The Gas-phase Raman Spectrum and Molecular Structure of Dibromodichlorotellurium(IV), $TeCl_2Br_2$

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Summary The Raman spectrum of gaseous $TeCl_2Br_2$ at 310°, reported for the first time, is consistent with the presence of a unimolecular species having C_1 symmetry.

DIBROMODICHLOROTELLURIUM(IV), $TeCl_2Br_2$,[1,2] represents the only known example of a Group VI mixed tetrahalide which is sufficiently stable in the vapour phase to allow a structural investigation by gas-phase laser Raman spectroscopy. By analogy with gaseous $TeCl_4$,[3] the species present in the vapour of $TeCl_2Br_2$ would also be expected to be molecular although suitable electron-diffraction data are not available. As far as we know the only spectral results available for $TeCl_2Br_2$ come from an i.r. study of the solid and of a benzene and dimethylformamide solution.[2]

The possible gas-phase dissociations

$$TeCl_2Br_2 \rightleftharpoons TeCl_2 + Br_2 \qquad (1)$$

$$TeCl_2Br_2 \rightleftharpoons TeBr_2 + Cl_2 \qquad (2)$$

$$2TeCl_2 \rightleftharpoons Te_2 + 2Cl_2 \qquad (3)$$

$$2TeBr_2 \rightleftharpoons Te_2 + 2Br_2 \qquad (4)$$

at temperatures near and above the boiling point of $TeCl_2Br_2$ (415°) were found to be negligible at the temperature of our gas-phase Raman experiment (310°). This was confirmed by the non-observation of the extremely intense and depolarised resonance fluorescence spectra of diatomic bromine, diatomic tellurium, and triatomic tellurium dibromide[4] which would be expected to be observed using 4880 Å laser excitation, even for vapour pressures of Br_2, Te_2, or $TeBr_2$ of the order of, or less than, 1 mm Hg. Our Raman data for $TeCl_2Br_2$ (Table) parallel those for $TeCl_4$ and show that the structure in the solid state differs from that in the vapour phase and in solution in C_6H_6 and MeCN, in which a molecular form is probable.[3] Let us consider the Raman data for $TeCl_2Br_2$ in the gaseous and solution phases in terms of the most probable stereochemistries based (a) on a regular trigonal bipyramid with an equatorial lone pair (A, B, and C) and (b) similar to (a) but in a distorted form.

The vibrational spectrum of $TeCl_2Br_2$[a]

Assignment	Raman[b] (gas, 310°)	Raman[b] (C_6H_6 solution)	I.r.[2] (C_6H_6 solution)	Raman[b] (MeCN solution)	I.r.[2] ($HCONMe_2$ solution)
$\nu TeCl_{eq}$	370s (p)	373s (p)		e	e
$\nu TeCl_{ax}$	285s (p)	286m (p)	279vsbr	275ms (p)	e
$\nu TeBr_{eq}$	242msh (p)	248ms (p)	255m	249s (p)	246s
$\nu TeBr_{ax}$	198m(p)	*ca.* 195m (p)[d]	234m	194ms (p)	195s
	ca. 150vw			164msbr (p)	
	ca. 130m.br (p)[c]				

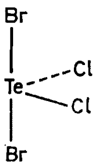
[a] The Raman spectrum of powdered $TeCl_2Br_2$ showed lines at 357mwsh, 338s, 242vs, 233msh, 226mwsh, 158w, 148w, 132w, 109w, 102w, 74s, and 51s.

[b] This study.

[c] This band was very broad and probably consists of more than one line.

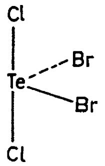
[d] Occurred on rising base-line.

[e] Region obscured by solvent.



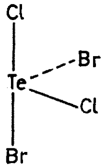
A

C_{2v}



B

C_{2v}



C

C_1

Although structure C seems unlikely, as one might expect the molecule to adopt the higher symmetry configuration, the gas- and solution-phase Raman data of the present study favour C for the following reasons. *All* of the observed Raman lines for $TeCl_2Br_2$ in the gaseous and solution phases were definitely polarised. Also, four polarised Raman-active stretching modes were observed, the frequencies of which correspond very closely with those to be expected for equatorial and axial Te–Cl stretching modes (370 and 285 cm^{-1}) and equatorial and axial Te–Br stretching modes (242 and 198 cm^{-1}), respectively.

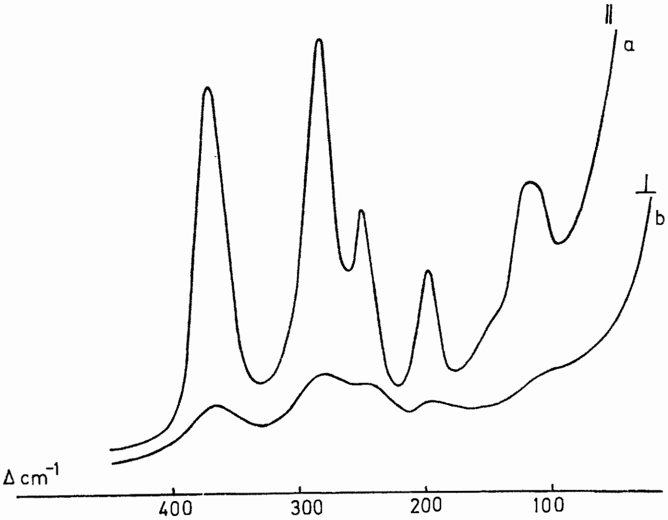
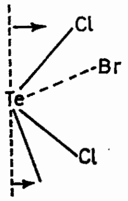


FIGURE. *The Raman spectrum of gaseous* $TeCl_2Br_2$ *at* 310°; (a) *parallel*; (b) *crossed polarisation measurement.*

In the analysis of the gas-phase data one should also consider the possibility that the axial bonds may be somewhat distorted from the 180° configuration as shown below:



D

A distortion of structure C of the kind shown in D which is tending towards a *distorted* square-pyramidal configuration about tellurium, would tend to reduce the lone-pair–bonding-pair interactions.[5] Note that similar distortions of structures A and B retain the symmetry C_{2v}. To summarise, we can say that the Raman data for molecular $TeCl_2Br_2$ are consistent with either of the low symmetry (C_1) structures C or D and not structure B which would have been predicted.[6]

$TeCl_2Br_2$(m.p. 292°) was prepared by the method of Aynsley.[1] Gas-phase Raman spectra were recorded for $TeCl_2Br_2$ at 310° on a Spex model 1401 using argon ion 4880 Å laser excitation.

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