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Mass spectrometric and IR spectroscopic characterisation of monomeric molecular ruthenium oxide tetrafluoride

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Abstract

Monomeric molecular ruthenium oxide tetrafluoride, prepared by the reaction of RuF_5 with glass at *c.* 300 °C, has been characterised by mass spectrometry and matrix-isolation IR spectroscopy. $RuOF_4$ exhibits C_{4v} symmetry, in common with all the known transition-metal oxide fluorides, with the O—Ru—F angle calculated to be equal to $110 \pm 6°$.

Introduction

The chemistry of ruthenium oxide tetrafluoride is of considerable importance since it is believed to play a significant role in the reprocessing of nuclear fuel by the fluoride-volatility method, and yet reports of its isolation in the laboratory describe widely differing properties. The first report by Holloway and Peacock [1] described a room-temperature-stable pale-green solid obtained from the reaction of ruthenium metal with BrF_3 in glass apparatus, which showed a vapour-pressure/temperature curve similar to that of other transition-metal oxide tetrafluorides and an X-ray powder diffraction pattern which differed from that of tetrameric RuF_5. Sakurai and Takahashi [2–4] reported that $RuOF_4$, prepared by the flow-fluorination of $RuO_2 \cdot nH_2O$, is only stable in the gas phase and exhibits an IR-active Ru=O stretch at 1040 cm^{-1}. Recently, Bougon *et al.* [5] have reported a room-temperature-stable brown solid, isolated from the room-temperature reaction of RuO_4 and KrF_2 in anhydrous HF, which exhibits an Ru=O stretch at 900 cm^{-1} and an X-ray powder diffraction pattern comparable with that of tetrameric RuF_5.

As part of our spectroscopic studies on a wide range of transition-metal fluorides and oxide–fluorides [6–9], we have investigated the vapours above heated platinum-metal pentafluorides. Ruthenium pentafluoride is reported [10] to exist mainly as a trimer in the gas phase, and the complicated matrix-isolated IR spectra are still being analysed. However, during attempts to

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'thermally crack' the trimer, we have obtained definitive evidence for ruthenium oxide tetrafluoride as a monomeric species, possessing C_{4v} symmetry, which is stable in the vapour phase at *c.* 300 °C.

Experimental

Details of our matrix-isolation equipment are described elsewhere [6]. Both nitrogen and argon (BOC, $>99.99\%$) were used as matrix gases. IR studies were carried out using a PE 983G spectrometer and a matrix rig fitted with CsI optics; matrix ratios were estimated to be well in excess of 1000:1. Mass-spectrometric studies were carried out on a VG SXP400 quadrupole instrument {mass range, 1–410 amu} interfaced to a microcomputer.

In a typical experiment, RuF_5 (0.5 g, 2.5 mmol, prepared by the static fluorination of ruthenium powder) was loaded in a dry box (<10 ppm H_2O) into a Pyrex spray-on vessel consisting of a small sample container closed with a PTFE tap and a long (*c.* 20 cm) 10 mm i.d. Pyrex tube connected directly to the vacuum manifold. The RuF_5 was heated to 35 ± 1 °C to maintain a slow, but measurable, flux of trimers, and the temperature of the spray-on tube could be maintained, by means of an electric furnace, within the range 20–350 °C.

Results and discussion

With both the sample and the spray-on tube at 35 °C, the mass spectrum of the vapour above ruthenium pentafluoride at 35 °C shows characteristic [11] ruthenium isotope patterns for RuF_5^+ and $(RuF_5)_2^+$ (the upper limit of the SXP400 mass spectrometer). On warming the spray-on tube, the relative ratios of these species remain virtually unchanged up to *c.* 300 °C. At this temperature a black metallic deposit appeared on the glass spray-on tube, all the peaks in the mass spectrum due to $(RuF_5)_2$ disappeared, and a series of new ruthenium isotope patterns centred around *m/z* ratios of 118, 137, 156, 175 and 194, assigned to RuO^+, $RuOF^+$, $RuOF_2^+$, $RuOF_3^+$ and $RuOF_4^+$ respectively, with additional intense peaks at *m/z* ratios of 47, 66, 85 and 104, corresponding to SiF^+, SiF_2^+, SiF_3^+ and SiF_4^+ respectively, appeared. The complete absence of ions with masses greater than 200, and up to the instrumental limit of 410 amu, even at very low electron energies, indicates that a monomeric ruthenium species had been formed.

Matrix-isolation IR studies were carried out on samples of RuF_5 using similar vaporisation conditions to those employed in the mass spectrometric experiments. IR spectra were obtained in both argon and nitrogen matrices, but spectral quality was generally better in nitrogen. When the sample and spray-on tube were held at 35 °C, complicated IR spectra, with a large number of peaks in the Ru–F stretching and bending regions, were observed.

An assignment of these bands on the basis of the recently claimed [10] trimeric structure for gaseous RuF_5 is in process. On warming the spray-on tube to 300 °C, all the peaks due to $(RuF_5)_3$ stopped growing (as evidenced by spectral subtraction) and, under low resolution in nitrogen matrices, new bands at *c.* 1060, 1021, 711, 685, 396 and 320 cm^{-1} were observed (Fig. 1). Identical spectra were obtained by pre-warming the spray-on tube to 300 °C prior to cool-down of the cryogenic head. The bands at 1021 and 396 cm^{-1} may be assigned to matrix-isolated SiF_4 [12]. By analogy with related monomeric MOF_4 species (Table 1), the remaining bands are assigned on the basis of position and intensity as, respectively, $\nu(Ru{=}O)$ (A_1), $\nu(Ru{-}F)$ (E), $\nu(Ru{-}F)$ (A_1) and $\delta(Ru{-}F)$ of C_{4v} $RuOF_4$.

It is possible to make an estimate of the angle between the C_4 axis and the ruthenium–fluorine bond, θ, from the observed relative intensities of the A_1 and E ruthenium–fluorine stretching modes, provided the interaction between the two A_1 stretching modes is neglected. We have shown that this is reasonable for the analogous $CrOF_4$ [6] and $ReOF_4$ [9] molecules, and that, under these conditions, the intensity ratio is given by eqn. (1).

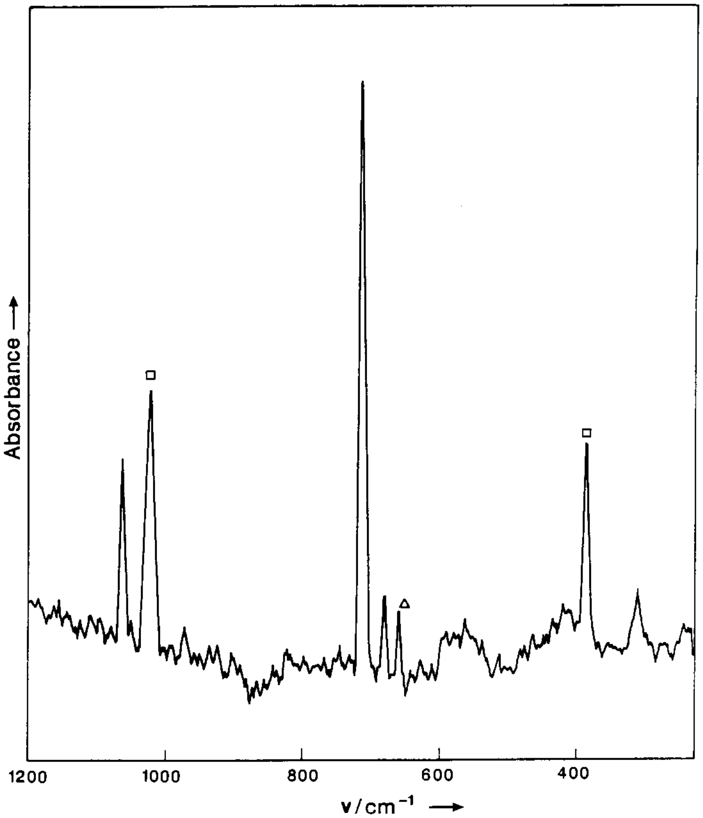

Fig. 1. Low-resolution IR spectrum for $RuOF_4$ in a nitrogen matrix: □ and △ bands assigned to SiF_4 and CO_2, respectively.

TABLE 1

A comparison of monomeric MOF_4 species

	Cr[a]	Mo[b]	W[b]	Re[c]	Ru[d]	Os[e]
$\nu_1(A_1)$	1028	1050	1050	1082	1060	1080
$\nu_2(A_1)$	686	714	726	685	685	695
$\nu_3(A_1)$	277	267	254	–	–	–
$\nu_7(E)$	746, 742	708	686	710	713, 710	685
$\nu_8(E)$	320	309, 304	309, 304	302	310	319
$\nu_9(E)$	271	238	236	245	–	–
O–M–F	104[f]	104[g]	104[g]	109±6	110±6	–

[a] Ref. 6.
[b] Ref. 17.
[c] Ref. 9.
[d] This work.
[e] Ref. 8.
[f] Ref. 13.
[g] Ref. 14.

$$\frac{I_E}{I_{A_1}}=\tan^2\theta\left(\frac{1}{M_F}+\frac{2\sin^2\theta}{M_{Ru}}\right)\bigg/\left(\frac{1}{M_F}+\frac{4\cos^2\theta}{M_{Ru}}\right) \quad (1)$$

The ratio of the areas under the E and A_1 bands in the spectra was measured as 9:1, from which a value of 70° may be calculated for θ and thus the O–Ru–F angle (β) may be estimated as 110°. There are inherent approximations in deriving the formulae for the intensities of the bands, such as neglect of anharmonicity, the factoring of stretching and bending modes, and the lack of interaction between the two A_1 symmetry stretching modes. There is also an attendant error in estimating the area under the two peaks. Considering these factors, it is prudent to place an error limit of at least ±6° on the derived value. However, the angle obtained appears reasonable when compared with the values obtained by electron diffraction for $CrOF_4$ (104°) [13], $MoOF_4$ (104°) and WOF_4 (104°) [14] and from vibrational data for $ReOF_4$ (109°) [9].

Under high resolution the two most intense bands show extensive structure (Fig. 2) which is attributed to the naturally occuring isotopes of ruthenium, and this structure provides an additional check on the angle θ value. The F and G matrix elements relevant to a general C_{4v} ZXY_4 molecule have been summarised [6], and in particular, the secular equation for the (factored-off) E stretching mode is:

$$\lambda_7=4\pi^2\nu_7{}^2=(F_r-F_{rr})(1/M_F+2\sin^2\theta/M_{Ru}) \quad (2)$$

This equation leads directly to θ (and hence to β) when frequency data for two different isotopic species are available.

Our high-resolution spectrum in the Ru–F stretching region is complex, and is interpreted as two equally intense, overlapping ruthenium isotope

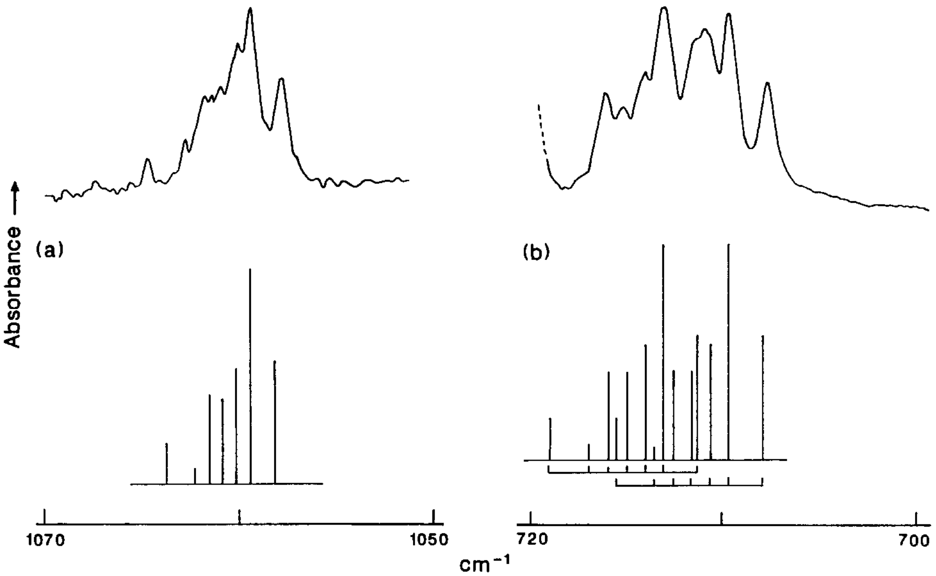

Fig. 2. High-resolution IR spectra for $RuOF_4$ in a nitrogen matrix: (a) 1070–1050 cm^{-1} with calculated line diagram (see text); (b) 720–700 cm^{-1} with calculated line diagram (see text).

patterns arising from a slight lifting of the E degeneracy. This is a phenomenon commonly found in nitrogen matrices [6], and the two components of the E mode λ_{7a} and λ_{7b} may be regarded as arising from two secular equations which have identical G matrix terms, but slightly different force constants F_{77a} and F_{77b}. Hence the isotope fine structure on each component of the doublet should yield the same value for θ. The line diagram accompanying Fig. 2(b) shows the calculated ruthenium isotope pattern for the split E mode assuming a uniform value of $\theta = 70°$ and equal F—Ru—F angles. The numerical data are summarised in Table 2. The agreement is clearly satisfactory and the isotope structure on each component is consistent with a single value of θ. Substituting this value into the A_1 secular equations yields a predicted isotope pattern for the Ru=O mode, and the line diagram accompanying Fig. 2(a) and numerical data in Table 2 are also in excellent agreement with the observed spectrum.

This work shows conclusively that gas-phase $RuOF_4$ is structurally similar to the other transition-metal oxide tetrafluorides and it is now pertinent to consider the previous counter-claims for this molecule. The reaction of ruthenium metal with BrF_3 affords RuF_5 [15]. However, it is well known that this reaction mixture can incandesce and that the heat generated would be more than adequate to allow a side-reaction of the RuF_5 with glass to give $RuOF_4$ contaminated with RuF_5 [1, 16]. The mass spectrum and similarity between the gas-phase IR [3] and our matrix-isolation IR spectra suggest that $RuOF_4$ may also be prepared by the flow-fluorination of $RuO_2 \cdot nH_2O$. The variation between our ν(Ru=O) stretch value and that obtained for the

TABLE 2

Observed and calculated IR bands (cm^{-1}) for matrix-isolated ruthenium oxide tetrafluoride

Observed[a]	Calculated[b]	Assignment
1064.7	1064.9	$\nu(^{96}\mathrm{Ru{=}O})\ \mathrm{A}_1$
1062.8	1063.0	$\nu(^{98}\mathrm{Ru{=}O})\ A_1$
1061.8	1062.1	$\nu(^{99}\mathrm{Ru{=}O})\ A_1$
1061.0	1061.2	$\nu(^{100}\mathrm{Ru{=}O})\ A_1$
1060.2	1060.3	$\nu(^{101}\mathrm{Ru{=}O})\ A_1$
1059.5	1059.5	$\nu(^{102}\mathrm{Ru{=}O})\ A_1$
1057.8	1057.8	$\nu(^{104}\mathrm{Ru{=}O})\ A_1$
[c]	718.9	$\nu(^{96}\mathrm{Ru{-}F})\ E$[d]
[c]	716.9	$\nu(^{98}\mathrm{Ru{-}F})\ E$[d]
716.0	715.9	$\nu(^{99}\mathrm{Ru{-}F})\ E$[d]
[c]	715.6	$\nu(^{96}\mathrm{Ru{-}F})\ E$
715.2	714.9	$\nu(^{100}\mathrm{Ru{-}F})\ E$[d]
714.0	713.9	$\nu(^{101}\mathrm{Ru{-}F})\ E$[d]
[c]	713.6	$\nu(^{98}\mathrm{Ru{-}F})\ E$
713.0	713.0	$\nu(^{102}\mathrm{Ru{-}F})\ E$[d]
[c]	712.6	$\nu(^{99}\mathrm{Ru{-}F})\ E$
711.6	711.6	$\nu(^{100}\mathrm{Ru{-}F})\ E$
710.9	711.2	$\nu(^{104}\mathrm{Ru{-}F})\ E$[d]
710.7	710.6	$\nu(^{101}\mathrm{Ru{-}F})\ E$
709.6	709.7	$\nu(^{102}\mathrm{Ru{-}F})\ E$
707.8	707.9	$\nu(^{104}\mathrm{Ru{-}F})\ E$

[a] This work N_2 matrix, peak position accuracy ± 0.2 cm^{-1}.

[b] Calculated with $O{-}Ru{-}F = 110°$, $F_{Ru-O} = 8.894$, $F_{Ru-F} = 4.225$, 4.186, $F_{Ru-O/Ru-F} = -0.207$, $F_{Ru-F/Ru-F} = 0.348$ mdyn Å^{-1}.

[c] Weak bands not resolved in our high-resolution studies.

[d] Assigned to a split E mode shifted by 3.3 cm^{-1} as described in the text.

brown $RuOF_4$ [5] suggest significant differences between gaseous/matrix-isolated and solid-state $RuOF_4$.

Acknowledgements

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