

splitting between the symmetric and asymmetric  $\text{SO}_2$  stretches has decreased from  $232\text{ cm}^{-1}$  in  $\text{BrOSO}_2\text{F}$  to only  $154\text{ cm}^{-1}$ . This indicates a trend toward a more ionic  $\text{SO}_3\text{F}$  group in the anionic complex. This is further indicated by a strong upward shift of the S-Br stretching mode from  $884\text{ cm}^{-1}$  in  $\text{BrOSO}_2\text{F}$  to  $1022\text{ cm}^{-1}$ . The corresponding SO stretching modes for  $\text{Br}(\text{OSO}_2\text{F})_4^{-7}$  show a similar trend. In addition, the sulfur-fluorine stretch, which has been found to be very sensitive toward changes in the covalent bond strength,<sup>22</sup> is found at  $781\text{ cm}^{-1}$ , exactly between the S-F stretching frequencies for  $\text{BrOSO}_2\text{F}$  and  $\text{CsSO}_3\text{F}$ .<sup>11</sup>

(22) P. A. Yeates, B. L. Poh, B. F. E. Ford, J. R. Sams, and F. Aubke, *J. Chem. Soc. A*, 2188 (1970).

The symmetric  $\text{SO}_2$  bending vibration is found at  $618\text{ cm}^{-1}$ , again higher than any other bending mode but noticeably reduced from the position in the spectrum of bromine(I) fluorosulfate.

Only one absorption mode is found in the bromine-oxygen region, a strong band at  $437\text{ cm}^{-1}$ , tentatively assigned as a symmetric bromine-oxygen stretch. The absence of any other vibrations in this region is consistent with a linear O-Br-O grouping, where neither the asymmetric stretch nor the O-Br-O bend is expected to be Raman active.

**Acknowledgment.**—Financial support from the National Research Council of Canada is gratefully acknowledged.

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## Raman Intensity Measurements on Group IV Tetrahalides

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Received October 6, 1970

The intensities of the totally symmetric stretching modes of the tetrachlorides, tetrabromides, and tetraiodides of carbon, silicon, germanium, tin, and titanium ( $\text{MX}_4$ ) have been determined relative to the  $806\text{-cm}^{-1}$  band of cyclohexane as internal standard. The measurements were made, wherever possible, using four different exciting lines. The results indicate that the relative intensities of these modes depend, in most cases, strongly on the exciting line used and in particular on the energy gap between the exciting frequency and the frequency of the first allowed electronic transition of each halide. The data have been used to determine bond polarizability derivatives ( $\bar{\alpha}'_{\text{MX}}$ ) at zero exciting frequency (infinite frequency for the first electronic transition) for each halide. These quantities, which vary in the order  $\text{MCl} < \text{MBr} < \text{MI}$  and  $\text{CX} \sim \text{SiX} < \text{GeX} < \text{SnX} < \text{TiX}$ , are discussed with reference to the degree of covalent character of the metal-halogen bonds and, more specifically, with the  $\delta$  function potential model for absolute Raman intensities. The  $a_1$  bands of the tetrachlorides have all been studied under high resolution, both as neat liquids and in cyclohexane solutions, and the variations in the structures of these bands from their expected isotopic pattern are discussed. In particular, the spectra of neat  $\text{SiCl}_4$  and neat  $\text{TiCl}_4$  have been obtained in the solid state and in the liquid state at three temperatures and the data have been interpreted to rule out a previous suggestion that these molecules are dimeric in the liquid state. The halogen-exchange reaction between  $\text{TiCl}_4$  and  $\text{TiBr}_4$  has been studied by monitoring the intensities of the  $a_1$  peaks of both the parent tetrahalides as well as those of the mixed halides  $\text{TiCl}_3\text{Br}$ ,  $\text{TiCl}_2\text{Br}_2$ , and  $\text{TiClBr}_3$ . By studying the spectra of mixtures of  $\text{TiCl}_4$  and  $\text{TiBr}_4$  with widely varying mole ratios, it is concluded that the mixtures consist of an almost random distribution of the five species.

### Introduction

The key quantity which, according to the Placzek theory,<sup>1</sup> determines the intensity and state of polarization of a Raman line is the derived polarizability tensor  $\alpha'$ , where  $\alpha' = (\delta\alpha/\delta Q)_0$ , the rate of change of the polarizability,  $\alpha$ , with respect to the normal coordinate  $Q$  at the equilibrium configuration. Like  $\alpha$ , this tensor possesses the invariants  $\bar{\alpha}'$  and  $\gamma'$ , which are its mean value and anisotropy

$$\begin{aligned}\bar{\alpha}' &= 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ (\gamma')^2 &= 1/2[(\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + \\ &\quad (\alpha'_{zz} - \alpha'_{xx})^2 + 6(\alpha'_{xy})^2 + \alpha'_{yz}^2 + \alpha'_{xz}^2]\end{aligned}$$

The theory leads to the result that for an assemblage of freely rotating molecules irradiated with polarized light, the total intensity,  $I$ , and the degree of depolarization ratio,  $\rho$ , of the Raman light scattered at right

angles to the incident direction are

$$\begin{aligned}I &= (\text{constant})[45(\bar{\alpha}')^2 + 7(\gamma')^2] \\ \rho &= \frac{3(\gamma')^2}{45(\bar{\alpha}')^2 + 4(\gamma')^2}\end{aligned}$$

In the special case of an isotropic molecule,  $\gamma = 0$ , and so for the symmetric stretching mode  $\gamma' = 0$ . Hence the Raman intensity of this mode is directly related to  $(\bar{\alpha}')^2$  and the depolarization ratio is zero. As the molecular group IV tetrahalides are isotropic, they form an ideal set of molecules for which to determine mean polarizability derivatives and bond polarizability derivatives ( $\bar{\alpha}'_{\text{MX}}$ ) and thus any relationship between the latter and bond character. An initial study along these lines was carried out by Woodward and Long<sup>2</sup> for five tetrachlorides and two tetrabromides of group IV, from which they concluded that their observed  $\bar{\alpha}'_{\text{MX}}$  values agreed, with one exception, with values calculated from the empirical equation  $\bar{\alpha}'_{\text{emp}} =$

(1) L. A. Woodward in "Raman Spectroscopy," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1967, p 1.

(2) L. A. Woodward and D. A. Long, *Trans. Faraday Soc.*, **45**, 1131 (1949).

$Cp(Z_M + Z_X)$ , where  $\alpha'_{\text{emp}}$  is the empirical value of  $\alpha'_{\text{MX}}$ ,  $Z_M$  and  $Z_X$  are the atomic numbers of the atoms in the molecule  $\text{MX}_4$ ,  $p$  is the percentage covalent character of the bond, and  $C$  is a proportionality constant determined by the  $\text{CCl}_4$  standard.

The intensity of the  $a_1$  mode of titanium tetrachloride did not conform with the rule. This unexpected disagreement, coupled with the fact that Woodward and Long's results referred to photographic plate determinations at only a single exciting frequency (Hg arc, 4358 Å), suggested that the matter should be reinvestigated by photon counting techniques using the variety of exciting lines now available in the form of laser sources. Accordingly, we have now studied the intensities of the  $a_1$  modes of 14 molecular tetrahalides ( $\text{MX}_4$ ,  $M = \text{C}, \text{Si}, \text{Ge}, \text{Sn}, \text{Ti}$ ,  $X = \text{Cl}, \text{Br}, \text{I}$ , with the exception of the photochemically unstable halide  $\text{Cl}_4$ ). Wherever possible, all measurements have been carried out using all four exciting lines 4880, 5145, 5682, and 6471 Å. These results clearly show that for all the halides, but more especially for the bromides and iodides, there is considerable resonance enhancement to the intensities of the  $a_1$  modes caused by the proximity of the exciting lines to the first allowed electronic transition of each molecule. The resonance enhancement is most pronounced for the titanium tetrahalides, on account of their very low-lying first electronic transitions.

The detailed isotopic intensity patterns of the  $a_1$  modes of the group IV tetrachlorides have also been studied under high resolution, both for the neat liquids as well as for cyclohexane solutions thereof, in order to look for evidence of molecular association in the neat liquids.

The final section of the work is concerned with the equilibrium between  $\text{TiCl}_4$  and  $\text{TiBr}_4$  and the mixed halides  $\text{TiCl}_3\text{Br}$ ,  $\text{TiCl}_2\text{Br}_2$ , and  $\text{TiClBr}_3$ , which has been monitored by measuring the intensities of the  $a_1$  modes of each species present in a mixture. The object was to establish whether the distribution was random or whether there is a preference for the parent or the mixed species.

### Experimental Section

**Preparation of Samples.**—Samples of the tetrahalides used for Raman intensity measurements were purified by vacuum distillation or sublimation. Spectroscopic grade cyclohexane was kept over calcium hydride to remove residual water. It was found that a satisfactory Raman signal could be obtained from solutions in an all-Pyrex-glass cell (volume 5–10 ml) in which the bottom surface had been blown approximately flat to minimize refraction of the entering laser beam; it was not necessary for this surface to be optically correct. For the chlorides and bromides, a weighed cell was attached to a suitable vacuum manifold and the tetrahalide was transferred into it by vacuum condensation. After weighing, cyclohexane was then added by the same process and the cell was sealed off under vacuum. The quantity of cyclohexane added was varied in accordance with the Raman intensity of the sample in order to have the same order of magnitude for the intensity of the sample and reference peak (806-cm<sup>-1</sup> band of cyclohexane).

The tetraiodides were insufficiently volatile to be transferred in this manner. Iodides of silicon, germanium, and tin were transferred to the cell as solids in a dry atmosphere, followed by evacuation, solvent addition, and sealing. Titanium(IV) iodide presented special difficulties because of its low solubility in cyclohexane and great ease of hydrolysis. Samples of this compound were purified by repeated distillation under vacuum in all-glass apparatus, followed by addition of anhydrous cyclohexane using break-seal techniques. After equilibration, the saturated solution was filtered through a glass sinter into a number of small sample tubes (ca. 2 ml), which were then sealed off. One of these

tubes was used for the Raman intensity measurements and another for recording the electronic spectrum (for which further dilution was necessary); the remaining samples were used to establish the concentration of the solution ( $2.86 \times 10^{-4} M$ ) by estimation of iodine.

The precise frequencies of the fundamentals of all the tetrahalides, recorded in dilute solution in cyclohexane and with similar instrumental settings, are listed in Table I.

TABLE I  
FUNDAMENTAL FREQUENCIES OF THE GROUP IV  
TETRAHALIDES IN CYCLOHEXANE SOLUTION (CM<sup>-1</sup>)<sup>a</sup>

Compd	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(t_2)$	$\nu_4(t_2)$
$\text{CCl}_4$	459	219	763, 792 <sup>b</sup>	315
$\text{CBr}_4$	268	124	671	185
$\text{SiCl}_4$	424	151	610	222
$\text{SiBr}_4$	249	90	486	136
$\text{SiI}_4$	170	62	406	92
$\text{GeCl}_4$	395	130	455	174
$\text{GeBr}_4$	235	79	330	112
$\text{GeI}_4$	159	60	264	81
$\text{SnCl}_4$	368	106	402	130
$\text{SnBr}_4$	221	65	282	86
$\text{SnI}_4$	151	43	221	63
$\text{TiCl}_4$	388	120	498 <sup>c</sup>	136
$\text{TiBr}_4$	231	74	389	90
$\text{TiI}_4$ <sup>d</sup>	162	51	323	67

<sup>a</sup> The values for  $\nu_1$  agree within 2 cm<sup>-1</sup>, for  $\nu_2$  within 4 cm<sup>-1</sup>, for  $\nu_3$  within 9 cm<sup>-1</sup>, and for  $\nu_4$  within 3 cm<sup>-1</sup> of the published values, these normally referring to data obtained for the neat molecules: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

<sup>b</sup> The doublet structure of  $\nu_3$  arises from Fermi resonance of  $\nu_3$  with  $\nu_1 + \nu_4$ . <sup>c</sup> The origin of any doublet structure is uncertain: F. A. Miller and G. L. Carlson, *Spectrochim. Acta*, 16, 6 (1960); B. Moszynska, *Bull. Acad. Pol. Sci., Ser. Sci., Math., Astron. Phys.*, 7, 455 (1959). <sup>d</sup> R. J. H. Clark and C. J. Willis, *J. Chem. Soc. A*, 838 (1971).

**Instrumentation.**—The Raman spectra were recorded using a Spex 1401 spectrometer with CRL Ar<sup>+</sup> and Kr<sup>+</sup> lasers. The scattered radiation was collected at 90° and focused by an  $f/0.95$  lens onto the entrance slit of the monochromator after having passed through a polarization scrambler. The 0.75-m Czerny-Turner monochromator employed two 1200 lines/mm Bausch and Lomb gratings blazed at 5000 Å. The method of detection was photon counting (cooled FW 130 phototube). For most measurements using the 6471-Å line and for all using the 6764-Å line, the standard back mirror of the Kr<sup>+</sup> laser was replaced by a red optimized one, so that the power available at these wavelengths was approximately 600 and 30 mW, respectively. The power of the 4880-, 5145-, and 5682-Å lines was approximately 1 W, 1.3 W, and 100 mW, respectively. The spectra were calibrated by reference to emission lines of neon. Peak areas were originally determined using a planimeter, but it was then found to be more convenient and probably more accurate to feed the output of the photomultiplier into an amplifier, then to a single-channel analyzer, and finally into a counter and to record the total number of counts on scanning through a peak (typically a 30-cm<sup>-1</sup> interval). Background signal was allowed for by scanning over a similar wave number interval on either side of the peak. All such measurements were carried out at least 12 times for each peak, using a bracketing procedure. The counter employed was an Ecko Electronics Ltd Automatic Scaler, Type N530F.

The relative spectral response of the instrument was determined by recording the spectra of a tungsten lamp held at three different temperatures (ca. 2000°K), the last being measured using a disappearing-filament optical pyrometer. The response curve was checked approximately by measuring the anti-Stokes to Stokes intensity ratios ( $I_{\text{AS}}/I_{\text{S}}$ )<sub>meas</sub> for a number of different fundamentals and comparing these ratios with those determined by the equation

$$\frac{I_{\text{AS}}}{I_{\text{S}}} = \left( \frac{\nu_0 + \Delta\nu}{\nu_0 - \Delta\nu} \right)^4 \exp(-hc\Delta\nu/kT)$$

All apparent intensity ratios were converted to true intensity ratios by means of the spectral response curve.

**Infrared Spectra.**—The infrared spectra of titanium tetraiodide was recorded on a Perkin-Elmer 225 spectrometer (1000–200  $\text{cm}^{-1}$ ) both as Nujol mulls and as cyclohexane solutions using cesium iodide or polythene plates or windows. The Nujol was held over potassium, and the mull was made up in a vacuum drybox. Spectra in the region below 200  $\text{cm}^{-1}$  were recorded on a Beckman-RIIC FS 720 interferometer as paraffin wax disks or on a Grubb-Parsons GM3 (200–70  $\text{cm}^{-1}$ ) spectrometer as Nujol mulls.

**Electronic Spectra.**—The electronic spectra of the tetrahalides were recorded using a Cary 14 spectrometer.

## Results and Discussion

**A. Raman Intensity Measurements on the  $a_1$  Modes.**—The measurement of absolute Raman intensities requires the use of a standard of known molar intensity, and without doubt the most satisfactory procedure is to use an internal standard; reproduction of precisely the same conditions of sample alignment and laser power and corrections for refractive index, etc., render the external reference procedure unsatisfactory. The internal standard must, however, not interact with the molecules under study. Accordingly we have chosen cyclohexane as internal standard because its interactions with the group IV tetrahalides must be extremely weak. The 806- $\text{cm}^{-1}$  band of cyclohexane was monitored in each case, the choice of this band being governed by the facts that it is sharp and structureless and no other peak of appreciable intensity occurs on its low-frequency side. The possibility that the molar intensity of a solute band may be a function of the mole fraction of solute present in the cyclohexane was eliminated in the cases of titanium tetrachloride and tetrabromide and carbon tetrachloride by studying solutions over a range of concentrations in the region 0.05–0.5 mol fraction; a linear relationship between concentration and intensity ratio was found in each case. It was accordingly assumed that for all other tetrahalides, solvent effects of this type were absent (as indeed has been shown previously for several other tetrahalides in carbon tetrachloride).<sup>2</sup>

The molar intensities of the group IV tetrahalides, corrected for instrumental response, are given in Table II relative to the 806- $\text{cm}^{-1}$  band of cyclohexane. The important result is that the relative intensities depend, in virtually all cases, very strongly on the exciting line used to gather the data; this result is contrary to the earlier findings of Woodward and Long<sup>2</sup> for  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , and  $\text{SnCl}_4$ . The dependence increases in the orders  $\text{MCl} < \text{MBr} < \text{MI}$  and  $\text{CX} < \text{SiX} < \text{GeX} < \text{SnX} < \text{TiX}$  and is obviously connected with the energy gap between the exciting frequency and the energy of the first allowed electronic transition ( $\nu_e$ ) in the tetrahalides (which is presumably ligand ( $\pi$ )  $\rightarrow$  metal ( $d_\pi$ )). This transition has been located for cyclohexane solutions of most of the bromides and all of the iodides, (see Table II), but for  $\text{CCl}_4$ ,  $\text{SiCl}_4$ ,  $\text{GeCl}_4$ ,  $\text{SiBr}_4$ , and  $\text{GeBr}_4$  it lies above 50,000  $\text{cm}^{-1}$ , the effective limit of the instrument. For these five halides,  $\nu_e$  has been taken as 50,000  $\text{cm}^{-1}$  in the subsequent analysis. Even in the case of carbon tetrachloride, there is a slight dependence of the relative molar intensities on the exciting frequency. However, in order to facilitate comparison of these data with earlier data and to simplify the calculations, we have adopted the standard procedure of referring all intensities to that of the  $a_1$

TABLE II: RELATIVE INTENSITIES OF THE  $a_1$  MODES AND BOND POLARIZABILITY DERIVATIVES FOR THE GROUP IV TETRAHALIDES AT FOUR EXCITING FREQUENCIES<sup>d</sup>

Halide	6471 Å				5682 Å				5145 Å				4880 Å				$\nu_e$ in $\text{C}_6\text{H}_{12}$ , $\text{cm}^{-1}$
	$I_2M_1/I_1M_2$ relative to 806 $\text{cm}^{-1}$ , $\text{C}_6\text{H}_{12}$	$f$	$\alpha'_{MX}$ , Å <sup>2</sup>	$I_2M_1/I_1M_2$ relative to 806 $\text{cm}^{-1}$ , $\text{C}_6\text{H}_{12}$	$f$	$\alpha'_{MX}$ , Å <sup>2</sup>	$I_2M_1/I_1M_2$ relative to 806 $\text{cm}^{-1}$ , $\text{C}_6\text{H}_{12}$	$f$	$\alpha'_{MX}$ , Å <sup>2</sup>	$I_2M_1/I_1M_2$ relative to 806 $\text{cm}^{-1}$ , $\text{C}_6\text{H}_{12}$	$f$	$\alpha'_{MX}$ , Å <sup>2</sup>	$I_2M_1/I_1M_2$ relative to 806 $\text{cm}^{-1}$ , $\text{C}_6\text{H}_{12}$	$f$	$\alpha'_{MX}$ , Å <sup>2</sup>	$I_2M_1/I_1M_2$ relative to 806 $\text{cm}^{-1}$ , $\text{C}_6\text{H}_{12}$	
$\text{CCl}_4$	1.61	1.00	2.04 <sup>a</sup>	1.69	1.00	2.04 <sup>a</sup>	1.775	1.00	2.04 <sup>a</sup>	1.837	1.00	2.04 <sup>a</sup>	1.00	1.00	2.04 <sup>a</sup>	1.00	>50,000
$\text{CBr}_4$	4.80	2.98	3.55	5.23	3.09	3.63	6.16	3.47	3.86	6.43	2.189	3.86	6.43	3.50	2.184	3.88	43,605
$\text{SiCl}_4$	1.91	1.19	2.105	2.17	1.28	2.185	2.41	1.36	2.25	2.61	1.116	2.25	2.61	1.42	1.115	2.30	>50,000
$\text{SiBr}_4$	4.59	2.85	3.28	5.40	3.19	3.48	5.66	3.19	3.49	6.62	2.454	3.49	6.62	3.60	2.448	3.71	>50,000
$\text{SiI}_4$	11.80	7.33	4.85	13.48	7.98	5.09	17.70	9.97	5.70	20.15	4.564	5.70	20.15	10.97	4.550	5.99	35,040
$\text{GeCl}_4$	4.59	1.237	3.10	5.45	3.22	3.295	5.67	3.19	3.28	6.32	1.232	3.28	6.32	3.44	1.231	3.41	>50,000
$\text{GeBr}_4$	8.55	5.31	4.27	10.20	6.04	4.58	11.79	6.64	4.81	12.16	2.688	4.81	12.16	6.62	2.682	4.81	>50,000
$\text{GeI}_4$	25.57	15.88	6.75	36.01	21.31	7.86	56.52	31.84	9.63	66.30	5.110	9.63	66.30	36.12	5.093	10.28	27,750
$\text{SnCl}_4$	6.84	4.25	3.59	8.01	4.74	3.79	9.39	5.29	4.01	10.19	1.369	4.01	10.19	5.55	1.367	4.11	48,355
$\text{SnBr}_4$	13.74	8.53	5.16	15.49	9.17	5.37	17.81	10.03	5.63	21.52	2.965	5.63	21.52	11.71	2.957	6.09	41,595
$\text{SnI}_4$	47.38	29.43	8.79	66.25	39.20	10.20	94.96	53.50	11.95								27,435
$\text{TiCl}_4$	10.59	6.58	4.66	12.97	7.67	5.04	17.64	10.05	5.77	19.39	1.255	5.77	19.39	10.55	1.254	5.92	34,840
$\text{TiBr}_4$	20.31	12.61	6.50	26.75	15.83	7.31	42.38	23.88	9.00	55.05	2.763	9.00	55.05	29.97	2.756	10.10	28,680
$\text{TiI}_4$	145.0	90.1	16.33														19,400

<sup>a</sup> Normalized to the experimental value of Chantry, quoted in ref 3. <sup>b</sup> Reproducible values could not be obtained owing to a tendency for the solution to boil in the laser beam. <sup>c</sup> Raman spectrum cannot be obtained using these exciting lines, owing to their close proximity in frequency to  $\nu_e$ , the first allowed electronic transition. <sup>d</sup>  $f = [(v_0 - \Delta\nu)/(v_0 - \Delta\nu)]^4 (\Delta\nu/\Delta\nu_0) [(1 - \exp(-hc\Delta\nu/kT)) / (1 - \exp(-hc\Delta\nu_0/kT))]$ ;  $I_2M_1/I_1M_2 = f(\alpha_2/\alpha_1)^2$ ;  $\alpha_2/\alpha_1 = (\mu_2/\mu_1)^{1/2} (\alpha'_{MX}/\alpha'_{MX})^{1/2}$ . All  $\Delta\nu$  values are taken from Table I.

mode of carbon tetrachloride at each exciting frequency. These results are also in Table II.

The relative intensities of the  $a_1$  modes of the tetrahalides have been converted to relative mean molecular polarizability derivatives ( $\bar{\alpha}'$ ) by use of the relationship

$$\frac{I_2}{I_1} = \frac{M_2}{M_1} \left( \frac{\nu_0 - \Delta\nu_2}{\nu_0 - \Delta\nu_1} \right)^4 \frac{\Delta\nu_1}{\Delta\nu_2} \times \frac{1 - \exp(-hc\Delta\nu_1/kT) (\bar{\alpha}'_2)^2 (1 + \rho_2) (3 - 4\rho_1)}{1 - \exp(-hc\Delta\nu_2/kT) (\bar{\alpha}'_1)^2 (1 + \rho_1) (3 - 4\rho_2)}$$

where  $M$  is the molar concentration,  $\nu_0$  is the exciting frequency, and  $\Delta\nu$  is the Raman shift of the mode under study; the subscript 2 refers to the halide and 1 to carbon tetrachloride. All depolarization ratios (polarized incident light and analyzed scattered light) for the  $a_1$  bands of the tetrahalides were taken as zero, i.e.,  $\rho_1 = \rho_2 = 0$ ; in practice all were measured and found to be  $<0.01$ . Finally, bond polarizability derivatives ( $\bar{\alpha}'_{MX}$ ) were obtained *via* the relationship

$$\frac{\bar{\alpha}'_2}{\bar{\alpha}'_1} = \left( \frac{\mu_2}{\mu_1} \right)^{1/2} \frac{\bar{\alpha}'_{(MX)_2}}{\bar{\alpha}'_{(MX)_1}}$$

where  $\mu_1$  and  $\mu_2$  are the reciprocals of the masses of the relevant X atoms. The results are given in Table I normalized to the value  $2.04 \text{ \AA}^2$  for  $\bar{\alpha}'_{\text{OCl}}$  for carbon tetrachloride. The basis for this absolute scale is the value  $1.00 \text{ \AA}^2$  for  $\bar{\alpha}'_{\text{CH}}$ , a value which is close to the experimentally determined value.<sup>4</sup>

In order to obtain  $\bar{\alpha}'_{MX}$  values in the absence of resonance enhancement to the intensities of the  $a_1$  modes, it is necessary to plot the apparent  $\bar{\alpha}'_{MX}$  values against the frequency function of Shorygin;<sup>5</sup> *viz.*

$$A = \frac{1 + (\nu_0/\nu_e)^2}{[1 - (\nu_0/\nu_e)^2]^2}$$

( $\nu_e$  is strictly an effective absorption frequency but is taken here in its customary sense of referring to the first allowed electronic transition of each molecule.)

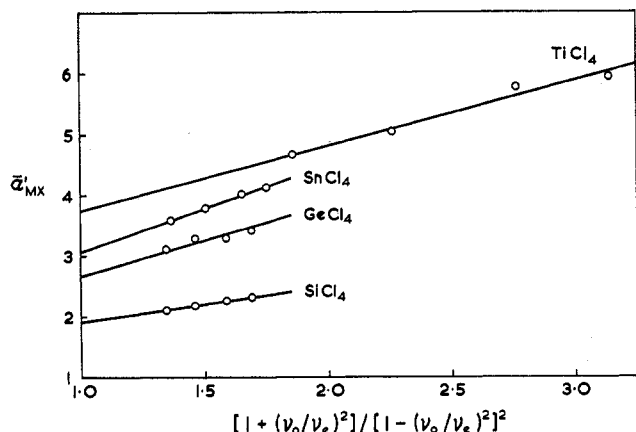


Figure 1.—Plot of  $\bar{\alpha}'_{MCl}$  vs.  $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ . The values for  $\nu_e$  are in Table II.

The plots for each chloride, bromide, and iodide are given in Figures 1–3, in which the relationship between  $\bar{\alpha}'_{MX}$  and  $A$  is seen to be linear as expected.<sup>5</sup> Extrapolation of each graph to  $A = 1$  (i.e.,  $\nu_0 = 0$  or  $\nu_e = \infty$ )

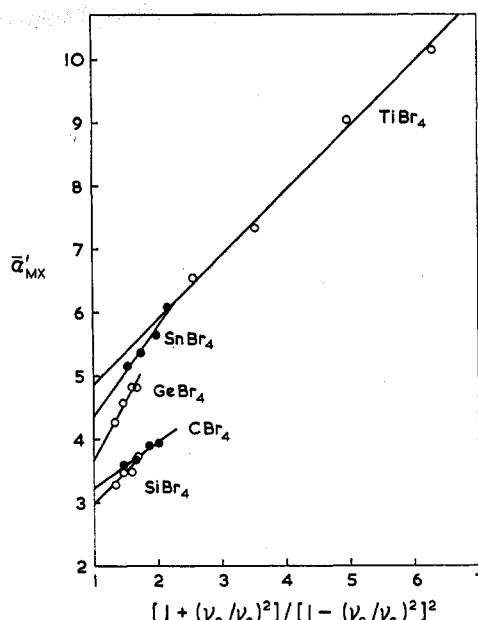


Figure 2.—Plot of  $\bar{\alpha}'_{MBr}$  vs.  $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ . The values for  $\nu_e$  are in Table II.

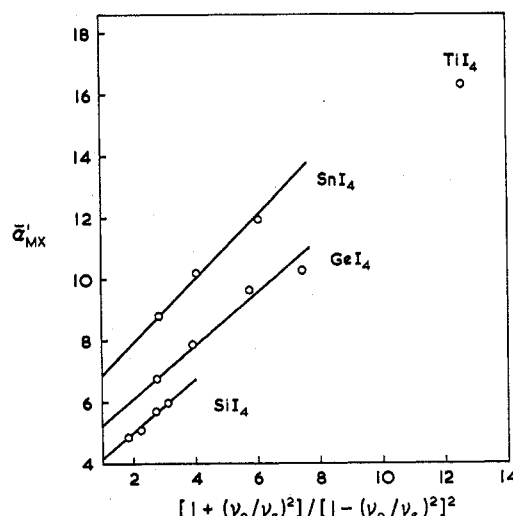


Figure 3.—Plot of  $\bar{\alpha}'_{MI}$  vs.  $[1 + (\nu_0/\nu_e)^2]/[1 - (\nu_0/\nu_e)^2]^2$ . The values for  $\nu_e$  are in Table II.

gives  $\bar{\alpha}'_{MX}$  values corrected for resonance enhancement, the results being given in Table III. Implicit in this analysis is the assumption that the reference line shows no resonance effects, an assumption which, as seen above, is good but not entirely valid; however, any errors introduced into  $\bar{\alpha}'_{MX}$  on this account are considered to be negligible.

The final  $\bar{\alpha}'_{MX}$  values are considerably lower than those found by Woodward and Long<sup>2</sup> (after correction to the present intensity scale). The reason for this lies mainly in the lack of correction for resonance enhancement of their observed intensities but may also be associated with their method for determining intensities. In order to check more carefully their empirical equation connecting  $\bar{\alpha}'_{\text{emp}}$  values with fractional covalent character ( $p$ ), where  $p = \exp(-1/4(\chi_M - \chi_X)^2)$ , and atomic numbers ( $Z$ ), *viz.*

$$\bar{\alpha}'_{\text{emp}} = Cp(Z_M + Z_X)$$

we have evaluated  $\bar{\alpha}'_{\text{emp}}$  for each halide using the more

(3) T. V. Long and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

(4) G. W. Chantry and R. A. Plane, *ibid.*, **32**, 319 (1960).

(5) J. Behringer, ref 1, p 168.

TABLE III  
 BOND POLARIZABILITY DERIVATIVES  $\bar{\alpha}'_{MX}$  ( $\text{\AA}^2$ ) FOR THE GROUP IV TETRAHALIDES

Molecule	xA	xB	100p	$r_e, \text{\AA}$	$\bar{\alpha}'_{MX}$				$\bar{\alpha}'_{emp}$
					Calcd	This work <sup>b</sup>	Exptl Ref 3	Ref 2	
CCl <sub>4</sub>	2.55	3.16	91.1	1.76	1.99	2.04	2.04	2.04	2.04
CBr <sub>4</sub>	2.55	2.96	95.9	1.94	2.76	3.23	3.33	4.08	3.83
SiCl <sub>4</sub>	1.90	3.16	67.2	2.01	2.03	1.90	1.96	1.96	2.03
SiBr <sub>4</sub>	1.90	2.96	75.5	2.15	2.75	2.98			3.60
SiI <sub>4</sub>	1.90	2.66	86.5	2.43	4.43	4.11			5.64
GeCl <sub>4</sub>	2.01	3.16	71.8	2.08	2.44	2.65	2.66	3.26	3.42
GeBr <sub>4</sub>	2.01	2.96	79.8	2.29	3.56	3.65			5.21
GeI <sub>4</sub>	2.01	2.66	90.0	2.50	5.09	5.22			7.45
SnCl <sub>4</sub>	1.96	3.16	69.8	2.30	3.19	3.06	3.37	3.87	4.55
SnBr <sub>4</sub>	1.96	2.96	77.9	2.44	4.18	4.34		6.73	6.45
SnI <sub>4</sub>	1.96	2.66	88.5	2.64	5.86	6.86			8.87
TiCl <sub>4</sub>	1.54	3.16	51.9	2.17 <sup>c</sup>	1.88	3.74		4.90	1.97
TiBr <sub>4</sub>	1.54	2.96	60.4	2.31	2.59	4.85			3.35
TiI <sub>4</sub>	1.54	2.66	73.1	(2.50) <sup>d</sup>	3.87	(8 ± 2) <sup>d</sup>			5.34

<sup>a</sup> *Chem. Soc., Spec. Publ.*, No. 11 (1958). <sup>b</sup> At zero exciting frequency. <sup>c</sup> Y. Morino and H. Uehara, *J. Chem. Phys.*, **45**, 4543 (1966). <sup>d</sup> Estimated.

exact Pauling electronegativity values ( $\chi$ ) of Allred.<sup>6</sup> The results are included in Table III. The resulting  $\bar{\alpha}'_{emp}$  values are in all cases except for the titanium tetrahalides (which are discussed later) considerably greater than our observed  $\bar{\alpha}'_{MX}$  values. This suggests that the above equation is oversimplified.

Good agreement is found between the present  $\bar{\alpha}'_{MX}$  values and those of Chantry (quoted in ref 3) for several tetrachlorides, although it is not clear whether his results were corrected for resonance enhancement. More particularly, the present  $\bar{\alpha}'_{MX}$  values agree well (again except the titanium tetrahalides) with those calculated assuming a  $\delta$  function potential model, *viz.*

$$\bar{\alpha}'_{MX}(\text{calcd}) = \frac{2}{3} \frac{\chi^{1/2} p}{Z_{eff} a_0} (1/2n) r^3$$

where  $\chi$  and  $p$  were previously defined,  $Z_{eff}$  is the effective nuclear charge, taken to be equal to the atomic number of the atom minus the number of inner shell electrons,  $a_0$  is the Bohr radius,  $1/2n$  is the bond order (taken to be unity), and  $r$  is the equilibrium internuclear distance. In the above expression,  $\chi^{1/2}/Z_{eff}$  is taken to be the geometric mean of the atomic values for atoms M and X. In this treatment,  $\bar{\alpha}'_{MX}$  is obtained by differentiating the parallel component of molecular polarizability arising from electrons in the bond; no contribution is allowed with respect to perpendicular components of the molecular polarizability or from non-bonding electrons. The agreement between the calculated and experimental values for  $\bar{\alpha}'_{MX}$  (given in columns 6 and 7 of Table III) is as good as could have been expected in view of the approximations inherent in the theory, and the considerable extrapolations involved in Figures 1–3 in order to eliminate the effects of resonance enhancement. It thus appears that measured values of  $\bar{\alpha}'_{MX}$  for bonds in molecules could be used to estimate their degree of covalency in cases where this is otherwise not known or alternatively to obtain bond orders.

Titanium tetrachloride, titanium tetrabromide, and almost certainly titanium tetraiodide (for which intensity measurements could only be made at a single

exciting frequency)<sup>7</sup> are exceptional in giving rise to experimental  $\bar{\alpha}'_{MX}$  values about double the values calculated using the  $\delta$  function potential model. This situation might be brought about by either or both of two factors. First, if halogen→metal  $\pi$  bonding is significant in the titanium tetrahalides, then  $n/2 > 1$ ; previous work<sup>4</sup> has indicated that a  $\pi$  electron makes a larger contribution to  $\bar{\alpha}'_{MX}$  values than does a  $\sigma$  electron. Second, the  $\sigma$ -electron hybridization scheme of the groups IVa and IVb tetrahalides are different.<sup>8</sup> Whereas in titanium tetrachloride the hybridization is  $d^3s$  with a slight admixture of  $sp^3$ , for the IVb subgroup, the hybridization is essentially  $sp^3$ . Which of these factors is the more important in amplifying the experimental  $\bar{\alpha}'_{MX}$  values we cannot at present decide. The possibility also remains that the very large intensity enhancement through the resonance Raman effect has not been adequately compensated for by the extrapolation procedure used;<sup>9,10</sup> this matter requires further investigation.

#### B. Isotopic Intensity Patterns of the $a_1$ Modes.—

The  $a_1$  vibrational mode of tetrahedral MCl<sub>4</sub> molecules involves the symmetrical stretching of all four MCl bonds. Owing to the isotopic distribution of chlorine in natural abundance (<sup>35</sup>Cl:<sup>37</sup>Cl = 75.53:24.47),  $\nu_1$  is expected to have five components, with approximately equal spacing, and an intensity pattern which reflects the isotopic composition of the tetrachloride, *viz.*, 32.54% M<sup>35</sup>Cl<sub>4</sub>, 42.17% M<sup>35</sup>Cl<sub>3</sub><sup>37</sup>Cl, 20.50% M<sup>35</sup>Cl<sub>2</sub><sup>37</sup>Cl<sub>2</sub>, 4.43% M<sup>35</sup>Cl<sup>37</sup>Cl<sub>3</sub>, and 0.36% M<sup>37</sup>Cl<sub>4</sub>. Such an intensity pattern is indeed found for the  $a_1$  mode of carbon tetrachloride, both as a frozen solid and as a neat liquid, as well as in cyclohexane solution.

Recent studies of the intensity patterns of the  $a_1$  modes of the other group IV tetrachlorides have indicated, surprisingly, that whereas GeCl<sub>4</sub> and SnCl<sub>4</sub> behave like CCl<sub>4</sub>, SiCl<sub>4</sub><sup>11</sup> and TiCl<sub>4</sub><sup>12</sup> do not; instead, the intensity patterns of these  $a_1$  modes are consistent with

(7) R. J. H. Clark and C. J. Willis, *J. Chem. Soc. A*, in press.

(8) G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **7**, 8 (1958).

(9) C. O. Quicksall and T. G. Spiro, *Inorg. Chem.*, **9**, 1045 (1970).

(10) A. C. Albrecht, *J. Chem. Phys.*, **34**, 1476 (1961).

(11) J. E. Griffiths and Y.-H. Pao, *ibid.*, **46**, 1679 (1967).

(12) J. E. Griffiths, *ibid.*, **49**, 642 (1968).

(6) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

their arising from a three chlorine atom system, *viz.*, 43.09%  $M^{35}\text{Cl}_3$ , 41.88%  $M^{35}\text{Cl}_2^{37}\text{Cl}$ , 13.57%  $M^{35}\text{Cl}^{37}\text{Cl}_2$ , and 1.46%  $M^{37}\text{Cl}_3$ . However, on dilution of silicon or titanium tetrachlorides to 20 mol % in carbon tetrachloride, the  $a_1$  patterns became normal. Griffiths<sup>11,12</sup> has interpreted these results to imply that neat  $\text{SiCl}_4$  and neat  $\text{TiCl}_4$  are dimeric with structures such that the  $a_1$  mode involves simultaneous movement of only three chlorine atoms. Earlier Raman studies of titanium tetrachloride have led to the suggestion<sup>13</sup> that instantaneous dipole-dipole forces are sufficiently strong to bring about a lowering of the molecular symmetry from  $T_d$  to  $C_{3v}$ .

In several respects, the first interpretation seemed to us to be untenable. First, the interpretation implied that neat  $\text{TiCl}_4$  and  $\text{SiCl}_4$  are completely dimeric, whereas they are completely monomeric on dilution to 20 mol % in  $\text{CCl}_4$ ; it seems improbable not only that there is no evidence for an equilibrium between the "two" forms but also that a dimeric form could be broken down by such a slight change of state as dilution to 20 mol % in  $\text{CCl}_4$ . Second, it seems improbable that the monomer would have its  $a_1$  vibration at precisely the same frequency as the "dimer." Third, we are not aware of any unequivocal independent evidence for association in neat  $\text{TiCl}_4$  or neat  $\text{SiCl}_4$ . Accordingly, we have reinvestigated the  $a_1$  patterns of the neat tetrachlorides and also those of cyclohexane solutions thereof.

The results are shown in Figure 4. The cyclohexane

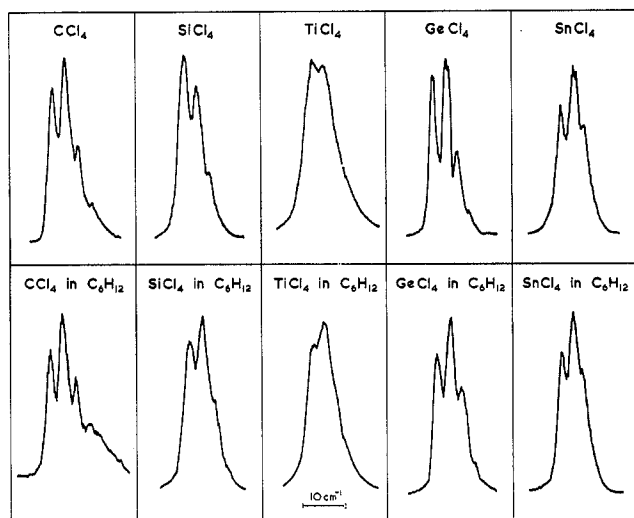


Figure 4.—The  $\nu_1(a_1)$  fundamentals of (a)  $\text{CCl}_4$ , (b)  $\text{SiCl}_4$ , (c)  $\text{TiCl}_4$ , (d)  $\text{GeCl}_4$ , and (e)  $\text{SnCl}_4$  as neat liquids at 22° and (f)  $\text{CCl}_4$ , (g)  $\text{SiCl}_4$ , (h)  $\text{TiCl}_4$ , (i)  $\text{GeCl}_4$ , and (j)  $\text{SnCl}_4$  as cyclohexane solutions (ca. 15 mol %) also at 22°. All spectra were recorded at 5145 Å (1.3 W) at a scanning rate of 2.5  $\text{cm}^{-1}/\text{min}$ . For the neat solutions, typical settings were slit widths 20, 70, and 20  $\mu$ , slit height 2 mm, scale 2K, and time constant 2 sec; for the cyclohexane solutions they were slit widths 40, 100, and 40  $\mu$ , slit height 2 mm, scale 1K, and time constant 4 sec ( $K = 1000$  counts/sec).

solutions of the tetrachlorides in all cases give rise to the expected isotopic patterns for the  $a_1$  mode and therefore require no further comment. The  $a_1$  isotopic patterns for the neat liquids, apart from being slightly better resolved, agree well with the previous findings; in particular, the unexpected pattern for silicon and titanium tetrachlorides has been verified.

In order to check the proposal of dimerization for silicon tetrachloride, we have studied the pattern of its  $a_1$  mode at  $-196$ ,  $-65$ ,  $22$ , and  $50^\circ$  (Figure 5). It is

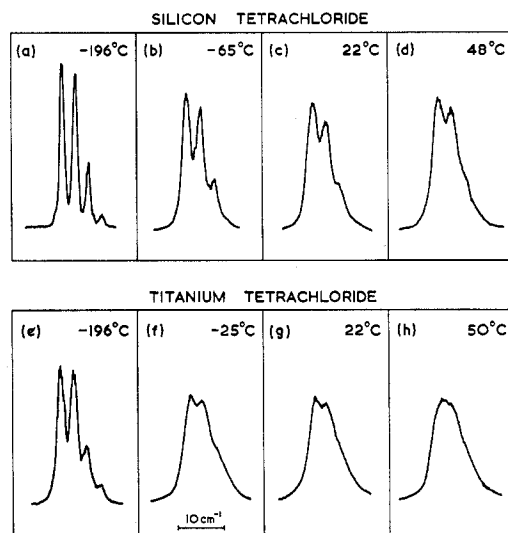


Figure 5.—The  $\nu_1(a_1)$  fundamentals of silicon tetrachloride at (a)  $-196$ , (b)  $-65$ , (c)  $22$ , and (d)  $48^\circ$  and that of titanium tetrachloride at (e)  $-196$ , (f)  $-25$ , (g)  $22$ , and (h)  $50^\circ$ . All spectra were recorded at 5145 Å except for (e) which was recorded at 6471 Å (300 mW). Instrumental settings for (a), (b), and (c) were slit widths 25, 100, and 25  $\mu$ , slit height 2 mm, time constant 2 sec, scale 10K, and scanning rate 5  $\text{cm}^{-1}/\text{min}$ ; for (d) they were the same except for the time constant of 1 sec and scale 5K; for (e) they were slit widths 5, 100, and 5  $\mu$ , slit height 2 mm, time constant 10 sec, scale 200, and scanning rate 0.4  $\text{cm}^{-1}/\text{min}$ ; for (f), (g), and (h) they were slit widths 25, 100, and 25  $\mu$ , slit height 2 mm, time constant 2 sec, scale 5K, and scanning rate 5  $\text{cm}^{-1}/\text{min}$  ( $K = 1000$  counts/sec). The temperature of  $-196^\circ$  for (a) and (e) indicates merely that the samples were held in a liquid nitrogen cell; the exact temperatures of the samples are not known but are undoubtedly above this and probably ca.  $-150^\circ$ .

seen that, apart from a general decrease in resolution associated with an increase in the intensity of underlying hot bands, a raising of the temperature brings about little if any change in the relative heights of the components. It seems almost inconceivable that any monomer-dimer equilibrium could be so unaffected by a temperature change covering almost the total liquid range of the halide ( $-70$  to  $+57.6^\circ$ ). Moreover, its boiling point is the *lowest* of all the tetrachlorides, a fact which hardly implies dimerization in the liquid state. Indeed, silicon tetrachloride has a relatively poor tendency to increase its coordination number, hence the failure of halogen redistribution reactions of silicon tetrahalides at room temperature.<sup>14</sup> We have also studied the Raman spectrum of liquid  $\text{SiCl}_4$  at  $-65^\circ$  over the range  $0$ – $800 \text{ cm}^{-1}$ ; no feature additional to the four expected fundamentals for a tetrahedral molecule is observed. This result rules out dimerization of the neat liquid, for in this case more fundamentals would be active. Similar results have been obtained for neat titanium tetrachloride at ca.  $-150$ ,  $-25$ ,  $22$ , and  $50^\circ$  (Figure 5). We therefore conclude that neither silicon nor titanium tetrachloride, as a neat liquid, is dimeric. It is significant, moreover, that an X-ray investigation of liquid  $\text{SiCl}_4$  has been interpreted in terms of molecular  $\text{SiCl}_4$  units and not in terms of dimeric units.<sup>15</sup> Al-

(13) B. Moszyńska, *Bull. Acad. Pol. Sci., Ser. Sci., Math., Astron. Phys.*, **7**, 455 (1959); B. Moszyńska and K. Szczepaniak, *ibid.*, **8**, 195 (1960).

(14) M. L. Delwaulle and F. Francois, *C. R. Acad. Sci.*, **219**, 335 (1944).

(15) V. P. Klochov and A. F. Skryshevsky, *Ukr. Fiz. Zh.*, **9**, 420 (1964).

TABLE IV  
CONCENTRATIONS OF MIXED HALIDES IN TiCl<sub>4</sub>-TiBr<sub>4</sub> MIXTURES<sup>a</sup>

Phase	% chlorine		%					K <sub>1</sub>	K <sub>2</sub>	K <sub>3</sub>
	As made up	Found from data	TiCl <sub>4</sub>	TiCl <sub>3</sub> Br	TiCl <sub>2</sub> Br <sub>2</sub>	TiClBr <sub>3</sub>	TiBr <sub>4</sub>			
N	26.1	26.3	...	6.2	21.2	44.2	28.4	...	0.61	0.31
N	40.1	40.1	[2.6]	17.4	31.1	35.8	13.2	...	0.64	0.32
N	45.0	45.6	[4.1]	23.4	32.8	30.5	9.3	...	0.67	0.33
S	48.8	48.7	[6.4]	25.5	32.4	28.0	7.7	...	0.68	0.32
N	50.8	51.4	[6.7]	29.3	33.1	24.7	6.2	...	0.66	0.34
S	53.0	52.8	[8.6]	29.3	32.9	23.3	6.1	...	0.63	0.37
N	58.4	58.9	10.9	37.4	31.5	16.9	3.3	0.25	0.64	0.36
S	58.7	58.8	12.5	34.8	31.5	17.8	3.4	0.33	0.62	0.34
S	61.8	63.0	15.2	39.9	29.2	13.4	2.2	0.28	0.63	0.35
N	68.7	69.2	22.3	43.5	24.0	9.1	1.1	0.28	0.69	0.33
S	68.8	68.9	22.8	41.7	25.0	9.1	1.5	0.33	0.61	(0.44)
S	71.1	71.3	25.8	43.0	22.9	7.3	0.9	0.32	0.60	(0.4)
S	74.4	74.6	30.7	43.6	19.6	5.5	0.6	0.32	0.62	(0.4)
S	76.3	76.4	33.9	43.3	18.0	4.2	0.4	0.33	0.57	(0.4)
N	83.7	83.6	48.3	39.4	10.6	1.6	...	0.33	(0.58)	...

<sup>a</sup> N = neat solution; S = cyclohexane solution. Concentrations of titanium tetrachloride given in brackets were obtained by calculation (see text). Values of K<sub>2</sub> and K<sub>3</sub> in parentheses were obtained from only small concentrations of one component and are not included in averages.

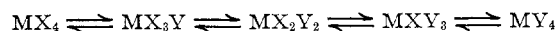
though the dilution experiments suggest that some distortion phenomenon is responsible for the unexpected intensity pattern of the a<sub>1</sub> modes of the neat liquids, we have not been able to define its exact nature. The finite values for the depolarization ratios for the tetrahalides—even for CCl<sub>4</sub><sup>16,17</sup> (albeit all <0.01)—are also indicative of intermolecular forces acting in the condensed phase so as to lower the molecular symmetry.

The most significant of the above results is the observation that for both SiCl<sub>4</sub> and TiCl<sub>4</sub>, the solid-state spectrum in the region of the a<sub>1</sub> mode is nearly identical with the low-temperature liquid spectrum. As solid titanium tetrachloride is known from X-ray crystallographic work to crystallize in a molecular lattice of tetrahedral units,<sup>18a</sup> the pattern of the a<sub>1</sub> bands must therefore arise from a four chlorine atom system. The unusual intensity pattern of this band for SiCl<sub>4</sub> and TiCl<sub>4</sub> probably arises from its being distorted by underlying hot bands, as the patterns become normal below 50°K.<sup>18b</sup> A site and factor group analysis of the complete spectrum at low temperatures, currently under study, should lead to a more precise understanding of the matter.

**C. Halogen Redistribution Reactions.**—By use of photographic Raman techniques, Delwaille and co-workers have demonstrated the existence of chlorobromides of carbon and silicon (which are isolatable) and of titanium, germanium, and tin (which are not). Subsequent work demonstrated the existence of chloroiodides<sup>19</sup> and bromoiodides<sup>20</sup> of silicon, germanium, and tin with similar properties. The characteristic feature of each halide and mixed halide, indeed frequently the criterion for the existence of the latter, is a very strong polarized Raman band attributed to the symmetric stretching of the metal-halogen bonds; it moves to progressively lower frequencies as bromine or iodine replaces chlorine in the mixed halide. The mixed halides of germanium, tin, and titanium may simply be

formed by mixing the appropriate parent tetrahalides at room temperature. The nine triple-mixed species, *i.e.*, ones of the type MX<sub>2</sub>YZ, have also been identified<sup>21</sup> for silicon, germanium, and tin by recognition of the unique values for their a<sub>1</sub> stretching modes.

Although the previous work has clearly shown the existence of mixed-halogeno species, it has provided no evidence as to whether either they or the parent species are the more stable or whether a random distribution (the so-called Calingaert distribution)<sup>22</sup> pertains. The equilibrium in question can be represented as



It is defined in terms of the equilibrium constants

$$K_1 = \frac{[MX_4][MX_2Y_2]}{[MX_3Y]^2}$$

$$K_2 = \frac{[MX_3Y][MX_2Y_3]}{[MX_2Y_2]^2}$$

$$K_3 = \frac{[MX_2Y_2][MY_4]}{[MX_2Y_3]^2}$$

which take the values K<sub>1</sub> = K<sub>3</sub> = 0.375 and K<sub>2</sub> = 0.444 for a random distribution. In the case of mixtures of the halides SnCl<sub>4</sub>, SnBr<sub>4</sub>, and SnI<sub>4</sub>, their <sup>119</sup>Sn nmr spectra have been interpreted<sup>23</sup> as demonstrating that a random redistribution of the halogen atoms takes place. The nmr technique is, however, not applicable in the case of the titanium halides. Accordingly, we have attempted to ascertain the nature of the halogen redistribution reaction in the TiCl<sub>4</sub>-TiBr<sub>4</sub> case by measurement of the area of the a<sub>1</sub> Raman peak of each parent halide and also that of the highest frequency a<sub>1</sub> peak of each mixed halide. These areas have been corrected for instrument response and then used to calculate K<sub>1</sub>, K<sub>2</sub>, and K<sub>3</sub>.

Two sets of mixtures were studied: one in which the pure halides were mixed together in the absence of solvent and a second set in which the halides were mixed in cyclohexane. The results (discussed below) were found to be independent of the presence of solvent. Although titanium tetrabromide is a solid (mp 39°), addition of even small amounts of the tetrachloride to it produced a homogeneous liquid at room temperature.

(21) C. Cerf and M.-B. Delhay, *Bull. Soc. Chim. Fr.*, 2818 (1964).

(22) G. Calingaert and H. A. Beatty, *J. Amer. Chem. Soc.*, **61**, 2748 (1939).

(23) J. J. Burke and P. C. Lauterbur, *ibid.*, **83**, 326 (1961).

(16) G. W. Chantry, *Spectrochim. Acta*, **21**, 1007 (1965).

(17) W. F. Murphy, M. V. Evans, and P. Bender, *J. Chem. Phys.*, **47**, 1836 (1967).

(18)(a) P. Brand and H. Sackmann, *Z. Anorg. Allg. Chem.*, **321**, 262 (1963); (b) R. J. H. Clark, B. K. Hunter, and C. J. Willis, *Chem. Commun.*, 201 (1971); H. J. Bernstein and H. F. Shurvell, personal communication.

(19) M. L. Delwaille, M. B. Buisset, and M. Delhay, *J. Amer. Chem. Soc.*, **74**, 5768 (1952), and references therein.

(20) M. L. Delwaille, M. F. Francois, and M. Delhay-Buisset, *J. Phys. Radium*, **15**, 206 (1954).

All spectra were recorded using 6471-Å radiation. As the frequencies of the  $a_1$  modes were relatively close together ( $\text{TiCl}_4$ , 390;  $\text{TiCl}_3\text{Br}$ , 325;  $\text{TiCl}_2\text{Br}_2$ , 291;  $\text{TiClBr}_3$ , 261;  $\text{TiBr}_4$ , 232  $\text{cm}^{-1}$ ), the level of background radiation was obtained by counting at a fixed frequency midway between peaks corresponding to the mixed halides. As the relatively weak  $\nu_3$  for titanium tetrabromide (392  $\text{cm}^{-1}$ ) is close to  $\nu_1$  for the tetrachloride (390  $\text{cm}^{-1}$ ), it was not possible to obtain an accurate estimate of the peak intensity for the tetrachloride in mixtures where more than 5% of the tetrabromide was present. In these cases, the values given in Table IV were calculated from the value of  $K_1$  found from other mixtures. Depolarization ratios for the  $a_1$  bands of the mixed halides were found to be of the order of 0.01–0.03. A typical spectrum is illustrated in Figure 6.

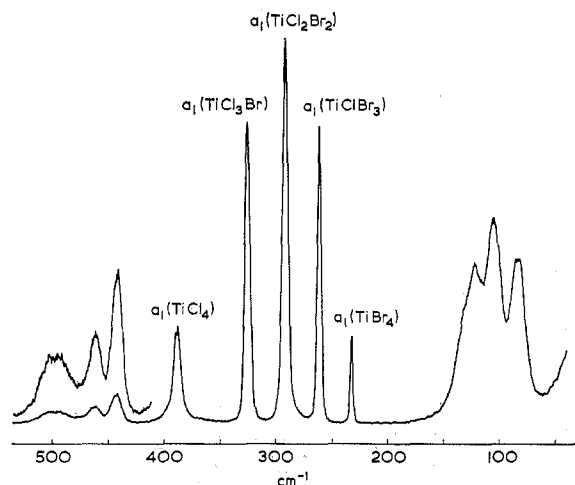


Figure 6.—Raman spectrum of a neat  $\text{TiCl}_4$ – $\text{TiBr}_4$  mixture at the mole ratio 59:41 over the range 0–550  $\text{cm}^{-1}$  at 23°. Power 300 mW at 6471 Å, slit widths 50, 100, and 50  $\mu$ , slit height open, time constant 1 sec, scale 10K (inset at 2K), scanning rate 40  $\text{cm}^{-1}/\text{min}$  ( $K = 1000$  counts/sec).

The remaining Raman-active vibrations of the various components produced peaks in the regions 60–120 and 400–500  $\text{cm}^{-1}$ , but their complex nature prevented any confident assignments from being made.

**Treatment of the Data.**—Since the mixed chloride–bromide species could not be isolated, it was not possible to measure their concentrations directly. The molar intensities were therefore evaluated by measuring peak intensities in a number of different mixtures, all containing cyclohexane, in which the total chloride:bromide ratio was varied in a known manner. For this purpose, a cell was made with a greaseless vacuum stopcock fitted with a neoprene diaphragm. Known amounts of titanium tetrabromide and cyclohexane were contained in the cell and titanium tetrachloride was condensed therein in increasing quantities; this procedure enabled spectra to be run at various chloride:bromide ratios.

Suppose the apparent peak intensity,  $I_1$ , of a particular component, mole fraction  $m_1$ , is given by

$$I_1 = h k_1 m_1$$

where  $h$  is a factor common to all components in that particular spectrum, depending on instrumental settings, exciting line intensity, etc., and  $k_1$  is a term including all factors peculiar to that component (molar

intensity, frequency corrections, etc.). Rearrangement gives

$$m_1 = I_1 / h k_1$$

so that, for a number of components in a mixture

$$\sum_1^n m_i = \frac{1}{h} \sum_1^n \frac{I_i}{k_i}$$

However, if all components are included

$$\sum_1^n m_i = 1$$

hence

$$h = \sum_1^n \frac{I_i}{k_i}$$

Substituting this expression for  $h$  gives

$$\frac{1}{k_1 m_1} = \frac{1}{I_1} \sum_1^n \frac{I_i}{k_i}$$

or

$$\frac{1 - m_1}{m_1} = \frac{k_1}{I_1} \sum_2^n \frac{I_i}{k_i}$$

If  $m_1$  represents the known mole fraction of the arbitrary standard, in this case the 806- $\text{cm}^{-1}$  band of cyclohexane, then by measuring all peak intensities at several different concentrations, a set of simultaneous equations relating the various  $k$  values may be obtained. This approach does not make any assumption about concentrations of any components, nor is it necessary to assume that they are in equilibrium together.

Using nine different mixtures, solution of the corresponding equations gave values of  $k_i/k_1$  for the three mixed chloride–bromide species, the tetrachloride and tetrabromide being previously determined on pure samples. After correction for instrument response, the intensities of the  $a_1$  bands relative to the 806- $\text{cm}^{-1}$  band of cyclohexane were found to be as follows:  $\text{TiCl}_4$ , 10.2;  $\text{TiCl}_3\text{Br}$ , 10.4;  $\text{TiCl}_2\text{Br}_2$ , 16.6;  $\text{TiClBr}_3$ , 16.2;  $\text{TiBr}_4$ , 21.0.

Using these values, the molar concentrations of the various components in cyclohexane solutions of the mixtures could then be calculated. For the pure tetrachloride and tetrabromide, measurement of peak intensities as a function of molar concentration had shown a linear relationship, indicating that the molar intensities were independent of concentration, and the same result was found in the cyclohexane solutions of the mixed halides. It was assumed, therefore, that the values of the molar intensities would remain the same in the mixtures where no cyclohexane was included, although, in the absence of the internal standard, direct experimental verification of this point is not possible. However, an overall check on the figures was made by computing the chlorine fraction in the mixture, defined as the atom ratio of total chlorine to total halogen present. Satisfactory agreement was found between the value of this ratio calculated from the derived concentrations of mixed species and that calculated from the known proportions in which the two tetrahalides were originally mixed.

Having found the concentrations of the individual



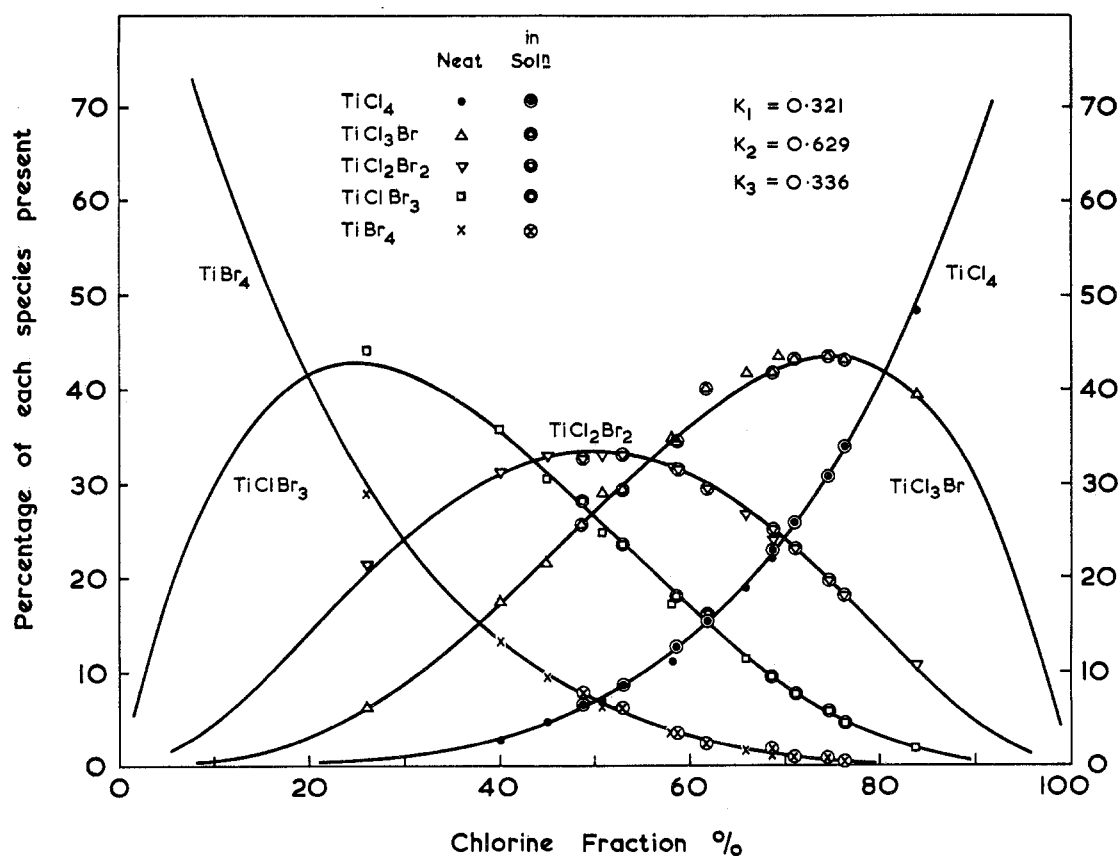


Figure 7.—Composition of  $\text{TiCl}_4$ – $\text{TiBr}_4$  mixtures at 23°. The solid curves represent the calculated concentrations of the species  $\text{TiCl}_4$ ,  $\text{TiCl}_3\text{Br}$ ,  $\text{TiCl}_2\text{Br}_2$ ,  $\text{TiClBr}_3$ , and  $\text{TiBr}_4$  at various mole fractions (given as percentages in the abscissa) of chlorine in a mixture. For a random distribution, the concentrations of each species, respectively, would be as follows (mole fraction of chlorine is  $x$ ):  $x^4$ ,  $4x^3(1-x)$ ,  $6x^2(1-x)^2$ ,  $4x(1-x)^3$ ,  $(1-x)^4$ . For a nonrandom distribution, the concentrations of the five species are modified (see text).

mixed-halide species, the three independent equilibrium constants were then calculated for the halogen-exchange process. The results are shown in Table IV. The average values found for these equilibrium constants were  $K_1 = 0.32$ ,  $K_2 = 0.63$ , and  $K_3 = 0.34$ , compared with the random distribution values of  $K_1 = K_3 = 0.375$  and  $K_2 = 0.444$ . Figure 7 shows the calculated distribution curves, based on average equilibrium constants, for the various species as the chlorine fraction varies from 0 to 100%, together with the experimental points. The equilibrium constants found therefore indicate essentially random distribution of the halogens, with a slightly lower concentration for the species  $\text{TiCl}_2\text{Br}_2$ . This small deviation of the data from that for a random distribution is most clearly demonstrated by a comparison of the experimentally found percentage of the species  $\text{TiCl}_2\text{Br}_2$  at a chlorine fraction of 50% with that calculated for a random distribution. The experi-

mental value is 33.1% (Table IV, Figure 7) whereas that for a random distribution is 37.5%.

**D. Conclusion.**—Raman intensity measurements on  $a_1$  bands of tetrahalides have proven to be sensitive probes to the degree of covalent character of metal-halogen bonds. The isotopic fine structure of the bands contains a great deal of structural information on the halides but has as yet only been shown to be fully interpretable for dilute solutions of the halides. Finally, it is shown that halogen-exchange equilibria can be studied and interpreted by way of Raman intensity measurements on the  $a_1$  modes of the parent and mixed halides.

**Acknowledgment.**—The authors thank Mr. B. W. Davies for assistance with some of the intensity measurements. C. J. W. thanks the University of Western Ontario for a leave of absence.