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Matrix-isolation studies on the vaporisation of alkali-metal tellurites: the characterisation of molecular M_2TeO_3 species (M = K, Rb or Cs)†

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Solid samples of alkali-metal tellurites (M_2TeO_3; M = K, Rb or Cs) have been heated *in vacuo* and the vaporisation products studied by mass spectrometry and matrix-isolation infrared spectroscopy. The molecular species M_2TeO_3 are identified by mass spectrometry as important products of vaporisation, and subsequent matrix-isolation studies, which incorporated oxygen-18 data, established both vibrational assignments and probable structures for these species. In particular, molecular K_2TeO_3 in argon has prominent IR absorptions at *ca.* 752, 742, 672, 360 and 306 cm^{-1} and a structure based on a pyramidal TeO_3 unit.

Alkali-metal tellurites (M_2TeO_3, where M = Cs, Rb or K) have been studied extensively in the solid phase. The crystal structures of rubidium tellurite,[1] potassium tellurite trihydrate,[2] caesium tellurite[3] and potassium tellurite[4] have been determined. Their structures all contain TeO_3^{2-} units, whereas other tellurium(IV) compounds, *e.g.* α-TeO_2, involve four oxygen atoms co-ordinating to each tellurium atom.[5] Studies concerned with heating alkali-metal tellurites in air have shown partial oxidation of Te^{IV} to Te^{VI} between 500 and 550 °C, a process which is reversed above 800 °C.[6,7] The salts were found to be stable up to 1000 °C in air.

Two Knudsen-cell mass spectrometric studies of the vaporisation of caesium tellurite have been reported. The first of these[8] established the existence of Cs_2TeO_3 as a probable molecular species, and obtained the standard enthalpy of vaporisation, whilst a more recent paper[9] established the congruent vaporisation of caesium tellurite and also studied the thermal dissociation of caesium tellurate. A calculation of the entropy of the gaseous ion TeO_3^{2-} has been reported[10] based on data taken from the solid phase.

The analogous alkali-metal selenites have previously been studied by matrix isolation and mass spectrometry,[11] where the predominant vapour phase species were found to be M_2SeO_3, with structures based on the pyramidal SeO_3^{2-} unit. In this study the vapour-phase species above the alkali-metal tellurites have been similarly investigated and the basic vibrational data for one particular system (K_2TeO_3) supplemented by experiments on the ^{18}O-enriched material in order to assist in the characterisation.

Experimental

The alkali-metal tellurites used in these studies were obtained by two separate routes. The majority of samples were prepared *in situ* by heating an equimolar mixture of the alkali-metal carbonate with tellurium dioxide *in vacuo* at *ca.* 800 °C according to the recommended procedure.[12] These samples were subsequently reground and heated in a platinum boat located inside an alumina tube which was heated inductively using a tantalum susceptor. Vaporisation took place *in vacuo* at temperatures typically in excess of ≈ 900 °C.

Samples of potassium tellurite were also obtained commercially (Aldrich, as hydrate) and vaporised in the same way, giving identical results. Oxygen-18-enriched potassium tellurite was prepared by dissolving the commercial sample in an excess of $H_2{}^{18}O$ (90 atom %) and leaving for 10 d. At the end of this period the water was removed by vacuum distillation and the sample vaporised as described above.

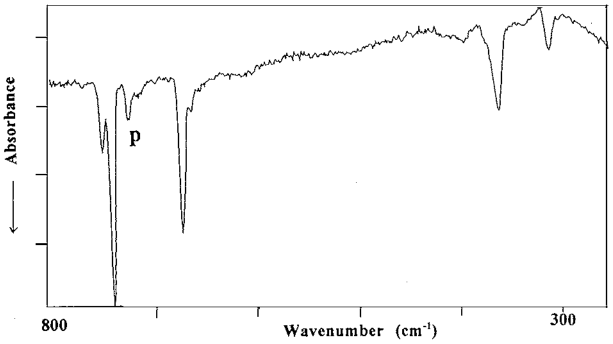

Fig. 1 Infrared spectrum of molecular K_2TeO_3 isolated in a nitrogen matrix. The feature denoted P is assigned to a polymer

The matrix-isolation apparatus and general methodology used for these experiments have been described elsewhere.[11,13] Both nitrogen and argon (BOC, 99.999%) were used as matrix gases in an estimated >1000-fold excess, and infrared spectra were recorded using a Perkin-Elmer PE983G instrument. Controlled-diffusion studies were carried out up to *ca.* 35 K. Mass spectra were obtained using the VG quadrupole models SXP600 and 12-12S operating in cross-beam mode.

Results

Our mass spectrometric studies on the vaporisation of alkali-metal tellurites were in good agreement with previous work.[8,9] For the caesium salt we observed a very intense signal corresponding to Cs^+, but a prominent signal was also obtained for the $Cs_2TeO_3^+$, together with weaker features corresponding to $Cs_2TeO_2^+$, TeO^+ and Te^+, which were assigned as fragments by varying the electron energy. The rubidium and potassium systems similarly yielded parent ions $M_2TeO_3^+$ and related fragments.

Matrix-isolation studies generally involved deposition times of up to 2 h, and during the initial stages IR spectra typically showed the characteristic absorptions of CO_2, notably at *ca.* 662 cm^{-1}, which corresponds to the bending mode. However, the evolution of CO_2 decreased with time, with the result that its absorptions could be effectively removed from subsequent spectra by subtraction.

Fig. 1 shows part of the nitrogen-matrix IR spectrum (800–250 cm^{-1}) obtained from the vaporisation of potassium tellurite, after removal of the CO_2 absorption. Two prominent bands are observed at 740.8 and 672.8 cm^{-1} and these are accompanied by weaker features at 750.9, 724.2, 713 (sh), 360 and 306

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† *Non-SI unit employed*: dyn = 10^{-5} N.

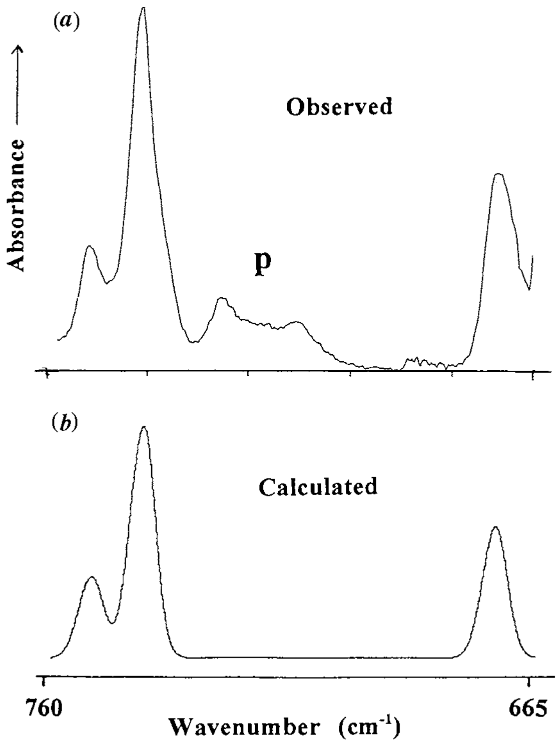


Fig. 2 Observed and calculated spectra in the Te–O stretching region for molecular K_2TeO_3 isolated in an argon matrix

cm^{-1}. Although all these bands showed essentially the same growth behaviour on deposition, controlled diffusion to *ca.* 35 K resulted in the continued growth of the bands at 724.2 and 713 cm^{-1}, but a *decrease* in the remaining five features. These latter bands at 750.9, 740.8, 672.8, 360 and 306 cm^{-1} are therefore assigned to a species A, which is chemically distinct from a second species B with absorptions at 724.2 and 713 cm^{-1}. On the basis of this diffusion behaviour species B is provisionally assigned as 'polymeric', whilst species A is identified as a possible monomer. It may be significant, however, that in this study or in the previous mass spectrometric reports[8,9] significant amounts of polymer were not detected in the vapour phase.

Corresponding features showing similar diffusion behaviour were also obtained from the rubidium and caesium systems and Table 1 summarises their band positions. Fig. 2(*a*) shows the higher-frequency spectral region obtained from K_2TeO_3 isolated in argon. This spectrum is very similar to that in nitrogen and the frequencies are included in Table 1. From these results it is evident that varying either the cation or the matrix environment produces only small shifts in vibrational frequency and we therefore assign all these features as vibrations involving essentially only Te/O motion in which there is little interaction with the matrix cage.

Fig. 3(*a*) shows the argon-matrix spectrum in the higher-frequency region obtained from the vapour above ^{18}O-enriched potassium tellurite. The CO_2 bands have not been subtracted out, but comparison with Fig. 2(*a*) reveals a number of additional peaks, notably at *ca.* 710 and 640 cm^{-1} and these are assigned to ^{18}O-enriched 'monomer'. Absorptions in the lower-frequency region of this spectrum were too weak to reveal well defined maxima.

Spectral Interpretation and Discussion

On the basis of the mass spectrometric studies, in which the $M_2TeO_3^+$ peaks are assigned as molecular ions, we provisionally identify the 'monomer' species A as matrix-isolated molecular tellurites M_2TeO_3. The frequencies of the three high-frequency bands (Table 1) lie in the Te–O stretching region, and may be compared to those in the pyramidal TeO_3^{2-} ion. In aqueous solution,[14] this ion has C_{3v} symmetry. The stretching modes transform as $A_1 + E$, with the A_1 stretch lying at 748 cm^{-1}, close to the highest-frequency mode of species A, and the E at 703 cm^{-1}, almost exactly between the more intense features at *ca.* 740 and 670 cm^{-1}.

Table 1 Vibration wavenumbers (cm^{-1}) observed in matrix-isolation studies on the vaporisation of alkali-metal tellurites

	K_2TeO_3		Rb_2TeO_3	Cs_2TeO_3
Species	N_2	Ar	N_2	N_2
A	750.9	752.0	750.3	748.9
	740.8	741.9	740.0	736.4
	672.8	672.0	672.2	673.6
	360	360	354	350
			347 (sh)	340 (sh)
	307	306	303	316
B	724.2	724.9	725.5	721.6
	713 (sh)	714	713.4	714.7

Accuracy: above 600 cm^{-1}, ± 0.5 cm^{-1}; below 600 cm^{-1}, ± 2 cm^{-1}.

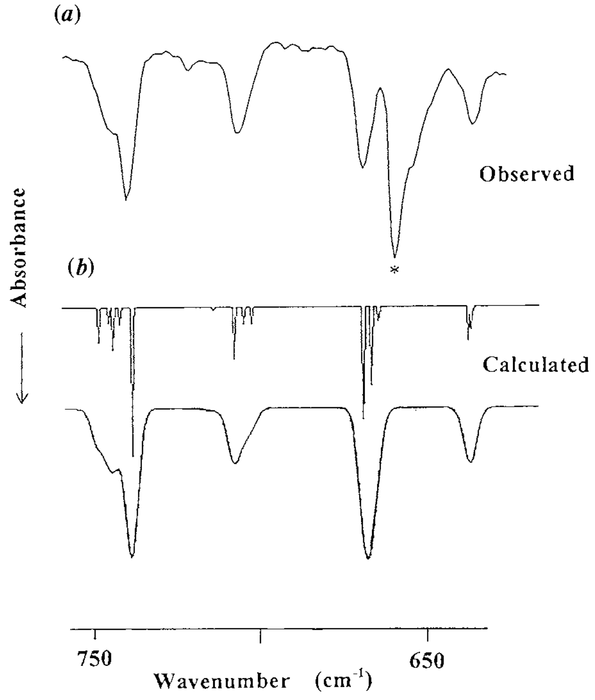
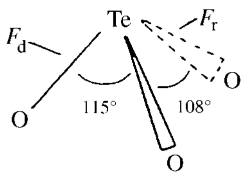


Fig. 3 Observed and calculated argon-matrix spectra for *ca.* 25% ^{18}O-enriched K_2TeO_3 species. The band denoted (*) is assigned to CO_2. Calculated spectra are displayed at bandwidths of 0.2 and 2.5 cm^{-1}

The general appearance of this spectral region is very similar to that previously observed for alkali-metal selenites,[11] and we propose a similar spectral interpretation for the tellurite spectra obtained here. Basically, we consider that co-ordination of the pyramidal TeO_3 unit by two cations reduces the symmetry to C_s, with a resulting splitting of the degenerate E mode into two components, $A' + A''$. The A_1 mode in the C_{3v} ion becomes A' in C_s, and as it is unlikely that two modes of the same symmetry end up close together in frequency, we assign the observed bands at *ca.* 750, 740 and 670 cm^{-1} as A', A'' and A' respectively. This symmetry ordering, in which the parent E mode splits such that $A'' > A'$, predicts that the lowering of symmetry is such as to produce one Te–O bond which has a *lower principal force constant* than the other two.

Fig. 4 shows three possible structures for molecular M_2TeO_3 species, all of which have C_s symmetry. The bis(monodentate) structure (*a*) has one terminal Te-O bond, which would be expected to be shorter and stronger than the two other

Table 2 Observed and calculated vibration wavenumbers (cm^{-1}) for ^{18}O-enriched K_2TeO_3 species isolated in argon matrices



Observed	Calculated (intensity)	Assignment
752.0	752.0 (1.1)	A′ $^{16}OTe^{16}O_2$
	748.9 (0.46)	A′ $^{18}OTe^{16}O_2$
747.6	747.6 (1.34)	A $^{16}OTe^{16}O^{18}O$
	745.6 (0.51)	A $^{18}OTe^{16}O^{18}O$
741.9	741.9 (3.6)	A″ $^{16}OTe^{16}O_2$
	741.9 (1.2)	A″ $^{18}OTe^{16}O_2$
	717.2 (0.1)	A′ $^{16}OTe^{18}O_2$
709.9	710.9 (1.57)	A $^{16}OTe^{16}O^{18}O$
	710.9 (0.04)	A′ $^{18}OTe^{18}O_2$
	708.1 (0.53)	A $^{18}OTe^{16}O^{18}O$
706.6 (sh)	705.6 (0.36)	A″$^{16}OTe^{18}O_2$
	705.6 (0.12)	A″$^{18}OTe^{18}O_2$
672.0	672.0 (3.57)	A′ $^{16}OTe^{16}O_2$
	669.6 (2.48)	A $^{16}OTe^{16}O^{18}O$
	667.4 (0.42)	A′ $^{16}OTe^{18}O_2$
640.1	640.4 (1.04)	A′ $^{18}OTe^{16}O_2$
	639.7 (0.71)	A $^{18}OTe^{16}O^{18}O$
	639.1 (0.12)	A′ $^{18}OTe^{18}O_2$

Frequency calculations assume a C_s pyramidal structure, with one unique angle (108 °) and two angles of 115 ° as shown above. The value of the unique stretching constant F_d is taken as 3.90 mdyn Å^{-1}, and the other force constants have values F_r 4.65, F_{rd} 0.41 and F_{rr} 0.20 mdyn Å^{-1}. Relative band intensities (in parentheses) assume randomised 25% ^{18}O enrichment.

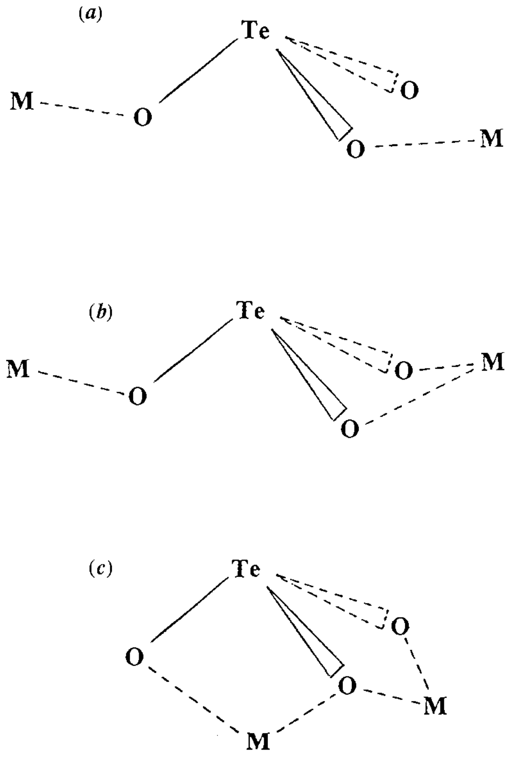


Fig. 4 Possible structures for molecular alkali-metal tellurites: (*a*) bis(monodentate)model, (*b*) mono-/bi-dentate model, (*c*) bis(bidentate) model

Te–O bonds which link to the cations, and is therefore unlikely to fit the observed spectrum. However, in the other two structures (*b*) and (*c*) the unique Te–O bond could be considered to be weaker than the other two. In structure (*b*) the unique bond bridges to a single cation and would be expected to have more single-bond character than the other two, whilst in the bis(bidentate) model (*c*) the unique O atom is close to two cations.

Fig. 2(*b*) shows a spectral simulation of the Te–O stretching region for K_2TeO_3 isolated in argon using a 'stretch only' force field.[11] The agreement is very satisfactory, but even this simple model requires a minimum of four independent stretching constants and the (arbitrary) choice of two angle parameters. Not surprisingly, there are a number of sets of such parameters which will generate a satisfactory spectral fit.

However, incorporation of the oxygen-18 data introduces several additional frequency constraints and Table 2 summarises our final results for the simulation of the vibrations of K_2TeO_3 isolated in argon. In this model the basic structural unit appears as a distorted pyramid with one significantly small angle (108 °) and where the principal stretching constant of the unique bond (F_d) is smaller than for the other two. Fig. 3(*b*) shows the spectral fit for the ^{18}O-enriched system using the parameters in Table 2, and the same parameters are employed for the simulation in Fig. 2(*b*).

In addition to neglecting any coupling with other vibrations, this 'stretch-only' model for the Te–O modes neglects the effect of anharmonicity, and in achieving a satisfactory spectral fit these uncertainties can be expected to be reflected as errors not only in the values of the force constants, but in the O–Te–O bond angles. Nevertheless, we believe that the prediction of one relatively small angle and two wider ones is correct and we note that this is also the model proposed for the analogous M_2SeO_3 species.[11] Calculations are currently in progress in an attempt to provide a theoretical justification for distinguishing between models (*b*) and (*c*) in Fig. 4 for both tellurites and selenites.[15]

The final assignment to be made concerns the spectral region 300–400 cm^{-1}. For K_2TeO_3 two bands are observed in this region, at 360 and 306 cm^{-1}, and for the rubidium and caesium salts similar features occur, with associated shoulders (Table 1). The $TeO_3{}^{2-}$ ion in aqueous solution has bending modes at 364 (A_1) and 326 (E) cm^{-1}, and we provisionally assign the band at 360 cm^{-1} as A′ (correlating with A_1 in C_{3v}) and that at 306 cm^{-1} as one (or both) of the components of the split E mode. This assignment is supported by the relative *intensities* of these two bands. In both the selenite system[11] and the related iodate system,[16] the A_1 XO_3 bending modes are found to be higher in frequency and more intense than the E.

Conclusion

These experiments first confirm that vaporisation of alkali-metal tellurites leads to the formation of molecular M_2TeO_3 and that the mass spectrometric studies are indeed looking at the parent ion. The matrix-isolation studies establish a number of fundamental vibrations, which are assigned on the basis of a distorted pyramidal structure for the TeO_3 unit. A detailed vibrational assignment concludes that in this structure one Te–O bond has a lower stretching constant than the other two, and two possible models are proposed which satisfy this condition. A second species was also identified in these matrix studies, which is believed to be a polymer. This species appears to be readily formed during controlled-diffusion studies and its presence in the matrix almost certainly occurs *via* limited aggregation during cocondensation, rather than as the result of trapping from the vapour phase.

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