# The Raman Spectra of Ruthenium and Osmium Tetroxides

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VIBRATIONAL studies on $RuO_4$ and $OsO_4$ have, hitherto, been rather incomplete.[1-4] No Raman data are available for $RuO_4$, and previous investigations of the Raman spectrum of $OsO_4$ were unable to resolve the two deformation modes, $\nu_2$ and $\nu_4$.[1] The only evidence on the frequency of the former (i.r. inactive) mode was its appearance as a very weak band in the vapour-phase i.r. spectrum.[4] Nevertheless, a considerable number of force-field calculations have been made on the basis of the known data.[3-8] The present work was carried out with the aim of putting these theoretical treatments on a sounder experimental basis.

Recent electron diffraction studies[9,10] have indicated no deviation from $T_d$ symmetry for either $RuO_4$ or $OsO_4$. Such a regular tetrahedral model gives rise to four fundamental vibrational frequencies: $\nu_1$ ($A_1$) and $\nu_2$ ($E$), M–O stretching modes, and $\nu_3$ and $\nu_4$ ($F_2$), deformation modes. All of these are active in the Raman spectrum, $\nu_1$ giving rise to a polarised band, but only $\nu_3$ and $\nu_4$ give rise to i.r. absorptions.

The observed Raman shifts for $RuO_4$ and $OsO_4$ are set out in the Table, and the spectra are illustrated in Figures 1 and 2.

The liquid-phase spectrum of $OsO_4$ was closely similar to that reported by Woodward and Roberts.[1] Attempts to resolve the 338 cm.$^{-1}$ band into the $\nu_2$ and $\nu_4$ components were unsuccessful using slit widths down to approximately 2 cm.$^{-1}$. The band at 958 cm.$^{-1}$ appeared as a shoulder to the much stronger 967 cm.$^{-1}$ band. The latter was strongly polarised, however, and when its intensity was reduced, using perpendicularly polarised

*Raman spectra of* $RuO_4$ *and* $OsO_4$ (*all frequencies in cm.*$^{-1}$)

| | | $RuO_4$ (liq.) | $RuO_4$ (solid) | $OsO_4$ (liq.) | $OsO_4$ (solid) |
|---|---|---|---|---|---|
| O–M–O deformations | $\nu_2$ | 326 ms, dp | 333 s | 338 m, dp | 348 s |
| | $\nu_4$ | 338 m, dp | | | 332 ms |
| M–O stretches | $\nu_1$ | 883 vs, pol | 884 vs | 967 vs, pol | 969 vs |
| | $\nu_3$ | 915 m, dp, br | 909 s<br>925 m | 958 m, dp | 957 ms |

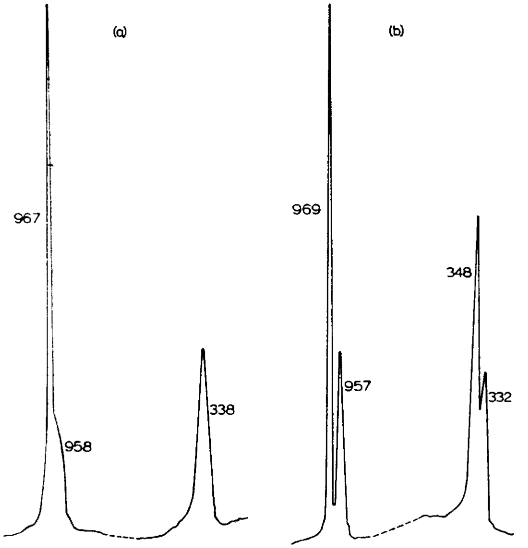

FIGURE 1. *Raman spectrum of* $OsO_4$, (a) *liquid*, (b) *solid.*

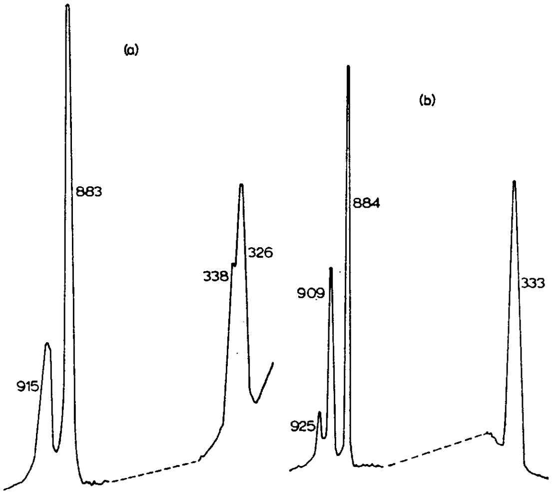

FIGURE 2. *Raman spectrum of* $RuO_4$, (a) *liquid*, (b) *solid.*

incident light, the degenerate stretching band was clearly resolved.

The spectrum of solid $OsO_4$ was somewhat different. The change of phase shifted the relative positions of the deformation bands so that they were clearly resolved, with peaks at 332 and 348 cm.$^{-1}$. Further, the latter band appeared as a doublet, with peaks (of approximately equal intensity) at 346 and 350 cm.$^{-1}$. This was presumably owing to the low site symmetry of the $OsO_4$ in the solid, which has been shown to be of monoclinic symmetry.[11] The 348 cm.$^{-1}$ band was therefore assigned to $\nu_2$ (of symmetry class $E$), leaving the 332 cm.$^{-1}$ component as $\nu_4$ ($F_2$). This agrees with the observations of Levin and Abramowitz,[4] who assigned i.r. absorptions at 353 and 329 cm.$^{-1}$ as $\nu_2$ and $\nu_4$ respectively. The doubly degenerate deformation mode is formally i.r. forbidden, and was extremely weak, its appearance being due to strong Coriolis interactions.

The stretching frequencies were also slightly shifted and sharpened by the change of phase, and became fully resolved, at 969 ($\nu_1$) and 957 cm.$^{-1}$ ($\nu_3$). Thus all four vibrational frequencies were distinguishable in the solid-phase spectrum.

Previous workers were unable to obtain the Raman spectrum of $RuO_4$,[2] as it is photosensitive to blue light. Use of the He–Ne laser line at 632·8 nm. to excite the spectrum overcame this difficulty, and samples of $RuO_4$ were found to be unaffected by more than three hr. of irradiation. The liquid-phase spectrum contained four bands, characteristic of a regular tetrahedral $XY_4$ species. Two bands were observed in the region of Ru–O stretching, at 883 and 915 cm.$^{-1}$. The latter was depolarised, and corresponded very closely to the i.r. absorption assigned to $\nu_3$.[2,3] The 883 cm.$^{-1}$ band was much stronger, and highly polarised. It can, therefore be definitely assigned to the symmetric Ru–O stretch ($\nu_1$), the frequency of which had previously been estimated (at 880 cm.$^{-1}$) from the position of an i.r. combination band.[3]

The region 300—400 cm.$^{-1}$ contained two bands, partially resolved, at 326 and 338 cm.$^{-1}$, both being depolarised. It is not easy to assign these unambiguously to $\nu_2$ and $\nu_4$. The vapour-phase i.r. frequency ($\nu_4$), at 330 cm.$^{-1}$, is of little use in distinguishing the two.[3] By analogy with $OsO_4$, the more intense band (that at 326 cm.$^{-1}$) is tentatively assigned to $\nu_2$. It is clear that the calculated value of 292 cm.$^{-1}$ for $\nu_2$[3] was considerably in error.

The spectrum of solid $RuO_4$, like that of $OsO_4$, differed appreciably from that of the liquid. In the Ru–O stretching region three bands appeared. The strongest, at 884 cm.$^{-1}$, clearly corresponded to $\nu_1$, while two bands at 909 and 925 cm.$^{-1}$ corresponded to $\nu_3$, split by the decreased symmetry of the molecular environment. Further comment on this cannot be made, however, until the crystal structure of $RuO_4$ is known. The splitting of the 915 cm.$^{-1}$ (liquid) band provided confirmation of its assignment to $\nu_3$, the degenerate Ru–O stretch. By contrast, the deformation region showed a simpler spectrum for the solid, only one band being observed at 333 cm.$^{-1}$. The phase change has shifted $\nu_2$ and $\nu_4$, bringing them into accidental degeneracy. This provides some additional evidence for the assignment of the 326 cm.$^{-1}$ (liquid) band to $\nu_2$, as in $OsO_4$ the corresponding band also increased in frequency on passing from liquid to solid.

The present results largely confirm the previous work on these compounds, while providing more direct evidence for several of the assignments. Further theoretical treatments of these molecules can therefore be carried out with much greater confidence.

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*Note added in proof:* A Paper entitled "Raman Spectra of Ruthenium Tetroxide and Related Species" by W. P. Griffiths [*J. Chem. Soc.* (*A*), 1968, 1663] reports conclusions essentially similar to those above.

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