The Raman spectrum and molecular structure of $\text{Me}_2\text{SiOReO}_3$ in the solid, liquid, solution, and gaseous phases

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The Raman spectrum of $\text{Me}_2\text{SiOReO}_3$ is found to be essentially the same in all of the above phases, proving that the non-linear SiReO bridge-bridged structure found in the solid phase is retained in the other phases and is not just the result of crystal packing requirements. The interpretation of the spectrum of $\text{Me}_2\text{SiOReO}_3$ is found to be particularly straightforward as the vibrational data can be considered to be intermediate between that of the parent, non-linear molecules ($\text{Me}_2\text{Si})_2\text{O}$ and ($\text{O}_2\text{Re})_2\text{O}$. In the present work, assignments for the ReO and SiO bridge stretching modes are proposed.


Laser Raman spectroscopy is now recognized by the inorganic chemist as being a valuable aid towards structural and vibrational assignment. The availability of high energy lasers now means that molecules can often be investigated in the vapor phase as well as in all other phases.

The Raman data for molecular $\text{Me}_2\text{SiOReO}_3$ in its various phases is extremely relevant to the stereochemical consequences of replacing silicon by rhenium(VII) which, like silicon, also has vacant d orbitals. It has been found that SiOSi angles generally fall in the range 130°-150° whereas the more limited data for ReORe angles has been found to vary from 130° in the linear Re(IV) anion (Cl$_4$ReOReCl$_4$)$^{4-}$ to approximately 120° in liquid and gaseous rhenium heptoxide (2), $\text{O}_2\text{ReOReO}_3$.

The recent X-ray data (3) for $\text{Me}_2\text{SiOReO}_3$ shows the presence of a molecular species with a SiReO bridge angle$^1$ of 164 ± 5°. Some degree of d orbital participation in the bonding was invoked to rationalize the wide SiReO angle.

It was thus of considerable interest to investigate the vibrational spectrum of $\text{Me}_2\text{SiOReO}_3$ in all of its possible phases to try to determine whether the non-linear SiReO skeleton found for the molecule in the crystal was retained in its other phases and was not just the result of crystal packing requirements. The present paper reports for the first time Raman data for trimethylsilyl-iranne, $\text{Me}_2\text{SiOReO}_3$.

The sensitivity of metal–oxygen bridge stretching frequencies to changes in the angle of the bridge has been demonstrated on a number of occasions (5). Thus an essential part of our discussion depends on a satisfactory assignment of the SiO and ReO bridge stretching modes in $\text{Me}_2\text{SiOReO}_3$ and the "parent" compounds.

Our approach to the problem was to obtain the Raman spectrum and Raman polarization data for $\text{Me}_2\text{SiOReO}_3$ in all possible phases and to compare the frequencies with those of ($\text{Me}_2\text{Si})_2\text{O}$ and ($\text{O}_2\text{Re})_2\text{O}$ whose vibrational spectra have been satisfactorily assigned (6, 2).

The X-ray data (3) for $\text{Me}_2\text{SiOReO}_3$ shows the crystal to be monoclinic with the centrosymmetric space group $C2/c$ ($C_{2v}^0$) and having four molecules in the primitive unit cell. In the crystal, the SiC bonds are staggered with respect to the terminal ReO bonds and the molecule has an overall symmetry of approximately $C_1$. Although there are four molecules in the primitive

TABLE I

<table>
<thead>
<tr>
<th>Approximate description*</th>
<th>$C_{3v}$ residue</th>
<th>$C_1$ molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>vSiMe + vReO$_3$</td>
<td>2a$_1$</td>
<td>2a' + 2a''</td>
</tr>
<tr>
<td>vSiMe + vReO$_3$</td>
<td>2e</td>
<td>2a' + 2a''</td>
</tr>
<tr>
<td>vSiO$_2$ + vReO$_3$</td>
<td>2a$_1$</td>
<td>2a'</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
<tr>
<td>$\delta$SiMe + $\delta$ReO$_2$</td>
<td>2e</td>
<td>$\gamma$ReO$_3$ + $\gamma$ReO$_3$</td>
</tr>
</tbody>
</table>

* = stretch; $\delta$ = deformation; $\rho$ = rock; $\rho$ = torsion.

1. The rhenium co-ordinates in $\text{Me}_2\text{SiOReO}_3$ were better defined than those of the light atoms because the heavy rhenium atom dominated the diffraction of X-rays and, as a result, the bond lengths and angles were not very precise.

2. The recent X-ray crystal structure (4) for technicium heptoxide, $\text{Tc}_2\text{O}_7$, shows the presence of oxygen bridged molecules, linear at the oxygen atom. The bridge oxygen atom was required to lie on a center of symmetry in the crystal.
TABLE 2
The Raman Spectra of \( \text{Me}_3\text{SiOReO}_3 \) in the solid, liquid, solution, and gaseous phases, \( \text{Re}_2\text{O}_7 \) in the gaseous phase, and \( (\text{Me}_3\text{Si})_2\text{O} \) in the liquid phase

<table>
<thead>
<tr>
<th>( \text{Me}_3\text{SiOReO}_3 )</th>
<th>Solid</th>
<th>Liquid</th>
<th>Solution</th>
<th>Gas</th>
<th>C(_2) assignment</th>
<th>Approximate description of mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Re}_2\text{O}_7 ) (2) ( \text{gas} ) (360°)</td>
<td>( \text{Me}_3\text{Si}_2\text{O} ) (6) liquid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1009 sp</td>
<td>1007 vs</td>
<td>1006 vsp</td>
<td>1007 vsp( \dagger )</td>
<td>1010 vsp</td>
<td>vReO</td>
<td>( a' )</td>
</tr>
<tr>
<td>972 m</td>
<td>959 m</td>
<td>960 mp</td>
<td>964 w</td>
<td>970 w</td>
<td>vReO</td>
<td>( a' + a'' )</td>
</tr>
<tr>
<td>1053( \dagger )</td>
<td>931 wsh</td>
<td>915 wp</td>
<td>934 vw</td>
<td>926 wp</td>
<td>vSiO</td>
<td>( a' )</td>
</tr>
<tr>
<td>518 sp</td>
<td>889 wp</td>
<td>857 w</td>
<td>857 vvw</td>
<td>831 w</td>
<td>p,CH(_3)</td>
<td>( a' )</td>
</tr>
<tr>
<td>( 835 \text{ mp?} )</td>
<td>834 vwp</td>
<td>( \sim 807 \text{ wp} )</td>
<td></td>
<td></td>
<td>p,CH(_3) or ( a' ) ( + a'' )</td>
<td></td>
</tr>
<tr>
<td>752 w</td>
<td>763 w</td>
<td>760 w</td>
<td>703 w</td>
<td>702 w</td>
<td>vSiMe</td>
<td>( a' + (a''?) )</td>
</tr>
<tr>
<td>683 mwp</td>
<td>658 mwp</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sim 800 \text{ vvw} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>456 wp</td>
<td>446 w</td>
<td>475 mwp</td>
<td>( \sim 475 \text{ wp} )</td>
<td>( \delta \text{ReO} )</td>
<td>vReO</td>
<td>( a' )</td>
</tr>
<tr>
<td>341 mbr</td>
<td>335 wp</td>
<td>350 s</td>
<td>343 mp</td>
<td>344 mp</td>
<td>( \delta \text{ReO} )</td>
<td>( 2a' + a'' )</td>
</tr>
<tr>
<td>322 wsh</td>
<td>322 vww</td>
<td>315 wsh</td>
<td>322 vww</td>
<td>326 wsh</td>
<td>( \delta \text{SiMe} )</td>
<td>( 2a' )</td>
</tr>
<tr>
<td>268 vw</td>
<td>293 wp</td>
<td>236 mwp</td>
<td>239 wp</td>
<td>299 wp</td>
<td>p,ReO</td>
<td>( a' )</td>
</tr>
<tr>
<td>( 248 \text{ msp} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>217 s</td>
<td>243 m</td>
<td>238 mp</td>
<td></td>
<td></td>
<td>( \delta \text{SiO} )</td>
<td>( a' + a'' )</td>
</tr>
<tr>
<td>( 185 \text{ msr} )</td>
<td>197 msh</td>
<td>193 vsbr</td>
<td>185 sp</td>
<td>190 msbr</td>
<td>( \delta \text{ReO} )</td>
<td>( a' + a'' )</td>
</tr>
<tr>
<td>177 wsh</td>
<td>176 wa</td>
<td>157 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \sim 113 \text{ vvw} )</td>
<td></td>
<td></td>
<td>134 w</td>
<td></td>
<td>( a' )</td>
<td></td>
</tr>
<tr>
<td>95 vvw</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>50 mp</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>117 w</td>
<td></td>
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</tr>
</tbody>
</table>

\( *p = \text{very, w = weak, m = medium, s = strong, sh = shoulder, br = broad, p = polarized.} \)
\( \dagger \text{Not resolved cleanly from band due to Pyrex glass in the region 520-700 cm}^{-1} \text{ as this was a high sensitivity scan.} \)

unit cell, no correlation splitting of the vibrational modes of the molecule into \( a_g + b_u \). Raman active crystal components was observed.

The main difference between the unsymmetrical bridge system found in \( \text{Me}_3\text{SiOReO}_3 \) and the symmetrical bridge systems found in \( (\text{Me}_3\text{Si})_2\text{O} \) and \( (\text{O}_2\text{Re})_2\text{O} \) lies in the fact that in the former the SiO and ReO bridge stretching modes are both totally symmetrical and can be expected to occur in the Raman spectrum as polarized lines. However, in the latter two species two bridge-stretching modes are still expected to occur (a high and low frequency mode), but only the lower frequency mode will be totally symmetrical.

Let us consider \( \text{Me}_3\text{SiOReO}_3 \) to be a rigid molecule without free rotation of the terminal \( \text{Me}_3\text{Si} \) and \( \text{O}_2\text{Re} \) groups about the respective metal–oxygen bonds. Then we can expect \( 13a' + 8a'' \) vibrational modes (below approximately \( 1100 \text{ cm}^{-1} \)) associated with the basic \( \text{C}_2\text{SiOReO}_3 \) skeleton. In addition there will be methyl rocking modes associated with the \( \text{Me}_3\text{Si} \) group which under \( C_{3v} \) symmetry (for the residue) have the symmetry species \( 2a_1 + 2e \). These are expected to occur in the range \( 870-720 \text{ cm}^{-1} \).

If there is very little vibrational coupling across the SiORe bridge, as would be expected by analogy with previous results on symmetrical bridge systems, then one can consider the two halves of the molecule as separate \( C_{3v} \) residues. We then arrive at the correlations for the normal modes of vibration of \( \text{Me}_3\text{SiOReO}_3 \) (below approximately \( 1100 \text{ cm}^{-1} \)) as shown in Table 1. The lowering of the symmetry of the terminal groups from \( C_{3v} \) to \( C_3 \) results in practice, in either a small splitting or slightly polarized character for some of the modes assignable to degenerate \( e \) modes of the \( C_{3v} \) residues. On this basis and taking into account the assignments for the related species \( (\text{Me}_3\text{Si})_2\text{O} \) and \( (\text{O}_2\text{Re})_2\text{O} \), we assign SiO and ReO bridge stretching modes in \( \text{Me}_3\text{SiOReO}_3 \) to polarized bands observed at 915
and 475 cm\(^{-1}\) (in the liquid) and 931 and 446 cm\(^{-1}\) (in the solid), respectively: cf. 
(Me\(_3\)Si)\(_2\)O \(v_{\text{sym}}\) 518 cm\(^{-1}\) and \(v_{\text{anti}}\) 1053 cm\(^{-1}\); 
(O\(_3\)Re)\(_2\)O \(v_{\text{sym}}\) 456 cm\(^{-1}\) and \(v_{\text{anti}}\) \(\sim\) 800 cm\(^{-1}\). 
Although the modes involving mainly stretching 
of the SiO and ReO bridge bonds both involve 
motion of the central oxygen atom and will be 
of mixed character, the above assignment is 
acceptable purely on a mass basis.

The remaining bands for Me\(_3\)SiReO\(_3\) are 
assigned as in Table 2 by analogy with the 
“parent” compounds whose Raman spectra are 
included in Table 2 for the purpose of comparison. The unassigned bands are the Me\(_3\)Si— 
and O\(_3\)Re— torsional modes and the totally 
symmetrical SiReO deformational mode, all of 
which are expected to occur below 180 cm\(^{-1}\).

The changes in frequency of the bridge 
stretching modes are small and variable between 
phases and correspond to a decrease of approx-
imately 10° (with respect to the solid) in the 
SiRe angle. The changes may be attributable 
to crystal packing requirements in the solid and 
termolecular interactions in the liquid and solution 
phases. However, the internal consistency of the Raman spectra for Me\(_3\)SiReO\(_3\) 
between phases shows unambiguously that the 
molecular structure is retained in all phases with 
only slight variations in the SiReO bridge angle.

**Experimental**

Rhenium heptoxide was prepared by oxidizing rhenium 
metal powder under anhydrous conditions and then 
sublimation of the pale yellow product in vacuo. Hexa-
methyldisiloxane was dried by refluxing over CaH\(_2\) and 
then distillation in vacuo. All solvents used, diethyl ether, 
chloroform, and benzene were also dried with CaH\(_2\) by 
standard procedures.

Trimethylsilylperbennate, Me\(_3\)SiOReO\(_3\), was prepared 
by refluxing Re\(_2\)O\(_5\) in excess hexamethyldisiloxane under 
anhydrous conditions (7). The crystallized Me\(_3\)SiReO\(_3\) 
was further purified by vacuum sublimation (obs. m.p. 
80.0 °C; litt. m.p. 79.5–80.5 °C).

Raman spectra were recorded on a Spex 1401 Raman 
spectrometer using ether argon-krypton or argon ion 
laser excitation. The spectra of liquid and gaseous 
Me\(_3\)SiReO\(_3\) were recorded at 100 and 180 °C, respectively, 
using cell and furnace designs similar to those 
described previously (2, 8).

Attempts to record laser Raman solution spectra in 
diethyl ether and chloroform were unsuccessful owing to 
rapid photodecomposition reactions. Solution data 
could, however, be obtained in hexamethyldisiloxane and 
benzene solution although photodecomposition reactions 
were still observed to be occurring very slowly in benzene 
solution. In order to identify any impurity bands, many 
solution spectra were recorded.

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