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Vapor Phase Vibrational Spectra for Re_2O_7 and the Infrared Spectrum of Gaseous $HReO_4$. Molecular Shapes of Mn_2O_7, Tc_2O_7, and Re_2O_7

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The Raman and infrared spectra of gas phase Re_2O_7 are reported. The experimental vibrational spectra of molecular Tc_2O_7 and Re_2O_7 are compared with calculated spectra. The results of these studies agree with a nonlinear M−O−M bridge for Tc_2O_7 and Re_2O_7. For infrared intensity calculations, the point charge approximation is used, while for the Raman calculations a combination of bond and atom polarizabilities is adopted. Pure Re_2O_7 was prepared from rhenium wire, but attempts to prepare it from rhenium powder and oxygen always led to infrared spectra showing serious contamination from a species containing an −OH linkage. Detailed experiments identified this molecule as $HReO_4$, a unique transition metal analogue of the perhalic acids, and a partial infrared spectrum of this molecule is reported.

Mn_2O_7[1] and Tc_2O_7[2] are two of four transition metal oxides known to have a molecular structure in the solid state. By contrast, crystalline Re_2O_7[3] is polymeric, containing both six- and four-coordinated rhenium. However, Re_2O_7 is low melting and quite volatile.[4] In 1969 it was shown[5] by Raman spectroscopy that the melt, like the vapor,[6] was monomeric. In the case of Mn_2O_7, the crystal structure[1] shows the presence of discrete molecules with an Mn−O−Mn bond angle of 120.7° and exact C_{2v} symmetry (the structure can be obtained from "linear" eclipsed Mn_2O_7 by bending at the M−O−M angle such that C_{2v} symmetry is retained). For crystalline Tc_2O_7, the Tc−O−Tc bond angle is 180° and the molecule has C_i symmetry.[2] If all the Tc−O terminal bonds were equivalent, the C_i molecule of the crystal would attain D_{3d} point symmetry with the bonds in the staggered configuration. A recent electron diffraction study of molecular Re_2O_7 in the vapor phase at 230 °C gave the Re−O−Re bond angle as 143.6° with the oxygen arranged to minimize repulsions.

Considering only the diffraction technique, it appears that there is a change from bent to linear to bent on passing from Mn through Tc to Re, but there are several interesting points to note. First, the structure of Mn_2O_7 is based on a close packing of oxygens so that this may define the M−O−M angle and the "eclipsed" configuration. In this connection, it is noted that there is an appreciable change in density between the crystal and the melt (2.79 g cm^{-3} by X-ray crystallography; 2.396 g cm^{-3} for the liquid[8] at 20 °C relative to water at 4 °C). Further, the bond angle for Mn_2O_7 as a thin film, or isolated in argon or nitrogen matrices, was estimated from infrared spectra[9] to be 150−160°. These results suggest that Mn_2O_7 as an isolated molecule may have a Mn−O−Mn bond angle substantially greater than that found in the crystalline solid. Second, for Tc_2O_7, the change to a linear M−O−M linkage and a staggered configuration may again be due to packing in the crystal. Thus Selig and Fried[10] in 1971 noted the similarity between the Raman spectra of Re_2O_7 and Tc_2O_7 as vapors, suggesting that in the isolated molecules both had the same (nonlinear) structure.

It is thus probable that Mn_2O_7, Tc_2O_7, and Re_2O_7 are all bent with an easily deformed M−O−M angle and, apart from steric factors associated with the terminal oxygens, free rotation about the M−O bridge bonds. In this connection, it is interesting that an earlier electron diffraction investigation[11] of Re_2O_7 at the higher temperature of 500 °C showed a nearly linear structure (165 ± 15°). Further, while the $Mo_2O_7^{2-}$ ion in $MgMo_2O_7$ shows a bond angle of 160.7° for the Mo−O−Mo bridge,[12] in the double salt $K_2Mo_2O_7{\cdot}KBr$ this linkage is linear.[13]

Mn_2O_7 is easily photolyzed and can be explosively unstable. Tc_2O_7 contains radioactive technetium. Thus electron diffraction or microwave studies on these molecules are unattractive, particularly as they contain nine atoms and may not have an electric dipole moment. Conventionally, vibrational spectroscopy has relied on rather qualitative arguments to deduce symmetry of molecules in the gas phase, unless high-resolution spectra can be obtained which are capable of rotational analysis. The rotational analysis of M_2O_7 is a formidable task and would require the use of cooled-beam or cell techniques to obtain analyzable spectra. We have used a sophisticated classical vibrational analysis program to model the normal modes of Tc_2O_7 and Re_2O_7, with qualitative estimates of infrared and Raman intensity (activity measures). Infrared intensities were modeled using the "point charge" model, and with only two types of atom in the molecule, it did not matter what charges

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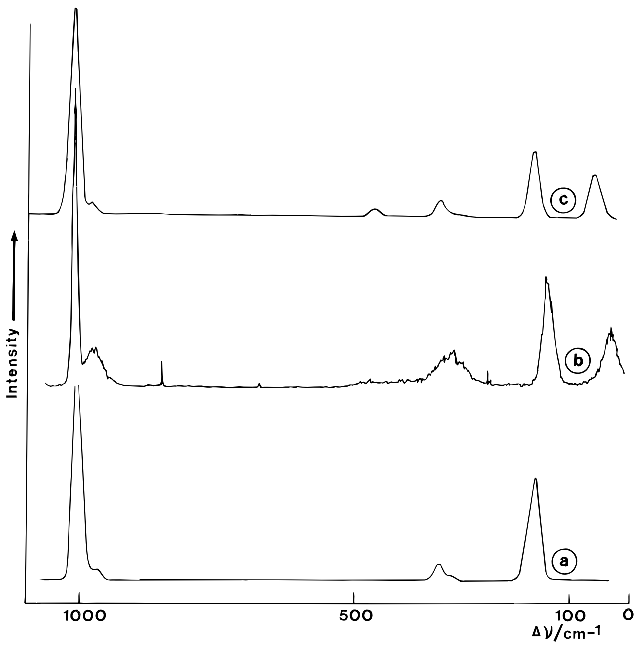

Figure 1. Observed (b) and calculated {bent (c) or linear (a)} Raman spectra of vapor phase Re_2O_7.

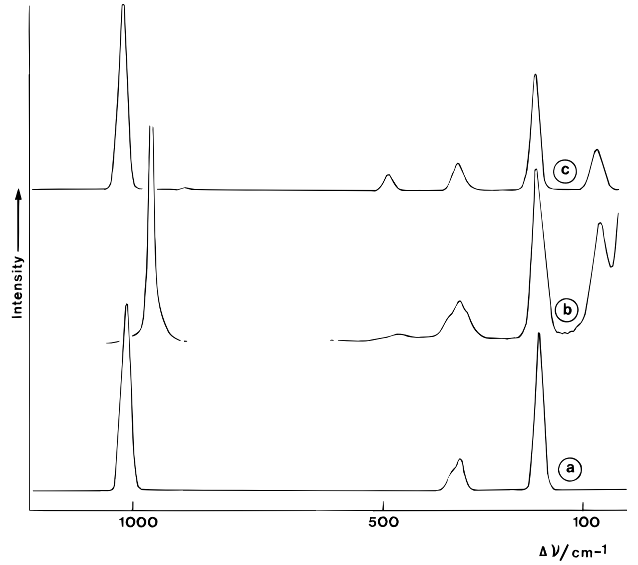

Figure 2. Observed[10] (b) and calculated {bent (c) or linear (a)} Raman spectra of vapor phase Tc_2O_7.

were used. The approach to Raman intensity used a combination of atom and bond polarizabilities, with one adjustable parameter defining the ratio of the two; this had the effect of matching the observed and calculated ratios for mainly stretching to mainly bending modes.[14] In Figures 1 and 2 the calculated spectra were drawn using a constant Gaussian half-width (hwhm) of 10 cm^{-1} for all bands. Force constants used in this analysis are listed in Table 1.

Experimental Section

Re_2O_7 was synthesized by heating a known weight of rhenium wire[15] in an oxygen atmosphere ($^{16}O_2$ or $^{18}O_2$) using an all-glass vacuum apparatus, apart from the sealed-in silicon windows required for infrared spectroscopy. The apparatus was then evacuated, and after the addition of a few Torr of oxygen, the cell and reaction tube were sealed off from the vacuum line. Re_2O_7 was then sublimed into the infrared cell and the reaction tube removed at a seal-off point. Infrared spectra were recorded using an FT1600 (Perkin-Elmer) or a 983G dispersive instrument (Perkin-Elmer) covering the total range 4000−200 cm^{-1}. The spectra were taken at successively increasing cell temperatures up to a maximum of ca. 250 °C. At the end of the experiment and after allowing the cell to cool, very pale yellow crystals could be seen condensed onto the walls, suggesting there had been negligible decomposition.

Table 1. Force Constants Used in the Frequency Calculations for M_2O_7 (M = Re, Tc)[a]

f_t	8.428 md $Å^{-1}$	δ_{tb}	0.797 md Å rad^{-2}	f_t-f_t	0.450 md $Å^{-1}$
f_b	4.142 md $Å^{-1}$	δ_{bb}	0.316 md Å rad^{-2}	f_t-f_b	0.733 md $Å^{-1}$
δ_{tt}	1.188 md Å rad^{-2}				

[a] Key: *f*, stretching; δ, deformational; t, terminal; b, bridge. Full C_{3v} symmetry was assumed for the O−ReO_3 residues. Force constants for $Mo_2O_7^{2-}$ in the crystal $K_2Mo_2O_7$.KBr[13] (for which a full assignment is possible) were upwardly adjusted and refined for best fit.

Samples for Raman spectroscopy were made up similarly using an all-glass apparatus. Spectra were obtained at a temperature of ca. 300 °C. An argon laser operating at 514.5 or 488 nm with an incident power of some 200 mW was used to excite the Raman spectra which were recorded using a Coderg T800 Raman spectrometer.

In some experiments (in both the infrared and the Raman) water or D_2O was deliberately added to the sample cell.

Results

Dirhenium Heptaoxide. The infrared spectra in the literature are not in good agreement. That of Beattie and Ozin[5] is open to question, as (possibly reactive) silver chloride windows were used. In the present experiments, a borosilicate cell with sealed-in silicon windows was used. The only disadvantage of this technique is the fact that silicon has an absorption in the 620 cm^{-1} region causing some obscuring of spectra. The results of the new infrared and Raman experiments are summarized in Table 2, which also contains data on the effects of adding water or D_2O. The new infrared data on Re_2O_7 are in modest agreement with the latest work in the literature.[16]

Figure 1 shows the observed and calculated Raman spectra of Re_2O_7 vapor. Calculated values are given for bond angles of 180 and 143.6° (as found in the latest[7] electron diffraction work). It is clear from this figure that the closest agreement is found for the nonlinear M−O−M bridge. In the infrared also, the complexity of the observed spectrum can only be matched by assuming a nonlinear geometry. The only other points to note here are (a) the assignment of an Re−O−Re symmetric stretch is not possible because of coupling with the in-phase ReO_3 symmetric deformation and (b) the torsional modes were not calculated and are assumed to have negligible intensity in both the infrared and the Raman.

Ditechnetium Heptaoxide. In this case, we have been unable to find an infrared spectrum of the vapor in the literature. Using the force field developed for Re_2O_7 and making only the mass change from Re to Tc give the calculated Raman spectrum for Tc_2O_7 shown in Figure 2. The agreement of the experimental spectrum[10] with that for the nonlinear configuration is excellent.

Gaseous $HReO_4$. In our initial studies, when we were attempting to synthesize Re_2O_7 from rhenium powder by

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(14) Details of this program are available from T.R.G.

(15) Use of rhenium powder led to the occurrence of O−H stretching modes in the infrared spectrum, presumably due to the presence of hydrogen in the rhenium sample even after outgassing at 500 °C in a pumping vacuum.

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Table 2. Observed and Calculated Infrared and Raman Frequencies (cm^{-1}) and Qualitative Intensities of Gaseous Re_2O_7, $HReO_4$, and $DReO_4$

Re_2O_7							
			I(calc)		$HReO_4$	$DReO_4$	
IR	Raman	calc	IR	Raman	IR	IR	descripn (coupling[a])
					3651 m	2695 m	ν(OH)
1050 vw, br[b]		1050	vw				$\nu_s(ReO_3)$ (−)
	1008 s, pol	1006		s, pol	*c*	*c*	$\nu_s(ReO_3)$ (+)
975 s	971 mw, dp	972 × 4	s	w	972 s	974 s	$\nu_{as}(ReO_3)$ (all)
868 s, br		863	s				ν_{as}(Re−O−Re)
					847 m, br		δ(ReOH)
					682 m, br	706 ms	ν(Re−OH)
						550? w, br	δ(ReOD)
480 m		463	ms				ν_s(Re−O−Re) + $\rho_z{}^d(ReO_3)$ (+)
345 m, sh	342 mw, br	351, 345, 343, 342	m, sh	mw			$\delta_{as}(ReO_3)$ (all)
305 ms		319	s				$\rho_z{}^d(ReO_3)$ (−)
		306	w				$\delta_s(ReO_3)$ (+)
		300	s				$\delta_s(ReO_3)$ (−)
	174 ms, dp	181 × 2		w			$\rho_x{}^d(ReO_3)$ (all)
		172		m, pol			ν_s(Re−O−Re) − $\rho_z{}^d(ReO_3)$ (+)
	61 m, pol	68		w, pol			δ(ReORe)

[a] Coupling refers to the in (+) or out (−) of phase coupling between the two ReO_3 units of Re_2O_7; (all) is used where the components overlap. [b] The surprising weakness of this band is verified by the calculations. ^{18}O substitution improves its visibility. [c] Within 972 cm^{-1} envelope at ca. 1000 cm^{-1}. [d] ρ_z refers to the rock of the ReO_3 unit in the Re−O−Re plane; ρ_x, out of the plane.

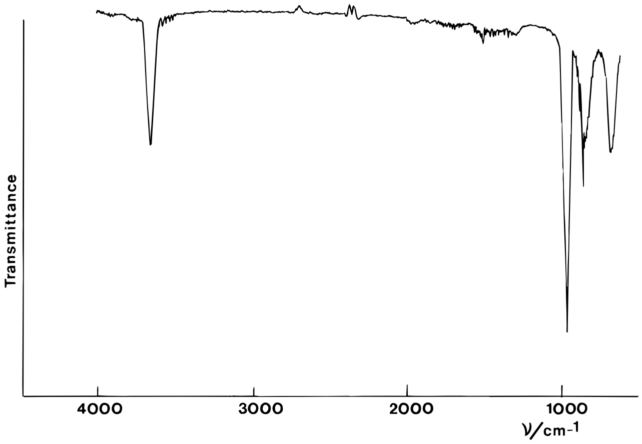

Figure 3. Infrared spectrum of $HReO_4$ vapor obtained by subtracting out the spectrum for Re_2O_7 from that of the equilibrium mixture above stoichiometric $HReO_4$ at ca. 250 °C.

combustion in oxygen, we obtained clear evidence of bands at 3651 and 682 cm^{-1} in addition to those expected in the infrared spectrum for Re_2O_7. The band at 3651 cm^{-1} is close to that found for species such as H_2SO_4[17] (3610 cm^{-1}), $HClO_4$[18] (3560 cm^{-1}), and HOBr[19] (3590 cm^{-1}). Further, it is known[4,20] that Re_2O_7 shows increased volatility in the presence of water, which has been shown to be due to the vapor phase molecule $HReO_4$. This molecule has also been reported in mass spectrometric studies.[21] We therefore examined the effects of adding H_2O or D_2O to our samples of Re_2O_7. In all cases, the infrared spectra obtained were a combination of the spectrum of Re_2O_7 with that of another species readily identified as $HReO_4$ or $DReO_4$. Partial isotopic substitution led to the observation of only two high-frequency bands, confirming the presence of one atom of hydrogen in this molecule. Figure 3 shows a spectrum of $HReO_4$ obtained by "subtracting out" the Re_2O_7 from the combined spectrum. This procedure leaves some doubt concerning the position of the symmetric ReO_3 stretching mode in $HReO_4$, which is clearly of low infrared intensity and is almost certainly within the pronounced PQR structured envelope for the antisymmetric mode. The symmetric mode is estimated to occur at ca. 1000 cm^{-1}. In the corresponding Raman spectra, it is not possible to recognize this or any other bands due to $HReO_4$, perhaps because the coincidence with Re_2O_7 bands is too close or because there is less $HReO_4$ present at the higher temperature required. The ReO_3 stretching modes of $XReO_3$ are rather insensitive to the substituent X. Thus for CH_3ReO_3[22] $\nu_s(ReO_3)$ is at 1003 cm^{-1} and $\nu_{as}(ReO_3)$ is at 975 cm^{-1}, while for ReO_3F[23] the corresponding frequencies are 1013 and 978 cm^{-1}. Thus the band at 972 cm^{-1} in Figure 3 can be assigned to ν_{as} with confidence. For ReO_3F the rhenium−fluorine stretching mode is assigned[23] at 701 cm^{-1} so that the 682 cm^{-1} band for $HReO_4$ is similarly assigned to ν(Re−OH), noting that there will be some mixing with M−O−H deformations which also occur in this region, for example CuOH[24] at 734 cm^{-1}. However, the more covalent HOBr[19] has its bending mode at 1164 cm^{-1}. The deuteration studies show that for $HReO_4$ the band assigned to ν(Re−OH) *increases* in frequency. This clearly indicates that the lower deformation for $DReO_4$ is able to couple strongly with the Re−(OD) stretch and enables the assignments for $HReO_4$ to be completed satisfactorily with δ(ReOH) at 847 cm^{-1} (see Table 2).

Conclusions

The results of the calculations taken in conjunction with the observed spectra accord well with a nonlinear M−O−M bridge for the heptaoxides in the gas phase. In the case of Tc_2O_7, the close correspondence between observed and calculated spectra is particularly noteworthy.

The demonstration of the presence of a molecule containing one atom of hydrogen (or deuterium) and the assignment of the major bands satisfactorily as $HReO_4$ confirm the presence of this molecule in Re_2O_7 gas phase samples containing H_2O or D_2O. Re_2O_7 is very hygroscopic, and we were not able to

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eliminate water from this system by successively subliming the partially hydrated Re_2O_7 *in vacuo*.

At the lower temperatures which we were able to use in the infrared work, there was probably up to 50% of the rhenium present as $HReO_4$. In this case, it was possible to "subtract out" the Re_2O_7 spectrum. This was not possible in the Raman experiments, which used higher temperatures and pressures. The intense Raman bands of $HReO_4$ and Re_2O_7 are expected to occur in similar regions of the spectrum. Further, the higher temperatures may have caused dissociation of $HReO_4$.

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