# Matrix Isolation and Mass Spectrometric Studies on the Vaporisation of $OsO_2F_3$: Characterisation of Molecular $OsO_2F_3$

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The vapour species produced by heating solid osmium trifluoride dioxide *in vacuo* have been isolated in low-temperature matrices and also studied by mass spectrometry. Both studies indicate a complex mode of decomposition, and in addition to the identification of $OsOF_4$ ($C_{4v}$) and $OsO_3F_2$ ($D_{3h}$) the i.r. spectra show additional features at 907 and 655 cm$^{-1}$ which are assigned as ν(Os=O) and ν(Os–F) respectively in molecular $OsO_2F_3$. A $D_{3h}$ structure is proposed for this species by comparison with other heavy-metal oxide fluorides.

Four oxide fluorides of osmium are currently known to exist.[1,2] These are $OsO_3F_2$, $OsOF_4$, $OsOF_5$, and $OsO_2F_3$, and the last of these, the dioxide trifluoride appears to be the least stable. This material is described by Falconer *et al.*[3] as an exceedingly moisture-sensitive yellow-green solid which has a Raman spectrum characteristic of a fluorine-bridged polymer. On heating this material *in vacuo* to *ca.* 330—380 K, extensive decomposition takes place and mass spectrometric studies[2] indicate the presence of $OsO_3F_2$, $OsOF_4$, and $OsF_6$ in addition to molecular $OsO_2F_3$. In contrast, the three other oxide fluorides can all be vaporised as monomeric species with only minimal decomposition.

The principal aim of this work was to investigate the vapour species produced on heating solid $OsO_2F_3$, using matrix-isolation i.r. spectroscopy, and in particular to obtain vibrational data for molecular $OsO_2F_3$. At the present time, the only clue regarding the shape of this molecule is a report of a small refocussing effect in an electric deflection experiment.[4] Matrix isolation is well suited to the semi-quantitative analysis of complex vapours by virtue of the narrow linewidths encountered in such studies, and we have recently obtained characteristic i.r. spectra for $OsO_4$,[4] $OsF_6$,[5] and the three other oxide fluorides,[6] some or all of which are anticipated to be present in this system. The matrix i.r. spectrum of the corresponding $d^0$ species $ReO_2F_3$ has also been reported,[7] and its structure shown to be based on $C_{2v}$ symmetry.

In view of the complexity of the system it was also felt necessary to carry out an independent mass spectrometric study on the vaporisation of $OsO_2F_3$ under the same conditions as the matrix i.r. experiments in order to assist spectral interpretation.

## Experimental

*Sample Preparation and Analysis.*—The preparation of pure solid samples in the Os–O–F system is not easy, and may be further complicated in the vapour phase by disproportionation and dismutation reactions. However, a pure sample of $OsO_2F_3$ was obtained by the route described by Sunder and Stevie,[2] although the conditions proved to be critical. In a typical preparation, $OsO_4$ (0.5 g, 2 mmol) was loaded into a 300-cm$^3$ Monel autoclave, followed by $OsF_6$ (0.6 g, 2 mmol) at 77 K. The system was allowed to warm slowly to room temperature and then heated at 418 ± 5 K for 16 h. After cooling to *ca.* 300 K a very small quantity of volatile material was removed by pumping, and the autoclave was then opened in a dry box (< 5 p.p.m. $H_2O$). A pale yellow-green solid was scraped out and stored in stainless steel containers in the dry box.

Samples were analysed for fluorine using the lanthanum alizarin complexone method[8] whilst osmium was determined spectrophotometrically after hydrolysis in dilute base, oxidation to $OsO_4$, and formation of the thiourea complex[9] (Found: F, 20.2; Os, 67.4. Calc. for $OsO_2F_3$: F, 20.4; Os, 68.1%). A Raman spectrum of the solid showed prominent bands at *ca.* 965, *ca.* 720, and *ca.* 390 cm$^{-1}$ similar to those reported previously.[3] The i.r. spectrum of the solid was obtained as a fine powder crushed between plastic plates (dry Nujol reacts vigorously with $OsO_2F_3$). Bands were observed at 995 and 955 (Os=O terminal), 720 (Os–F terminal), and 480—580 cm$^{-1}$ (broad, Os–F bridging).

*Mass Spectrometric and Matrix-isolation Studies.*—Mass spectrometric studies were carried out using a VG SXP400 quadrupole instrument interfaced with a microcomputer. In a typical experiment, a sample of $OsO_2F_3$ was loaded into a pre-fluorinated stainless steel container and pumped under high vacuum (< 10$^{-6}$ Torr) overnight at room temperature. Samples were then slowly heated by an external furnace, and during this stage, the vapour species traversed a line-of-sight path of 15 cm before entering the ionisation region of the mass spectrometer. Temperatures were measured by a thermocouple attached to the outer wall of the stainless steel holder, and during heating, mass spectra were recorded continuously.

The general features of our matrix-isolation equipment have been described elsewhere.[10] In this present study, the vaporisation conditions for $OsO_2F_3$ were identical to those used in the mass spectrometric studies, and samples were co-deposited with nitrogen or argon (BOC 99.999%) as matrix materials. However, by incorporating a 'V' shaped CsI window as the cooled deposition surface it was possible to record i.r. matrix spectra continuously during sample deposition and thus monitor changes in vapour composition in a similar way to the mass spectrometric studies. The spectrometer used in these studies was a Perkin-Elmer 983G instrument interfaced with the appropriate data station.

## Results and Discussion

*Mass Spectrometry.*—The original mass spectrometric studies on $OsO_2F_3$ by Sunder and Stevie[2] indicated that at *ca.* 333 K the species present in the vapour phase are $OsO_3F_2$, $OsO_2F_3$, and $OsOF_4$. This conclusion was based on the observation of the appropriate parent ions and also of the fragments $OsO_3F^+$, $OsO_2F_2^+$, and $OsOF_3^+$ which, as expected, formed the base peaks in the spectra of these oxide fluorides. At higher temperatures (*ca.* 380 K) there was evidence for the formation of $OsO_4$ and $OsF_6$.

In our studies, gentle warming to *ca.* 313 K produced small amounts of $OsO_4^+$, and on further heating to *ca.* 333 K, $OsOF_3^+$ was first observed, indicating the presence of $OsOF_4$. At 350 K, $OsF_4^+$ and $OsF_5^+$ were noted, and finally at *ca.* 370 K, $OsO_3F_2^+$

and $OsO_2F_3^+$ appeared together with $OsO_3F^+$ and $OsO_2F_2^+$, signalling the presence in the vapour of $OsO_3F_2$ and $OsO_2F_3$. Further heating beyond 380 K produced no additional spectral features.

Comparison between the two sets of experimental data shows that there is satisfactory overall agreement regarding the identity of the vapour species, although the temperatures at which the various ions were observed differ between the two studies: in general, our temperatures being somewhat higher than those reported by Sunder and Stevie.[2] This difference may partly be due to a small temperature lag in our experiments, but more probably arises from the lower overall sensitivity of our mass spectrometer. One observation not accounted for in this way is the 'early' (*ca.* 313 K) appearance of $OsO_4^+$ in our experiments. This most probably arises from the formation of $OsO_4$ as a result of surface hydrolysis in those parts of our inlet system which could not be adequately passivated.

At the end of each mass spectral run, the sample, including furnace and thermocouple, could be transferred directly to the matrix equipment for corresponding i.r. studies.

*Infrared Spectroscopy.*—Matrix i.r. studies were carried out on samples of $OsO_2F_3$ using identical vaporisation conditions to those employed in the mass spectrometric studies, and the results obtained from freshly loaded samples were very similar to those from samples transferred from the mass spectrometer. I.r. spectra were obtained in both argon and nitrogen matrices, but spectral quality was generally better in nitrogen. In a typical experiment, samples were first pumped extensively at $< 10^{-6}$ Torr, and subsequently deposited on the cooled window area with a large excess ($> 1\,000 \times$) of matrix gas. During deposition, the sample temperature was slowly raised from *ca.* 300 to 400 K, and the spectral range 1 100—600 cm$^{-1}$ scanned repetitively.

The first i.r. absorption to appear was at *ca.* 960 cm$^{-1}$ when the sample temperature had reached *ca.* 315 K, and this band may be identified unambiguously as the $T_2$ Os=O stretch in $OsO_4$ by comparison with earlier work.[4,6] At *ca.* 335 K, three bands at 1 078, 695, and 685 cm$^{-1}$ began to grow simultaneously. These are similarly identified as the i.r.-active stretching modes in $OsOF_4$.[6] Further heating to *ca.* 355 K generated new features in the Os–F stretching region at 738, 730, 715, 711, and 670 cm$^{-1}$ which appeared to have no counterparts in the Os=O region. These absorptions are therefore assigned to binary osmium fluorides. Comparison with previous work[5] indicates that they cannot be solely due to $OsF_6$, for which the i.r.-active $T_{1u}$ stretch lies at 712, 725 cm$^{-1}$ when isolated in a nitrogen matrix, and we therefore believe that a lower fluoride such as $OsF_5$ may be present. Although there are no established i.r. data for this molecule, this assignment is consistent with the appearance of ion peaks $OsF_5^+$ and $OsF_4^+$ at a similar temperature in the mass spectrometric studies.

Finally, at *ca.* 385 K, four further bands were observed to grow, but by varying experimental conditions, such as sample heating rate, it was possible to show that these arose from two different species. One of these is characterised by peaks at 907 and 655 cm$^{-1}$, whilst the second absorbs at 932 and 640 cm$^{-1}$. This latter species is identified as $OsO_3F_2$ by comparison with published data[4] and its presence in this system further confirmed by the appearance of $OsO_3F_2^+$ in the mass spectrum. The remaining bands at 907 and 655 cm$^{-1}$ are assigned to monomeric $OsO_2F_3$ as discussed below.

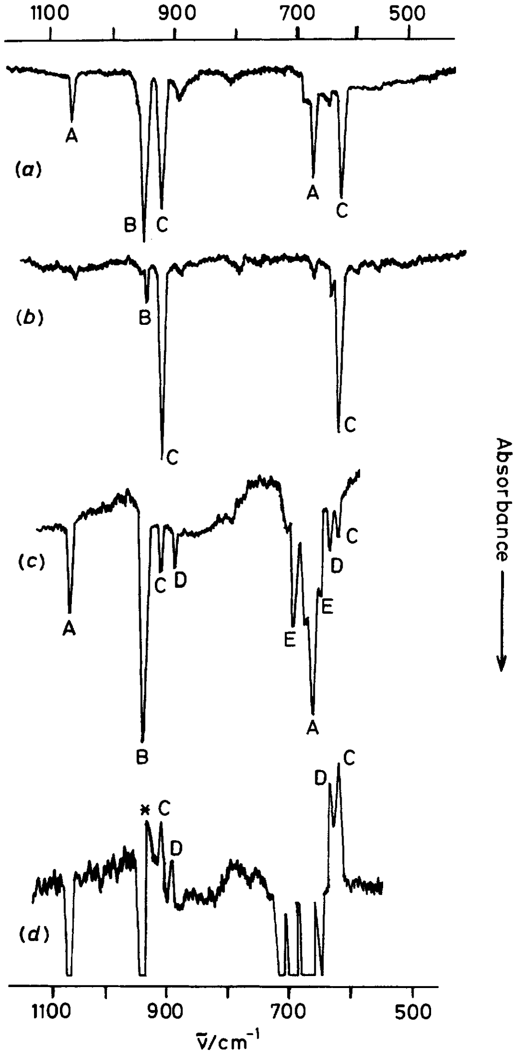

**Figure.** Nitrogen matrix i.r. spectra obtained from osmium oxide fluoride systems. Spectrum obtained (*a*) from a mixture of $OsOF_4$ + $OsO_3F_2$, (*b*) from $OsO_3F_2$, (*c*) from $OsO_2F_3$, and (*d*) difference spectrum obtained from $OsO_2F_3$ system. The feature denoted (*) arises from incomplete subtraction owing to different band widths. The species present are identified as A, $OsOF_4$; B, $OsO_4$; C, $OsO_3F_2$; D, $OsO_2F_3$; and E, binary osmium fluoride

The Figure shows representative i.r. spectra obtained from various osmium oxide fluoride systems including $OsO_2F_3$. In particular, Figure (*d*) displays a difference spectrum in which the lower temperature species ($OsO_4$, $OsOF_4$, and the binary fluoride) have positive absorbances, whilst the species evolved at higher temperatures in the same experiment have negative absorbances. The Table summarises the vibration frequencies observed in this work.

*Spectral Interpretation.*—The bands at 907 and 655 cm$^{-1}$ are assigned to $OsO_2F_3$ by virtue of their parallel growth rates in the spectral regions corresponding to Os=O and Os–F modes, and by the appearance of the parent $OsO_2F_3^+$ ion in the mass spectrometric studies. If these two bands are the only symmetry allowed i.r. stretching modes for $OsO_2F_3$, then it may readily be shown[7] that only a $D_{3h}$ structure is possible. However, despite the narrow band widths encountered in these experiments there is a possibility that other i.r. bands associated with the 907 and 655 cm$^{-1}$ features are masked by the presence of the other trapped species. It is therefore important to consider alternative symmetries for $OsO_2F_3$.

In particular, $ReO_2F_3$ has been shown to possess a $C_{2v}$ geometry, and in a low-temperature nitrogen matrix[7] has prominent i.r. absorptions at 992 ($B_2$), 701 ($A_1$), and 674 ($B_1$)

**Table.** I.r. absorptions (cm$^{-1}$) observed during[a] matrix-isolation studies on the vaporisation of $OsO_2F_3$

| Temperature/K | | | | | |
|---|---|---|---|---|---|
| 293 | 315 | 335 | 355 | 385 | Assignments |
| | | 1 078 | 1 078 | 1 078 | $A_1$ $OsOF_4$ |
| | 960 | 960 | 960 | 960 | $T_2$ $OsO_4$ |
| | | | | 932 | $E'$ $OsO_3F_2$ |
| | | | | 907 | $A_2''$ $OsO_2F_3$ |
| | | | 738 | 738 | ν(Os–F)[b] |
| | | | 730 | 730 | ν(Os–F)[b] |
| | | | 715 | 715 | ν(Os–F)[b] |
| | | | 711 | 711 | ν(Os–F)[b] |
| | | 695 | 695 | 695 | $A_1$ $OsOF_4$ |
| | | 685 | 685 | 685 | $E$ $OsOF_4$ |
| | | | 670 | 670 | ν(Os–F)[b] |
| | | | | 655 | $E'$ $OsO_2F_3$ |
| | | | | 640 | $A_2''$ $OsO_3F_2$ |
| | | | 559 | 559 | ν(Os–F–Os)[b] |
| | | | 468 | 468 | ν(Os–F–Os)[b] |
| | 330 | 330 | 330 | 330 | $T_2$ $OsO_4$ |
| | | 319 | 319 | 319 | $E$ $OsOF_4$ |

[a] The temperatures quoted are those at which the various peaks were observed to be increasing in intensity. [b] Unassigned Os–F modes of an unidentified binary osmium fluoride.

cm$^{-1}$ with somewhat weaker features at 1 029 ($A_1$), and 621 ($A_1$) cm$^{-1}$. A comparison between the i.r. fundamentals of $OsOF_5$ ($d^1$) and $ReOF_5$ ($d^0$), both of which have $C_{4v}$ symmetry, shows a close similarity. No two corresponding fundamentals are more than 25 cm$^{-1}$ apart,[11] and the absorptions of $OsOF_5$ are consistently lower in frequency than those of $ReOF_5$. If $OsO_2F_3$ has the same $C_{2v}$ structure as $ReO_2F_3$ one might therefore expect it to show prominent i.r. bands in the regions *ca.* 960—990, 670—700, and 640—670 cm$^{-1}$, and less intense features at *ca.* 1 000 cm$^{-1}$ and at 600—620 cm$^{-1}$. In view of the complexity of our Os–F region, it is possible that such additional Os–F bands might be obscured, but it would then be difficult to suggest an assignment for the band at 907 cm$^{-1}$. Even if this were the more intense ($B_2$) of the Os=O modes in $C_{2v}$ $OsO_2F_3$, it seems unlikely that it should be found over 50 cm$^{-1}$ below its anticipated region. Such a reduction in frequency could, however, arise from a change in geometry, and we believe that these results indicate a $D_{3h}$ symmetry for $OsO_2F_3$, with $A_2''$ (Os=O) at 907 cm$^{-1}$ and $E'$ (Os–F) at 655 cm$^{-1}$.

The only evidence against this proposed structure comes from an electric deflection study[2] on heavy-metal oxide fluorides, which includes data on $OsO_2F_3$, $OsO_3F_2$, and $ReO_2F_3$. In these experiments, a small refocussing effect (*ca.* 5 ± 3%) was obtained for the neutral precursors of the ions $OsO_2F_2^+$, $OsO_3F^+$, and $ReO_2F_2^+$, and was interpreted as evidence for a permanent electric dipole in all three species, thus precluding $D_{3h}$ symmetry. However, it was subsequently shown *via* i.r. and Raman selection rules, and also by $^{18}O$ isotope patterns, that $OsO_3F_2$ adopts a $D_{3h}$ structure in low-temperature matrices.[4] One must therefore conclude either that some other mechanism is responsible for causing refocussing at this low level in the vapour species, or alternatively, that the matrix imposes $D_{3h}$ symmetry on $OsO_3F_2$. Whilst it is impossible to reject the second alternative, a recent review[12] of matrix data has concluded that there are 'no convincing cases in which molecular symmetry differs in gas and matrix phases'. Moreover it is known that thermal population of low-lying vibrational levels in otherwise non-polar species (*e.g.* $TiF_4$) can cause a refocussing effect,[13] and we therefore believe that these electric deflection experiments do not rule out a $D_{3h}$ structure for $OsO_2F_3$.

It may also be relevant to note[14,15] that in octahedral dioxo complexes $MO_2X_4$, metals with a $d^0$ configuration prefer a *cis* structure, whilst *trans* dioxo linkages are observed as the number of *d* electrons rises, and it is also significant that *trans*-$MO_2X_4$ species have appreciably *lower* M=O stretching frequencies than their *cis* counterparts. Although the symmetry arguments put forward to account for these observations are *not* strictly transferable to five-co-ordination, it is interesting to note that the *cis* structure for $ReO_2F_3$ ($d^0$) and the proposed *trans* structure for $OsO_2F_3$ would be consistent with this trend.

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