The Raman spectrum and molecular structure of $Me_3SiOReO_3$ in the solid, liquid, solution, and gaseous phases

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The Raman spectrum of $Me_3SiOReO_3$ is found to be essentially the same in all of the above phases, proving that the non-linear SiORe 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 $Me_3SiOReO_3$ is found to be particularly straightforward as the vibrational data can be considered to be intermediate between that of the parent, non-linear molecules $(Me_3Si)_2O$ and $(O_3Re)_2O$. 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 $Me_3SiOReO_3$ 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 180° in the linear Re(IV) anion (1) $(Cl_5ReOReCl_5)^{4-}$ to approximately 120° in liquid and gaseous rhenium heptoxide (2), $O_3ReOReO_3$.

The recent X-ray data (3) for $Me_3SiOReO_3$ shows the presence of a molecular species with a SiORe bridge angle[1] of 164 ± 5°. Some degree of d orbital participation in the bonding was invoked to rationalize the wide SiORe angle.

It was thus of considerable interest to investigate the vibrational spectrum of $Me_3SiOReO_3$ in all of its possible phases to try to determine whether the non-linear SiORe skeleton found for the molecule in the crystal was retained in its other phases and was not just the result of crystal packing requirements.[2] The present paper reports

for the first time Raman data for trimethylsilyl-perhennate, $Me_3SiOReO_3$.

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 $Me_3SiOReO_3$ and the "parent" compounds.

Our approach to the problem was to obtain the Raman spectrum and Raman polarization data for $Me_3SiOReO_3$ in all possible phases and to compare the frequencies with those of $(Me_3Si)_2O$ and $(O_3Re)_2O$ whose vibrational spectra have been satisfactorily assigned (6, 2).

The X-ray data (3) for $Me_3SiOReO_3$ shows the crystal to be monoclinic with the centrosymmetric space group $C2/c$ (C_{2h}^6) 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_s. Although there are four molecules in the primitive

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[1] The rhenium co-ordinates in $Me_3SiOReO_3$ 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, Tc_2O_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 1

Correlations for the normal modes of vibration of $Me_3SiOReO_3$

Approximate description*	C_{3v} residue	C_s molecule
vSiMe + vReO$_t$	$2a_1$	$2a'$
vSiMe + vReO$_t$	$2e$	$2a' + 2a''$
vSiO$_b$ + vReO$_b$	$2a_1$	$2a'$
δSiMe + δReO$_t$	$2a_1$	$2a'$
δSiMe + δReO$_t$	$2e$	$2a' + 2a''$
ρ_rSiMe + ρ_rReO$_t$	$2e$	$2a' + 2a''$
ρ_rSiMe + ρ_rReO$_t$	$2a_2$	$2a''$
ρ_rMe	$2a_1$	$2a'$
ρ_rMe	$2e$	$2a' + 2a''$
δSiORe	a_1	a'

*v = stretch; δ = deformation; ρ_r = rock; ρ_t = torsion.

TABLE 2

The Raman Spectra of Me₃SiOReO₃ in the solid, liquid, solution, and gaseous phases, Re₂O₇ in the gaseous phase, and (Me₃Si)₂O in the liquid phase*

| Re₂O₇ (2) gas (360°)	(Me₃Si)₂O (6) liquid	Me₃SiOReO₃				C_s assignment	Approximate description of mode
		Solid	Liquid (100°)	Solution	Gas (180°)		
1009 sp		1007 vs	1006 vsp	1007 vsp‡	1010 vsp	vReO	a'
972 m		959 m	960 mp	964 w‡	970 w	vReO	a' + a''
	1053† ⎱ 518 sp ⎰	931 wsh	915 wp	934 vw	926 wp	vSiO	a'
	889 wp	857 w	857 vw			ρrCH₃	a''
		831 w	834 vwp			⎰ ρrCH₃	a'
	835 mp? }			~807 wp		⎱ ρrCH₃ or vSiMe	a' or a''
		763 w	760 w				
	752 w ⎱ 683 mp ⎰	703 w	702 w			vSiMe	a' + (a''?)
	658 msp ⎰	642 m	635 sp	638 msp	639 msp	vSiMe	a'
~800 vvw ⎱ 456 wp ⎰		446 w	475 mwp		~475 w§	vReO	a'
341 mbr ⎱ 322 wsh ⎰ p 268 vw	335 wp	350 s	343 mp	344 msp	347 mp	⎰ δReO	2a' + a''
		315 wsh	322 vwsh	326 wsh	328 wsh	⎱ δSiMe	a'
			293 wp		299 wp	ρrReO	a'
	248 msp ⎱ 217 s ⎰	243 m	238 mp			δSiMe	a' + a''
185 ms ⎱ 177 wsh ⎰ p	197 msh ⎱ 176 vs ⎰ p	193 vsbr	185 sp	190 msbr	180 msbrp	⎰ ρrReO ⎱ ρrSiMe	a'' + a'
		157 w?			150 vw?	ρrSiMe	a''
113 vvw ⎱ 95 vvw ⎰ 50 mp ⎰		134 w				δReOSi or terminal torsions	
		117 w					

*v = very, w = weak, m = medium, s = strong, sh = shoulder, br = broad, p = polarized.
†Observed only in infrared spectrum.
‡These refer to the recorded values in (Me₃Si)₂O solution, as this region was obscured by benzene lines.
§Not resolved clearly from band due to Pyrex glass in the region 520–470 cm⁻¹ as this was a high sensitivity scan.

unit cell, no correlation splitting of the vibrational modes of the molecule into $a_g + b_g$, Raman active crystal components was observed.

The main difference between the unsymmetrical bridge system found in Me₃SiOReO₃ and the symmetrical bridge systems found in (Me₃Si)₂O and (O₃Re)₂O 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.

Me
Me — Si —O— Re — O
Me   1.69 164±5° 1.67   O
                                O
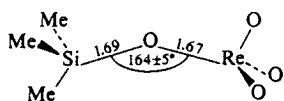
Let us consider Me₃SiOReO₃ to be a rigid molecule without free rotation of the terminal Me₃Si— and O₃Re— groups about the respective metal–oxygen bonds. Then we can expect 13a' + 8a'' vibrational modes (below approx-

imately 1100 cm⁻¹) associated with the basic C₃SiOReO₃ skeleton. In addition there will be methyl rocking modes associated with the Me₃Si 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 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 Me₃SiOReO₃ (below approximately 1100 cm⁻¹) as shown in Table 1.

The lowering of the symmetry of the terminal groups from C_{3v} to C_s 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 (Me₃Si)₂O and (O₃Re)₂O, we assign SiO and ReO bridge stretching modes in Me₃SiOReO₃ to polarized bands observed at 915

and 475 cm^{-1} (in the liquid) and 931 and 446 cm^{-1} (in the solid), respectively: *cf.* $(Me_3Si)_2O$ v_{sym} 518 cm^{-1} and v_{anti} 1053 cm^{-1}; $(O_3Re)_2O$ v_{sym} 456 cm^{-1} and v_{anti} ~ 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 $Me_3SiOReO_3$ 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_3Si— and O_3Re— torsional modes and the totally symmetrical SiORe 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 approximately 10° (with respect to the solid) in the SiORe angle. The changes may be attributable to crystal packing requirements in the solid and intermolecular interactions in the liquid and solution phases. However, the internal consistency of the Raman spectra for $Me_3SiOReO_3$ between phases shows unambiguously that the molecular structure is retained in all phases with only slight variations in the SiORe 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.

Trimethylsilylperhennate, $Me_3SiOReO_3$, was prepared by refluxing Re_2O_7 in excess hexamethyldisiloxane under anhydrous conditions (7). The crystallized $Me_3SiOReO_3$ was further purified by vacuum sublimation (obs. m.p. 80.0 °C; lit. 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 $Me_3SiOReO_3$ 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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