# Mass Spectra and Vibrational Spectra of '$TeCl_2Br_2$'. The Vibrational Spectrum of Tellurium Tetrachloride

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Mass spectrometric studies show the presence of more than one compound in the vapour above $TeCl_2Br_2$. In agreement with this observation, at least five 'stretching modes' are found from Raman and i.r. studies of '$TeCl_2Br_2$' in the gas-phase. A previous assignment of stereochemistry on the basis of the Raman spectrum of $TeCl_2Br_2$ cannot be confirmed. Matrix i.r. and Raman spectra, and gas-phase i.r. spectra (using an i.r. cell with sealed-in silicon windows), are reported for tellurium tetrachloride. The results do not disagree with a $C_{2v}$ formulation for this molecule.

THE molecular systems $TeCl_4$ and $TeCl_2Br_2$, containing ten valence electrons, are stereochemically interesting. Gas-phase and solution Raman spectra and solution i.r. spectra on $TeCl_2Br_2$ were initially interpreted on the basis of a molecule having $C_1$ symmetry, deriving from a trigonal bipyramid with a vacant equatorial position.[1] This molecular shape would be unique as it implies the presence of one bromine and one chlorine in both axial and equatorial positions. Subsequently, on the basis of normal co-ordinate calculations, it was suggested that the spectra could be interpreted as due to the presence of two $C_{2v}$ isomers one of these again being unique in having equatorial chlorines, with axial bromines.[2] In the case of $TeCl_4$ the compound is monomeric in the gas-phase and it is known from Raman studies[3] that the molecule does not have tetrahedral symmetry. However no gas-phase i.r. data were reported.

The compound $TeCl_2Br_2$ is normally prepared by the oxidation of $TeCl_2$ with bromine.[4] The situation is somewhat complicated by a recent report[5] stating that $TeCl_2$ is not a stable crystalline compound under normal conditions. We find that a material which is apparently identical with $TeCl_2Br_2$ described above[4] may be obtained by heating a mixture of $TeCl_4$ and $TeBr_4$ to 300 °C in a sealed tube for a few minutes.

It is well known that it is possible to obtain pure compounds of the type $MX_{4-n}Y_n$ (where X and Y are halogens) for carbon and silicon, using for example, fractional distillation procedures. However this is not true in the case of the corresponding germanium and tin compounds where, although the presence of several molecular species can be detected spectroscopically,[6] the individual compounds have not been obtained as pure discrete entities. In the case of a mixture of $SnCl_4$ and $SnBr_4$ at room temperature equilibrium is obtained in less than ten seconds. $^{119}Sn$ N.m.r. studies show the presence of all the possible permutations in approximately the statistically expected ratios.[7]

On the basis of these observations we felt it unlikely that the ten electron system molecule $TeCl_2Br_2$ would be the only component present in the vapour of this composition under the somewhat drastic conditions necessary for a gas-phase Raman spectrum. We therefore examined the gas-phase i.r. spectrum of this compound under conditions approximating to those of the Raman study. Two strong bands were observed in the i.r. spectrum (140—590 cm$^{-1}$) at 316s and 380m cm$^{-1}$. A low resolution (10 cm$^{-1}$) gas-phase Raman spectrum showed bands at 203 (4·5), 253 (3·6), 289 (10), and 377 (7·9) cm$^{-1}$ closely agreeing with the spectrum previously reported. It appears that a total of at least five vibrations in the metal–halogen stretching region are observed, which is unacceptable for a species with four bonds. A moderate resolution (4 cm$^{-1}$) Raman spectrum showed the presence of additional shoulders. It is likely that a mixture of compounds is present. We attempted to differentiate between the various compounds present by studying the Raman spectra of $TeCl_{2+n}Br_{2-n}$ for various Cl : Br ratios. This was largely unsuccessful for example at a composition approximating to that required for $TeCl_3Br$ a Raman spectrum similar to that found for '$TeCl_2Br_2$' was obtained, but with altered relative intensities.

Although we are not aware of how it is possible to study the molecular shape in such a gaseous mixture of several compounds, we felt that mass spectrometry would at least help in identifying the principal constituents. The vapour above pure $TeBr_4$ yielded only $TeBr^+$ and $TeBr_2^+$ peaks in addition to those for $Br_2^+$. In the case of pure $TeCl_4$ peaks were observed for $TeCl_3^+$ (100), $TeCl_2^+$ (27), and $TeCl^+$ (6), the relative intensities being shown in parentheses. The results for $TeCl_2Br_2$ are summarised in Table 1, giving main peaks at $TeCl_3^+$ (16), $TeBrCl_2^+$ (9·6), and $TeBr_2Cl_2^+$ (9·2). The presence of species other than $TeCl_2Br_2$ in the vapour is thus demonstrated. Unfortunately the origin of the species $TeBrCl_2^+$ is not clear, it could be either $TeCl_3Br$ or $TeCl_2Br_2$ or both. Similarly the origin of the $TeCl_3^+$ peak could be $TeCl_4$ or $TeCl_3Br$,

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[2] G. A. Ozin and A. Vander Voet, *J. Mol. Structure*, 1971, **10**, 397.

[3] I. R. Beattie, J. R. Horder, and P. J. Jones, *J. Chem. Soc.* (*A*), 1970, 329.

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[6] M. L. Delivaulle, M. B. Buisset, and M. Delhaye, *J. Amer. Chem. Soc.*, 1952, **74**, 5768.

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as the parent ion was not observed for pure $TeCl_4$. However, the results suggest that previous deductions of molecular shape made for this system were based on an erroneous interpretation of the observations.

TABLE 1

Mass spectrum of $TeCl_2Br_2$

| Species | Major mass number | Relative intensity (total) |
|---|---|---|
| $Br_2^+$ | 158, 160, 162 | 2·4 |
| $TeCl^+$ | 161, 163, 165 | 1·3 |
| $TeCl_2^+$ | 196, 198, 200, 202 | 2·5 |
| $TeBr^+$ | 207, 209, 211 | 1·3 |
| $TeCl_3^+$ | 233, 235, 237 | 16·0 |
| $TeBrCl^+$ | 242, 244, 246 | 1·4 |
| $TeBrCl_2^+$ | 277, 279, 281 | 9·6 |
| $TeBr_2^+$ | 286, 288, 290 | 0·5 |
| $TeBrCl_3^+$ | 312, 314, 316, 318 | 4·3 |
| $TeBr_2Cl_2^+$ | 356, 358, 360, 362 | 9·2 |

Predictions of molecular shape for $TeCl_4$ lead to a $C_{2v}$ species derived from a trigonal bipyramid with a vacant equatorial position. Thus

$$\Gamma_{\text{mol}} = 4a_1 + 2b_2 + 2b_1 + a_2$$

all bands being Raman and i.r. active except for the mode $a_2$ which is Raman active only. The gas-phase Raman spectrum (Table 2) shows the presence of four polarised bands. The two high frequency Raman bands could be regarded as the symmetric equatorial stretch (382 cm$^{-1}$) and the symmetric axial stretch (290 cm$^{-1}$). Correspondingly the two strong i.r. bands in the gas-phase are antisymmetric stretching modes. The equatorial stretch at 382 cm$^{-1}$ is accidentally degenerate with the Raman band, while the 314 cm$^{-1}$ band is assigned to the antisymmetric axial stretch.

TABLE 2

I.r. and Raman spectra (cm$^{-1}$) of $TeCl_4$

| Tentative assignments | Raman | | | Infrared | | |
|---|---|---|---|---|---|---|
| | Gas-phase | Matrix | | Gas-phase | Matrix | |
| | | Ar | $N_2$ | | Ar | $N_2$ |
| $a_1$ Equatorial stretch | 382vs,pol | 391s | 389s | | 391w | 390vw |
| $b_2$ Equatorial stretch | | 384w | 380vw | 382m | 382m | 380w |
| | | 378sh | 374sh | | 378w | 375vw |
| | | | | | 365w | 361w |
| | | | | | 360vw | 357vw |
| | | | | | 315s | |
| $b_1$ Axial stretch | | | | 314vs | 307vs [a] | 303vs |
| | | | | | | 298sh |
| $a_1$ Axial stretch | 290vs,pol | 291vs | 295vs | | | |
| | | 287m | 291s | | | Cut off *ca.* 200 cm$^{-1}$ |
| | | | 287sh | | | |
| $a_1$ Equatorial deformation | 158m,pol | 179m | 175w | | | |
| | 130sh | 162mw | 159w | | | |
| $a_1$ Axial deformation | 72w,pol | Cut off *ca.* 100 cm$^{-1}$ | | | | |

[a] Complex band.

We hoped that matrix isolation studies on these bands might show details of isotope fine structure. However, the expectation was not realised in a way which we could interpret. The results (Table 2) support the accidental degeneracy at 382 cm$^{-1}$ in the gas-phase Raman and i.r. spectra. They also confirm the gas-phase data and suggest the presence of at least seven fundamental modes of vibration for the molecule, four of which from the gas-phase data are polarised.

## EXPERIMENTAL

$TeCl_2Br_2$ was prepared either (a) from '$TeCl_2$' by bromination [4] or (b) by heating a mixture of $TeCl_4$ and $TeBr_4$ in a sealed tube to 300 °C for a few minutes. Observed m.p.s (a), 305—309; (b), 304—307; lit.,[4] (a), 292 °C. Compounds were handled by vacuum techniques or in glove-boxes. Gas-phase i.r. spectra were obtained for $TeCl_4$ and $TeCl_2Br_2$ using unmodified Beckman IR 11 or Perkin-Elmer 225 spectrometers together with a 7 cm long evacuated borosilicate cell having fused in silicon windows. Spectra were taken for sample temperatures in the range 250—305 °C and pressures of the order of 100 Torr. Gas-phase Raman spectra of $TeCl_2Br_2$ were obtained using 4880 Å excitation and a Spex monochromator. Several samples were studied in the temperature range 250—305 °C. One sample used for an i.r. gas-phase experiment was studied at a similar temperature in the Raman effect using the cell from a gas-phase i.r. experiment. The Raman spectrum was closely similar to that obtained in the Raman experiments at higher pressures.

Matrix isolation Raman spectra were obtained at 15 K using a Cary 82 spectrometer (6471 Å excitation) in conjunction with a cryostat * based on the Displex CS 202 closed cycle helium refrigerator (Air Products). Matrix isolated i.r. spectra were obtained using the same cryostat with the Beckman IR 11 spectrophotometer. High purity argon and nitrogen (B.O.C.) were used as matrix gases. Glass (Pyrex) effusion cells were used for all matrix-isolation experiments. Mass spectra were obtained on a Bendix time-of-flight mass spectrometer using Knudsen cells made of stainless steel. A temperature of 130—135 °C was used for all mass spectral experiments.

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* Details to be published.