New Electronic Spectra of Gaseous SeBr, TeCl, TeBr, and TeI

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Summary U.v. spectra of SeBr, TeCl, TeBr, and TeI have been observed during the flash photolysis of the corresponding polyhalides, and vibrational analyses of the spectra are summarised.

FEW electronic spectra of the monohalides of Group VIB elements are known at present. A single transition, $^2\Pi$–$X^2\Pi_1$, of the molecules ClO, BrO, and IO has been recorded in emission from flames[1] and in absorption following flash photolysis of mixtures of the halogens and oxygen.[2] Bands of SCl photographed in the flash photolysis of S_2Cl_2 have been tentatively assigned to a similar transition.[3] The i.r. spectrum of OF,[4] the microwave spectrum of ClO,[5] and the e.s.r. spectra of OF, ClO, BrO, IO, SF, and SeF [6] have also been recorded. We now report the observation of the u.v. absorption spectra of SeBr, TeCl, TeBr, and TeI, photographed during the flash photolysis of the vapours of the corresponding polyhalides.

The spectrum of SeBr consists of two groups of violet-degraded bands, having (0,0) members at 2115·1 Å (47265 cm^{-1}) and 2164·1 Å (46195 cm^{-1}). Bands of the lower wavelength group are more numerous and intense, and analysis shows that $\Delta G_{1/2}' = 389$ and $\Delta G_{1/2}'' = 316$ cm^{-1}. The higher wavelength group consists of two bands separated by 390 cm^{-1}. These two groups are interpreted as transitions from the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ levels of the ground state to a common upper state, B.

The spectra of TeCl and TeBr are very similar to that of SeBr, each consisting of two groups of violet-degraded bands with vibrational parameters which are identical within the error of measurement. For TeCl, the (0,0) bands of B–$X^2\Pi_{3/2}$ and B–$X^2\Pi_{1/2}$ occur at 2256·8 and 2345·4 Å respectively, $\Delta G_{1/2}' = 455$ cm^{-1} and $\Delta G_{1/2}'' = 386$ cm^{-1}. In the case of TeBr the wavelengths of the (0,0) bands are 2316·9 and 2413·0 Å, $\Delta G_{1/2}' = 313$ and $\Delta G_{1/2}'' = 267$ cm^{-1}.

TeI displays a more extensive B–$X^2\Pi_{3/2}$ system than the other monohalides, some twenty bands being present. The (0,0) band lies at 2433·5 Å and the values of $\Delta G_{1/2}'$ and $\Delta G_{1/2}''$ are 257 and 216 cm^{-1} respectively. Only one weak band of B–$X^2\Pi_{1/2}$ is present. A second extensive band system, C–$X^2\Pi_{3/2}$, is also observed, with the (0,0) member at 2289·0 Å, $\Delta G_{1/2}' = 251$ and $\Delta G_{1/2}'' = 216$ cm^{-1}.

Molecular parameters of SeBr, TeCl, TeBr, and TeI

Molecule	State	T_e (cm^{-1})	ω_e (cm^{-1})	A (cm^{-1})
SeBr	B	47227	393	a
	$X^2\Pi$	0	317	$a + 1070$
TeCl	B	(44298)	(455)	b
	$X^2\Pi$	0	(385)	$b + 1674$
TeBr	B	43125	314	c
	$X^2\Pi$	0	267	$c + 1719$
TeI	C	43658	252	
	B	41057	260	
	$X^2\Pi$	0	217	

Values in parentheses are of T_0, $\Delta G_{1/2}'$ and $\Delta G_{1/2}''$.

Molecular constants derived from the analysis of the various systems are shown in the Table. a, b, and c represent the (probably small) spin-orbit intervals of the B states.

The band systems just described are clearly not of the same type as the known $^2\Pi_1$–$X^2\Pi_1$ systems of the halogen monoxides. The latter transitions involve a decrease in ω_e on excitation and lie to much longer wavelengths. It is likely that the B–X and C–X systems of the selenium and tellurium halides are Rydberg transitions.

We thank the Royal Society and the S.R.C. for grants for equipment; K.R. thanks the S.R.C. for a maintenance award.

(*Received, March 9th*, 1970; *Com.* 328.)

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