.981	0.947	1.022	1.003	0.969
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	0.87 ± 0.12 ^a		0.946	0.879	1.022	0.967	0.898
	C ₆ H ₅ Cl+CHCl ₃	0.80 ± 0.17 ^b		0.953	0.894	1.022	0.974	0.914
1002	C ₆ H ₅ Cl		1.07 ^a	0.981	0.947	1.008	0.989	0.955
	C ₆ H ₅ Cl+n-C ₇ H ₁₆		1.01 ^a	0.946	0.879	1.008	0.954	0.886
	C ₆ H ₅ Cl+CHCl ₃		1.13 ^a	0.953	0.894	1.008	0.961	0.902
1095	C ₆ H ₅ Cl	0.90 ± 0.05 ^a		0.981	0.947	1.006	0.987	0.953
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	0.85 ± 0.11 ^b		0.946	0.879	1.006	0.952	0.884
	C ₆ H ₅ Cl+CHCl ₃	0.87 ± 0.16 ^b		0.953	0.894	1.006	0.959	0.900
1584	C ₆ H ₅ Cl	0.90 ± 0.10 ^a	1.00 ^a	0.981	0.947	1.001	0.982	0.949
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	0.90 ± 0.11 ^a	1.11 ^a	0.946	0.879	1.001	0.947	0.880
	C ₆ H ₅ Cl+CHCl ₃	0.88 ± 0.18 ^b	1.13 ^a	0.953	0.894	1.001	0.954	0.895
652	CDCl ₃	1.00 ± 0.05 ^c		0.961	0.910	1.026	0.980	0.930
	CDCl ₃ +C ₆ H ₅ Cl	0.87 ± 0.06 ^d		0.953	0.894	1.026	0.970	0.910
2254	CDCl ₃	0.89 ± 0.14 ^c	0.83 ^e	0.961	0.910	1.000	0.961	0.910
	CDCl ₃ +C ₆ H ₅ Cl	0.75 ± 0.37 ^d	0.89 ^e	0.953	0.894	1.000	0.953	0.894

^a - $t_1 = 25^\circ$ $t_2 = 78^\circ$ ^c - $t_1 = 28^\circ$ $t_2 = 52^\circ$ ^e - $t_2 = -20^\circ$ $t_2 = +25^\circ$

^b - $t_1 = 25^\circ$ $t_2 = 60^\circ$ ^d - $t_1 = 28^\circ$ $t_2 = 68^\circ$ $I' = 1 - \exp(-1.44 \nu/t)^{-1}$

In Table IV for each band the following data for Raman and for infrared records are given: the spectral slit widths (columns 3 and 8), the apparent halfwidths at two temperatures (columns 4 and 9, and 5 and 10) and the shape factors at these temperatures (columns 6 and 11, and 7 and 12). For Raman bands the width of the exciting mercury line (1.3 cm⁻¹) recorded with a slitwidth of 2 microns was withdrawn. The accuracy of infrared measurements was about 2.5%.

TABLE IV

Band cm ⁻¹		Raman spectra					Infrared spectra				
		spec- tral slit width cm ⁻¹	($\Delta\nu_{1/2}$) _{t₁} cm ⁻¹	($\Delta\nu_{1/2}$) _{t₁} cm ⁻¹	r _{t₁}	r _{t₂}	spec- tral slit width cm ⁻¹	($\Delta\nu_{1/2}$) _{t₁} cm ⁻¹	($\Delta\nu_{1/2}$) _{t₂} cm ⁻¹	r _{t₁}	r _{t₂}
1	2	3	4	5	6	7	8	9	10	11	12
196	C ₆ H ₅ Cl	6.6	22.0±0.7 ^f	26.0±1.8 ^f	1.02 ^f	1.03 ^f					
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	6.6	25.2±0.4 ^f	29.3±1.5 ^f	0.97 ^f	1.02 ^f					
	C ₆ H ₅ Cl+CHCl ₃	4.2	22.6±1.3 ^g	26.4±1.6 ^g	1.04 ^g	1.08 ^g					
414	C ₆ H ₅ Cl	3.1	9.9±0.7 ^f	10.4±0.7 ^f	1.23 ^f	1.30 ^f	3.5	12.0 ^f	12.4 ^f	1.38 ^f	1.42 ^f
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	3.1	10.0±0.4 ^f	9.9±1.0 ^f	1.19 ^f	1.23 ^f	3.5	10.2 ^f	11.3 ^f	1.41 ^f	1.38 ^f
	C ₆ H ₅ Cl+CHCl ₃	3.1	8.8±0.9 ^g	10.0±1.6 ^g	1.15 ^g	1.14 ^g	3.5	11.3 ^f	11.7 ^f	1.41 ^f	1.42 ^f
615	C ₆ H ₅ Cl	6.1	9.6±0.3 ^f	11.2±0.5 ^f	1.24 ^f	1.24 ^f					
	C ₆ H ₅ Cl+CHCl ₃	6.1	10.0±0.5 ^g	11.4±0.5 ^g	1.22 ^g	1.25 ^g					
704	C ₆ H ₅ Cl	3.3	5.3±0.3 ^f	5.7±0.2 ^f	1.37 ^f	1.37 ^f					
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	3.3	5.2±0.3 ^f	5.2±0.4 ^f	1.36 ^f	1.40 ^f					
	C ₆ H ₅ Cl+CHCl ₃	3.3	5.5±0.5 ^g	5.3±0.8 ^g	1.30 ^g	1.29 ^g					
1002	C ₆ H ₅ Cl						2.0	3.6 ^f	4.4 ^f	1.24 ^f	1.23 ^f
	C ₆ H ₅ Cl+n-C ₇ H ₁₆						2.0	4.0 ^f	4.6 ^f	1.28 ^f	1.26 ^f
	C ₆ H ₅ Cl+CHCl ₃						2.0	3.6 ^f	4.4 ^f	1.19 ^f	1.18 ^f
1095	C ₆ H ₅ Cl	3.4	8.2±0.3 ^f	10.3±0.4 ^f	1.29 ^f	1.32 ^f					
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	3.4	8.9±0.4 ^f	10.3±0.6 ^f	1.27 ^f	1.33 ^f					
	C ₆ H ₅ Cl+n-CHCl ₃	3.4	8.4±0.7 ^g	9.0±1.0 ^g	1.19 ^g	1.20 ^g					
1584	C ₆ H ₅ Cl	3.6	12.2±0.5 ^f	16.7±1.0 ^f	1.24 ^f	1.29 ^f	3.0	11.5 ^f	12.4 ^f	1.12 ^f	1.15 ^f
	C ₆ H ₅ Cl+n-C ₇ H ₁₆	3.6	13.8±0.6 ^f	19.7±1.4 ^f	1.31 ^f	1.42 ^f	3.0	11.7 ^f	12.3 ^f	1.14 ^f	1.15 ^f
	C ₆ H ₅ Cl+CHCl ₃	3.6	13.1±1.0 ^g	15.1±2.3 ^g	1.19 ^g	1.20 ^g	3.0	10.6 ^f	12.2 ^f	1.14 ^f	1.17 ^f
667	CHCl ₃	3.2	4.9±0.1 ^h	5.3±0.1 ^h	1.35 ^h	1.35 ^h					
	CHCl ₃ +C ₆ H ₅ Cl	3.2	5.0±0.1 ⁱ	5.5±0.2 ⁱ	1.30 ⁱ	1.33 ⁱ					
652	CDCl ₃	3.2	6.1±0.1 ^h	6.3±0.1 ^h	1.35 ^h	1.35 ^h					
	CDCl ₃ +C ₆ H ₅ Cl	3.2	6.1±0.2 ⁱ	6.6±0.2 ⁱ	1.30 ⁱ	1.33 ⁱ					
2254	CDCl ₃	4.0	8.2±0.7 ^h	7.7±0.7 ^h	1.20 ^h	1.14 ^h	1.0	8.6 ^j	8.9 ^j	1.18 ^j	1.11
	CDCl ₃ +C ₆ H ₅ Cl	4.0	9.6±0.8 ⁱ	8.4±1.0 ⁱ	1.10 ⁱ	1.13 ⁱ	1.0	12.0 ^j	10.4 ^j	1.24 ^j	1.06

f — t₁ = 25°, t₂ = 78° h — t₁ = 28° t₂ = 52° j — t₁ = -20° t₂ = +25°

g — t₁ = 25° t₂ = 60° i — t₁ = 28° t₂ = 68°

Discussion

The comparison of experimental band parameters measured in different solvents and temperatures lets us determine the nature and structure of complexes present in the studied solutions. According to the dielectric theory the ratio of the infrared band intensities in

liquid to that in gas phase equals $(1/n)(F/E)^2$, where n should be treated as the refractive index of the medium (liquid or solution), E is the external electric field and F the internal field. For Raman band intensity ratio beside the above formula also $(1/n)(F/E)^4$ was proposed (Illinger 1965; Mirone 1966; Fini, Mirone, Patella 1968). For the internal field several expressions were suggested. In this work the simplest formula of Chako (1934) $F = [(n^2+2)/3]$ is used for calculations, as this formula only is valid for alternating electric field of high frequency. So the columns 6 and 7 of the Table II and 5 and 6 of the Table III were calculated from the refractive index values gathered in the Table I.

The comparison of the column 4 with the columns 6 and 7 of the Table II shows that when chlorobenzene is dissolved in chloroform the intensity decrease of Raman bands of chlorobenzene is greater than that calculated. For chloroform increase of intensity greater than that calculated is observed. This proves that in such a solution there is a change in specific interactions. It can be suggested that in pure chlorobenzene autocomplexes exist and the chlorobenzene molecules form mixed complexes with chloroform molecules. For all but one Raman band of chlorobenzene in heptane solution the observed intensity variation is in agreement with calculated values within experimental error.

For the 414 cm^{-1} band the decrease in both studied solutions is greater than for other bands. This can be interpreted as the result of breaking the autocomplexes. It should be noticed that the formation of mixed complexes does not compensate the effect of breaking the autocomplexes. This proves that different parts of the chlorobenzene molecule are active in formation of these two kinds of complexes.

The raising of temperature should not affect the intensity of infrared bands in harmonic approximation (Illinger, Freeman 1962), whereas the intensity of Stokes Raman bands should increase according to Placzek's factor

$$\frac{1 - \exp(1.44 \nu/t_1)}{1 - \exp(1.44 \nu/t_2)}$$

(Placzek 1934; Bernstein, Allen 1955) when the temperature is raised from t_1 to t_2 .

Placzek's factor was derived for free molecules in gas phase. In liquids and solutions it must be modified by the influence of intermolecular interactions. This is presented in columns 8 and 9 of the Table III. They contain the values of Placzek's factor for each frequency (column 7) multiplied by internal field effects (columns 5 and 6, respectively). The agreement, within experimental error, of columns 8 and 9 with the column 3 shows that the change of temperature in the applied range does not influence the specific interactions. The error limits do not allow to decide which formula $(1/n)(F/E)^2$ or $(1/n)(F/E)^4$ fits the experimental data better.

The variations of Raman band intensities let us thus conclude about the existence of complexes in liquid and solutions, but gives almost no hints as regards the structure of these complexes. In chlorobenzene molecule the C—Cl bond or the π -electrons can be active in complex formation. In chloroform molecule the C—H bond or the CCl_3 group can be directed towards chlorobenzene molecule. Additional information to solve the problem of structure of the complexes can be obtained from the examination of the halfwidth variations.

The broadening of Raman bands at increased temperature was explained by Sobelman (1953). His theory relates the band width with the relaxation time. The change of relative position of molecules is an effect of chaotic Brownian rotation of the molecule round different axes. Some rotations are more probable than others. If such a rotation produces a change in the projection of the polarizability derivative tensor for a given vibration on the direction of observation, the width of the band related to this vibration will be changed by the temperature. This theory was extended by Rakov (1964) on infrared bands, the polarizability derivatives being replaced by dipole moment derivatives. He showed also that the broadening of the bands is highly affected by the decreasing viscosity achieved by raising the temperature or adding low viscosity solvent.

In accordance with these theories we observe a noticeable broadening of Raman bands 196, 615 and 1584 cm^{-1} of chlorobenzene when temperature is raised or when chlorobenzene is dissolved in *n*-heptane (Table IV). The discussion of the 1095 cm^{-1} band is rather complicated, as the shape of this band is due to Fermi resonance (Lisitz 1967). For the infrared bands the broadening at elevated temperature is not so much differentiated as for Raman bands. The broadening of the 196 and 1584 cm^{-1} Raman bands of chlorobenzene suggests that for this molecule more probable is the rotation round the axis perpendicular to the ring plane than round the axis of symmetry of the molecule. In the latter case rotation would not change the value of the polarizability projection and the width of the band would not become larger. The width of the 1584 cm^{-1} band in chloroform solution is affected by the temperature considerably less than in pure chlorobenzene and its heptane solution. On this basis it may be suggested that the axis perpendicular to the ring remains the most probable axis of rotation for the free molecules present in heptane solution and for the autocomplexes present in pure chlorobenzene, but in chloroform solutions it is not the axis of rotation any longer. It follows then that the symmetry of autocomplexes resembles the symmetry of free molecules, but is altered for mixed complexes. This is plausible only in the case when the autocomplexes have a sandwich structure formed by means of π ring electrons and the mixed complexes are formed with the C-Cl bond of chlorobenzene molecule (Fig. 2). This conclusion is in agreement with the previous statement that different parts of chlorobenzene molecule are active in the formation of autocomplexes and of mixed complexes.

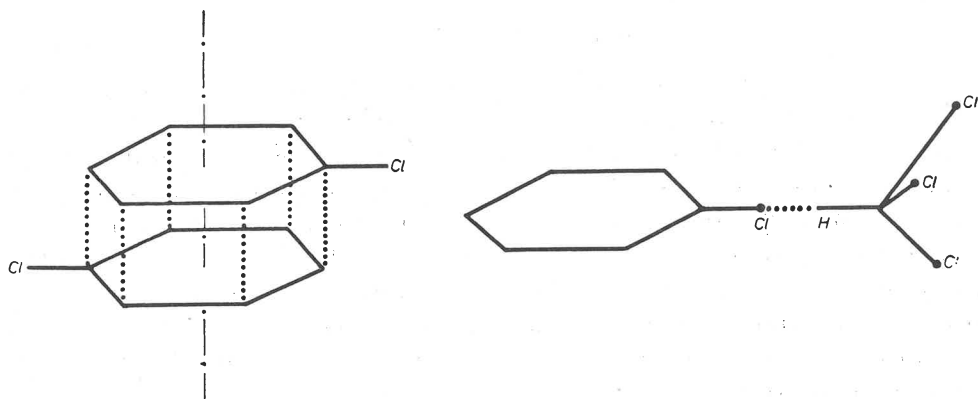


Fig. 2

When we compare the vibrations of 652 and 2254 cm^{-1} bands for the pure d-chloroform and its chlorobenzene solution, we notice that the latter is shifted and broadened, whereas the former is almost unaffected by the solvent. This is evidence that it is the C-D bond of the chloroform molecule which is active in complex formation with chlorobenzene molecule.

The shift of the 2254 cm^{-1} band in solution of chloroform in chlorobenzene both in Raman and in infrared spectra can be interpreted as the result of forming specific complexes between the two kinds of molecules. There is no explanation for the decrease of the frequency of the 196 cm^{-1} chlorobenzene band at elevated temperature. It followed from intensity variations that the temperature changes only the universal interactions. The temperature increase goes along with the decrease of refractive index. Thus the change of universal interactions described by the change of internal field should cause an increase and not the decrease of frequency. The examination of the frequency shifts gives us no new information about the complexes formed in studied liquids and solutions.

No interpretation of the shape contour variations can be found as yet in the literature. As the errors in determination of r value are about 5%, a significant decrease of r value is observed only for some bands. The decrease of the shape factor value means that the share of the wings increases. We suggest that this may be the result of the appearance of new vibration-rotational branches due to complexes formed in the studied liquids. Such new branches were discerned in vibrational-rotational B bands in the infrared spectrum of the gaseous mixtures of HCl with noble gases, where complexes are formed due to van der Waals forces (Bratož 1965; Gordon 1966). In our case it is impossible to discern such branches, but their appearance may clear up the observed variation of band shape. So the value of the shape factor of the 1584 cm^{-1} band of chlorobenzene in chloroform solution smaller than in the pure liquid confirm the conclusion based on intensity variations that a complex is formed in this solution. The smaller value of the shape factor of the 1584 cm^{-1} chlorobenzene Raman band in pure liquid than in heptane solution can be considered as a confirmation that in this solution the chlorobenzene autocomplexes are disrupted. We see then that we cannot draw more information from the shape factor changes than from intensity variation.

The comparison of the infrared and Raman band intensity variations

The comparison of intensity variations of the bands of the same frequency obtained by two methods (absorption and scattering) is very difficult. The studied bands must be intense enough in infrared and Raman spectra to be measured by both methods with sufficient accuracy. Moreover in the solutions studied in the infrared the concentration of the solute is normally so low that for such concentration the bands are not observed in Raman spectra. It follows then that the comparison of variations of the parameters of such bands cannot be done on the basis of results now available in the literature and special investigations are needed. In this work we have compared the bands of the same liquids and solutions of equimolar composition only. Also temperature variation was similar when Raman band and infrared band variations were observed.

The comparison of the column 4 with column 5 of the Table II and of the column 3

with 4 in the Table III shows that variation of intensities in Raman and infrared bands of the same frequency can have different values or even different directions. This fact can be explained in the following way, basing on the theory of dielectrics. According to Böttcher (1952) the dipole moment $\vec{\mu}$ and the polarizability α of a free molecule are altered under influence of the internal field into μ^* and α^*

$$\mu^* = \frac{\mu}{1-f\alpha}, \quad \alpha^* = \frac{\alpha}{1-f\alpha},$$

where f is a function of dielectric constant and molecular radius.

When we differentiate the modified molecular parameters μ^* and α^* with respect to the normal coordinate Q , we receive quantities proportional to the square root of band intensities. Thus, for the ratio of band intensity in the condensed phase to that in the gas phase we receive the following expressions:

$$\text{for Raman bands } \left[\frac{\partial \alpha^*}{\partial Q} : \frac{\partial \alpha}{\partial Q} \right]^2 = \left[\frac{1}{(1-f\alpha)^2} \right]^2$$

$$\text{for infrared bands } \left[\frac{\partial \mu^*}{\partial Q} : \frac{\partial \mu}{\partial Q} \right]^2 = \left[\frac{1}{1-f\alpha} + \frac{\mu f}{(1-f\alpha)^2} \frac{\partial \alpha / \partial Q}{\partial \mu / \partial Q} \right]^2.$$

We see that the expression for Raman bands does not contain any vibration parameters. The internal field should then change all band intensities of a given molecule in a similar manner. This fact was verified by the experiment as discussed above.

On the other hand, the square root of the intensity ratio of infrared bands depends on the derivatives of the polarizability and of the dipole moment of a free molecule with respect to the normal coordinate. This ratio can be represented in the more general form

$$\left(\frac{A_l}{A_g} \right)^{1/2} = B + C \frac{\partial \alpha / \partial Q}{\partial \mu / \partial Q}.$$

In similar form also other formulae derived on the basis of internal field theory (Buckingham 1960; Bakhshiev 1968; Dervil, Vincent-Geisse 1968) can be expressed. The analysis of vibrational spectra lets us calculate the values of $\partial \alpha / \partial Q$ and $\partial \mu / \partial Q$ but not their signs. It follows that in the infrared spectrum the internal field can affect the intensity of particular bands of a molecule in a different manner. This variety of intensity changes for particular infrared bands of a molecule when solvent and/or temperature were changed was observed in this work and in a former publication (Mierzecki 1964).

The internal field and the intermolecular complexes

As we have seen in the precedent discussion the concept of internal field presents a good method of describing the universal interactions. Moreover, it can be a means for discerning between the universal and specific interactions. On the other hand, no other method for such classification of interactions can be proposed. The reason why the concept of internal field influenced by continuous dielectric medium is accepted in dielectric theories is that we are unable to calculate the contributions of all intermolecular complexes formed in liquids or solutions. In fact for each pair of molecules a distance can be found for which

the attraction interactions are equilibrated by repulsion of their atomic cores. So each pair of interacting molecules does form an intermolecular complex by means of particular parts of the two molecules. This is true even in the case when the attraction between the molecules is a consequence of dispersion interactions only. These interactions are caused by the quantum mechanical coupling of zero level oscillations of molecular oscillators. For large molecules the molecular oscillator may often be a particular group or bond of a molecule. In consequence, the dispersion interactions can be regarded as the interactions between these groups or bonds of two molecules. Thus, the interactions between each pair of molecules will always have a specific character.

What is the reason for the fact that in many cases such interactions do not manifest themselves as specific in the spectra? We suppose that the mean life time of the complex supplies a criterion for differentiating the spectral features of complexes. A complex can be observed as a spectroscopic species if its mean life time is longer than the period of the electromagnetic wave of the applied spectroscopic method. The frequency and the molar intensity of the bands of such a complex should have definite values, like the bands of free molecules. In this case only the spectroscopists consider a complex as due to "specific" interactions.

If the mean life time of the complex is shorter than the period of the electromagnetic wave, the applied method allows to record only the averaged values of band parameters of all species present in the solution. We propose to call such complexes "statistical complexes", and those of longer mean life time "spectroscopic complexes", for as we have seen, all complexes have in fact a specific character. In the presence of statistical complexes the band frequencies and molar intensities depend on the amounts of each species. They are then a function of concentration of the solute.

It should be noticed that the measurements of dielectric constant and refractive index always give the averaged values for all species present in the liquid or solution. These quantities alone are usually inserted in the formulae for internal field. Thus, the results calculated from these formulae can agree only with measurements of variations of averaged parameters, *i. e.* in the case when statistical complexes are only formed. Consequently, the internal field effect can be regarded as a method of examination of the influence of statistical complexes on band parameters. A difference between the so-called specific and universal interactions is thence only methodologic and not intrinsic.

For the spectroscopist the main problem is to decide if in the studied liquid spectroscopic or statistical complexes are formed. We have seen that the spectroscopic complexes should manifest themselves by characteristic frequencies and molar intensities. Unfortunately, in but a few cases can such new bands with defined parameters be observed. These parameters are mainly obscured by two effects. First, the spectroscopic complexes form statistical complexes with other free molecules or complexes. Thus, the spectroscopic features for both kinds of complexes are usually concomitant. Second, the bands of spectroscopic complexes often cannot be separated from those of free molecules when the difference in frequency of these bands is very small.

As we have seen a comparison of the internal field formulae frequently, but not always, gives us a sufficient bases for deciding which kind of complexes is formed. In some cases the

examination of other band parameters and the concentration dependence can provide essential hints to solve this problem and to determine the structure of intermolecular complexes.

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REFERENCES

- Bakhshev, N. G., Girin, O. P., Libov, V. S., *Optika i Spektrosk.*, **14**, 476, 634, 745 (1963); **16**, 1016 (1964); **20**, 623 (1966).
- Bakhshev N. G., *et al.*, *Optika i Spektrosk.*, **24**, 910 (1968); **25**, 45, 207 (1968).
- Bernstein, H. J., Allen, G., *J. Opt. Soc. Amer.*, **45**, 237 (1955).
- Böttcher, C. F. J., *Theory of Electric Polarization*, Elsevier, Amsterdam 1952.
- Brahms, S., *Bull. Acad. Polon. Sci., Ser. Sci. Math. Astr. Phys.*, **7**, 449 (1959).
- Bratož, S., Martin, M. L., *J. Chem. Phys.*, **44**, 1061 (1965).
- Buckingham, A. D., *Proc. Roy. Soc. (London)*, **A255**, 32 (1960).
- Chako, N. R., *J. Chem. Phys.*, **2**, 644 (1934).
- Dervil, E., Vincent-Geisse, J., *J. Chim. Phys.*, **65**, 1417 (1968).
- Fini, G., Mirone, P., Patella, P., *J. Mol. Spectr.*, **24**, 144 (1968).
- Gordon, R. G., *J. Chem. Phys.*, **44**, 3083 (1966).
- Hallam, H. E., in ed. M. Davies, *Infrared Spectroscopy and Molecular Structure*, Elsevier, Amsterdam 1963.
- Illinger, K. H., *J. Mol. Spectr.*, **15**, 440 (1965).
- Illinger, K. H., Freeman, D. E., *J. Mol. Spectr.*, **9**, 191 (1962).
- Josien, M. L. and *altr.*, *J. Chem. Phys.*, **22**, 1169, 1264 (1954); *J. Chim. Phys.*, **52**, 162 (1955); *Bull. Soc. Chim. (France)*, 178, 1539 (1955); 188 (1958); 1516 (1959); in ed. Magnini, *Advances in Molecular Spectroscopy*, London 1962, p. 840; in ed. Hadzi, *Hydrogen Bond*, Pergamon Press, London 1959, p. 129.
- Kahiaty, Y., Shimozawa, T., Suzuki, R., *J. Mol. Spectr.*, **23**, 372 (1967).
- Lascombe, J., Devaure, J., Josien, M. L., *J. Chim. Phys.*, **61**, 1271 (1964).
- Lisitza, M. P., Kharchenko, N. P., *Opt. i Spekt.*, Sb. Stat. III, 232 (1967).
- Mierzecki, R., *Acta Phys. Polon.*, **25**, 821 (1964).
- Mirone, P., *Spectrochim. Acta*, **22**, 1897 (1966).
- Placzek, G., in: *Marx Handbuch der Radiologie*, Band VI, Leipzig 1934.
- Rakov, A. V., *Trudy FIAN*, **27**, 111 (1964).
- Ratajczak, H., Orville-Thomas, W. J., *Trans. Faraday Soc.*, **61**, 2603 (1965).
- Ramsay, D. A., *J. Amer. Chem. Soc.*, **74**, 72 (1952).
- Rea, D. G., *J. Mol. Spectr.*, **4**, 507 (1960).
- Rossini, F. D., Pitzer, K. S., Arnett, R. L., Braun, R. H., Pimentel, G. C., *Selected Values of Physical and Thermodynamical Properties of Hydrocarbons*, Pittsburg 1953.
- Schmidt, E. W., Brandmüller, J., Nonnemacher, G., *Z. Elektrochem.*, **64**, 726 (1960).
- Schubert, M., *Exp. Techn. Phys.*, **6**, 203 (1958).
- Sechkarev, A. V., *Opt. i Spekt.*, **19**, 721 (1965).
- Sobelman, I. I., *Izv. AN SSSR, ser. fiz.*, **17**, 554 (1953).
- Sokolovskaya, A. I., *Trudy FIAN*, **27**, 63 (1964).
- Sushchinskij, M. M., *Trudy FIAN*, **12**, 54 (1960).
- Szczepaniak, K., Rezaev, N. I., *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astr. Phys.*, **11**, 407 (1963).