Vibrational Spectra and Stretching Force-constants of Tetrahalogeno-complexes of Manganese(II)

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REGULAR tetrahedral structures for $MnCl_4^{2-}$, $MnBr_4^{2-}$, and MnI_4^{2-} are supported by i.r.[1] and u.v. absorption[2] evidence. Of the four fundamental frequencies only two (ν_3 and ν_4 of species f_2) are permitted in the i.r. whereas all four are permitted in the Raman effect, where $\nu_1(a_1)$ is expected to be the strongest feature and easily recognisable by its high degree of polarization. Hitherto no Raman spectra have been reported for these species. The present Communication gives Raman findings and confirmatory evidence from i.r. combination frequencies. It also points out a striking difference in force-constant trend, as compared with all other known tetrahedral MX_4 sets with X = Cl, Br, I.

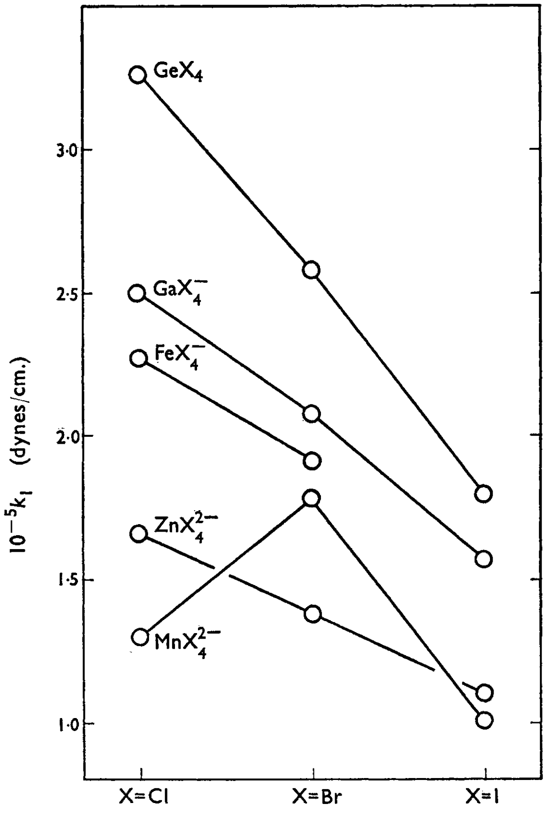

FIGURE. *Force constants* k_1 *of tetrahalogeno-species.*

The Mn^{II} complexes were prepared as alkyl ammonium salts and analysed by standard methods.[3] All are soluble in solvents such as MeCN, CH_2Cl_2, and $CHCl_3$. The yellow colours of the solutions made it impracticable to excite the Raman spectra with the blue Hg 4358 Å line, so that Hg 5461 Å (Cary 81 spectrometer) and He 5876 and 6678 Å (special grating spectrograph[4]) were used. Results with solid samples using the He–Ne laser line at 6328 Å (Cary Laser spectrometer) are also reported. I.r. spectra (33—800 cm.$^{-1}$) were recorded with a Beckman I.R. 11 spectrometer.

Some typical results are shown in the Table. Salts with other cations gave similar results. Our i.r. findings for the active fundamentals ν_3 and ν_4 are in satisfactory agreement with previous work.[1] For solid samples we observed crystal-effect splittings of ν_3 which had not always been reported previously. For $MnBr_4^{2-}$ and MnI_4^{2-} the highest-frequency i.r. combination bands ($\nu_3 + \nu_1$) appear only weakly; but our assignments of them are reasonable in these cases, where both ν_3 (i.r.) and ν_1 (Raman) are directly and independently observed. A similar assignment of the analogous combination band of $MnCl_4^{2-}$, which is relatively more intense, therefore gives support to the assignment of the single observed Raman frequency of $MnCl_4^{2-}$ as ν_1. Since this Raman line appeared only rather weakly, it might have been regarded as doubtful from the Raman spectra alone.

As ν_1 is the sole frequency of species a_1, it is possible to calculate from it a stretching force constant $k_1 = 4\pi^2\nu^2 m$, where m is the mass of the halogen atom. Using the Raman solution values $\nu_1 = 249$ cm.$^{-1}$ for $MnCl_4^{2-}$, $\nu_1 = 195$ for $MnBr_4^{2-}$ and $\nu_1 = 116$ for MnI_4^{2-}, we obtain respectively $k_1 = 1{\cdot}31$, $1{\cdot}79$, and $1{\cdot}01$ (10^5 dynes/cm.).

The trend of these k_1-values is anomalous, as compared with all other known sets of MX_4 species with X = Cl, Br, I. The anomaly is shown in the Figure, which includes for comparison typical results for sets of species which are (i) uncharged (M = Ge^{IV}), (ii) singly charged (M = Ga^{III}) and, like MnX_4^{2-}, doubly charged (M = Zn^{II}), (for ν_1-values see ref. 5). In these and all other known sets, k_1 falls monotonically and nearly linearly in the order X = Cl, Br, I; whereas the Mn^{II} species alone show an anomalous rise from X = Cl to X = Br. The Figure also includes values of k_1 for the tetrachloro- and tetrabromo-complexes of Fe^{III}.[6] Despite the fact that these are isoelectronic with the Mn^{II} complexes, they do not show the anomaly.

TABLE

Typical results and assignments

Mn^{II} Complex	Method (R = Raman)	Cation	State of Sample	Observed frequency (cm.$^{-1}$)	Assignment
$MnCl_4^{2-}$	R. Hg 5461 Å	Et_3NH^+	MeCN soln.	249 w pol.	ν_1 a_1
	R. He–Ne laser[a]	Et_3NH^+	solid	256 w	ν_1 a_1
	R. He–Ne laser[b]	K^+	$MnCl_2$–2KCl melt	255 pol.	ν_1 a_1
	Infrared	Et_3NH^+	Nujol mull	$\left.\begin{matrix}301\\278\end{matrix}\right\}$ vs	ν_3 f_2
				120 s	ν_4 f_2
				$\left.\begin{matrix}558\\539\end{matrix}\right\}$ mw	$\nu_3+\nu_1$ F_2 whence ν_1 ~259
$MnBr_4^{2-}$	R. He 5876 Å[c]	$Bu^n_4N^+$	$CHCl_3$ soln.	226 m	ν_3 f_2
				195 s pol.	ν_1 a_1
				81 ms	ν_4 f_2
				65 m	ν_2 e
	R. He–Ne laser[a]	$Bu^n_4N^+$	solid	195 m	ν_1 a_1
	Infrared	$Bu^n_4N^+$	Nujol mull	$\left.\begin{matrix}221\\209\end{matrix}\right\}$ vs	ν_3 f_2
				89 s	ν_4 f_2
				$\left.\begin{matrix}428\\416\end{matrix}\right\}$ w	$\nu_3+\nu^1$ F_2 whence ν_1 ~207
MnI_4^{2-}	R. He 5876 Å	$Bu^n_4N^+$	$CHCl_3$ soln.	116 ms	ν_1 a_1
	R. He 6678 Å	$Bu^n_4N^+$	$CHCl_3$ soln.	58 mw	ν_4 f_2
				46 mw	ν_2 e
	R. He–Ne laser[a]	$Bu^n_4N^+$	solid	107 s	ν^1 a_1
	R. He–Ne laser[a]	Et_4N^+	solid	108 s	ν_1 a_1
	Infrared	Et_4N^+	Nujol mull	$\left.\begin{matrix}193\\188\end{matrix}\right\}$ vs	ν_3 f_2
				56 s	ν_4 f_2
				$\left.\begin{matrix}296\\286\end{matrix}\right\}$ vw	$\nu_3+\nu_1$ F_2 whence ν_1 ~101

w = weak; m = medium; s = strong; v = very; pol = polarised.

[a] M. Gall, private communication; [b] J. H. R. Clarke, private communication; [c] G. Davidson, Thesis, Oxford, 1967.

In terms of a valency-type force-field with interactions, the constant k_1 becomes $k_r + 3k_{rr}$, where k_r represents individual bond-stretching and k_{rr} represents stretch–stretch interaction. Preliminary calculations suggest that the anomaly in the k_1-values is probably mainly attributable to the k_{rr} constants.

The work is being extended to tetrahalogeno-complexes of other transition-metal ions.

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[3] N. S. Gill, R. S. Nyholm, and P. Pauling, *Nature*, 1958, **182**, 168; N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.

[4] L. A. Woodward and M. J. Ware, *Spectrochim. Acta.*, 1963, **19**, 775.

[5] H. Siebert, "Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer, 1966, p. 66.

[6] L. A. Woodward and M. J. Taylor, *J. Chem. Soc.*, 1960, 4473; M. Gall, private communication (For $FeBr_4^{2-}$, ν_1 = 202 cm.$^{-1}$).