Infrared and Ultraviolet–Visible Spectroscopic Studies on Manganese Heptoxide (Mn_2O_7)

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Infrared and u.v.–visible spectra are reported for Mn_2O_7 both in the solid phase and as a monomeric species isolated in low-temperature matrices. The i.r. spectra are consistent with the expected bridged structure, and indicate a relatively wide $O_3Mn{-}O{-}MnO_3$ angle. Characteristic i.r. absorptions are found at *ca.* 955 cm^{-1} [$\nu_{asym}(Mn{=}O)$], *ca.* 890 cm^{-1} [$\nu_{sym}(Mn{=}O)$], and *ca.* 775 cm^{-1} [$\nu_{asym}(Mn{-}O)$]. The electronic spectrum of Mn_2O_7 shows a number of charge-transfer bands with partially resolved vibrational progressions, and their features are compared with those of related manganese(VII) oxo-species.

Dimanganese heptoxide has been known for over 100 years as the highly explosive material formed when potassium permanganate reacts with concentrated sulphuric acid.[1] Perhaps as a result of this reputation, there appear to be no structural data on this compound in any phase, and it has received very little attention from spectroscopists. Nevertheless a number of physico-chemical properties have been established [2] (*e.g.* vapour pressure), despite the fact that its sensitivity to shock is comparable to that of mercury fulminate.

During the course of our matrix-isolation studies on manganese halide oxides we noted that MnO_3F reacted with Pyrex to produce a material with properties similar to those reported for Mn_2O_7 (*e.g.* colour, volatility) and that matrix i.r. spectra could be obtained for this impurity. We therefore carried out an independent i.r. and u.v.–visible study on Mn_2O_7 prepared by traditional methods.

Experimental

The i.r. and u.v.–visible spectra of Mn_2O_7 were obtained by two slightly different methods. For our initial studies, small samples of the volatile oxide were prepared from the reaction between $KMnO_4$ and H_2SO_4 [3] using a grease-free vacuum line fitted with polytetrafluoroethylene stopcocks. In a typical synthesis, concentrated H_2SO_4 (10 cm^3) was placed in a reaction tube at room temperature, and pumped for 30 min to remove dissolved gases. This tube was then cooled to *ca.* −20 °C (CCl_4 slush) and powdered $KMnO_4$ (*ca.* 3 g) added in small portions. The solution became deep green, and the reaction tube was re-evacuated. The reaction mixture was then allowed to warm slowly to 0 °C, during which time Mn_2O_7 slowly distilled out of the tube and could be collected as a red-brown solid in break-seal ampoules cooled by liquid N_2. In subsequent spectroscopic studies, these samples were sublimed from a 0 °C bath on to the cold central window of our cryostat.[4]

Although no explosions were encountered using this method, there was always a possibility that handling the pure material might result in detonation, and the majority of spectra were therefore obtained using a different procedure. Here, the vapour distilling out of the H_2SO_4–$KMnO_4$ reaction mixture was condensed directly on to the cryostat window. Previous experiments had established that H_2SO_4 alone is involatile at *ca.* 0 °C, and this procedure gave results which were identical to neat Mn_2O_7 vaporisations.

The spectra of solid Mn_2O_7 were obtained by condensing the vapour directly on to the central window cooled to *ca.* 12 K, whilst deposits of the matrix-isolated molecules were obtained by co-condensation with an excess (*ca.* × 1 000) of argon or nitrogen. In both types of experiment, spectra were also recorded after annealing. For the matrix samples, this involved warming to *ca.* 30 K, but for the pure solid the temperature was allowed to increase to *ca.* 250 K before recooling to *ca.* 12 K.

Infrared and u.v.–visible spectra were recorded on Perkin-Elmer instruments PE 225 and PE 554 respectively, whilst the low temperatures necessary for this work were obtained using Air Products closed-cycle Displex systems as previously described.[4]

Results and Discussion

Infrared Spectroscopy.—The i.r. spectrum obtained when Mn_2O_7 was sublimed directly on to the cooled (12 K) central window *in the absence* of matrix gas consisted of four prominent, broad features at 955, 890, 785, and 765 cm^{-1}, and weaker absorptions at 560, 370, 345, and 325 cm^{-1}. Upon warming to *ca.* 250 K, the two bands at 785 and 765 cm^{-1} coalesced to a single broad feature at *ca.* 750 cm^{-1}, whilst the other spectral features sharpened and shifted slightly in frequency. These changes were not reversed by recooling to *ca.* 12 K, and Figure 1(*a*) shows a typical spectrum.

The frequencies and relative intensities of the four high-frequency bands (Table 1) are very similar to those previously found by Krebs and Hasse [5] for solid ' permanganic acid.' In their work, bands at 565, 770, 882, and 943 cm^{-1} were assigned to a discrete Mn_2O_7 unit in a compound formulated as $Mn_2O_7{\cdot}2H_2O$. The two lowest-frequency stretching modes were assigned as ν_{sym} and ν_{asym} respectively for the (non-linear) Mn–O–Mn bridge, whilst those at 882 and 943 cm^{-1} were assigned as ν_{sym} and ν_{asym} for a terminal MnO_3 group. These authors also mention that the i.r. spectrum of the solid anhydrous heptoxide is similar, but give no details. Our stretching frequencies for the annealed solid are in good agreement with these results, and additional support for the assignment of the terminal Mn–O stretches comes from the spectrum of MnO_3F, where ν_{sym} and ν_{asym} lie at 905.2 and 952.5 cm^{-1} respectively.[6]

The four low-frequency bands observed in our solid spectrum lie in the region expected for MnO_3 bending modes. In MnO_3F, such modes are assigned at 337.7 and 373.7 cm^{-1}.[6]

Figure 1(*b*) shows a nitrogen matrix i.r. spectrum of Mn_2O_7. The principal regions of absorption are similar to those found in the solid, although even under low resolution it is evident that some of the matrix bands show multiplet structure. In particular, the most intense band centred at *ca.*

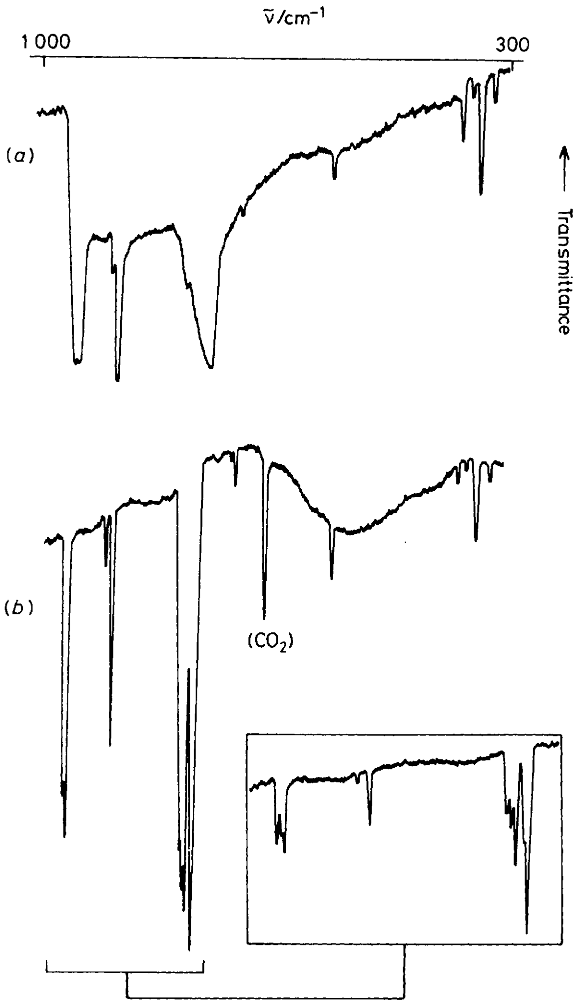


Figure 1. Infrared spectra of Mn_2O_7 (300—1 000 cm^{-1}): (*a*) annealed solid, (*b*) isolated in a nitrogen matrix

775 cm^{-1} was found on closer examination (see inset) to consist of five components, whilst the bands at *ca.* 890 and 955 cm^{-1} show doublet and triplet structure respectively. In argon matrices the same general features were observed, and structure was again noted on some of the bands. However, the components of these multiplets differed both in frequency and relative intensity from their counterparts in nitrogen, and annealing experiments (to *ca.* 35 K) failed to simplify the picture.

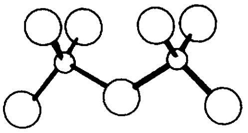
Despite the obvious complexity of some of the matrix bands, the overall similarity between the absorptions in the solid and the matrix suggests that the same molecular species is present, and the spectra are broadly consistent with a structure for Mn_2O_7 in which terminal MnO_3 groups are linked by a (C_{2v}) oxygen atom bridge. There are no published structural data on Mn_2O_7, but an estimate of the bridge angle can in principle be made using either the solid or the matrix i.r. spectrum.

If one assumes that the two stretching modes of the Mn–O–Mn bridge are harmonic, and are effectively uncoupled from the remaining vibrational modes, and also that the bond-dipole model is a useful guide to i.r. intensities, it may then be shown[7] that equation (1) is applicable where I is the

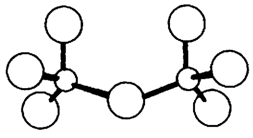
$$I_{asym}/I_{sym} = \tan^2\theta(M_O + 2M_{Mn}\sin^2\theta)/(M_O + 2M_{Mn}\cos^2\theta) \quad (1)$$

Table 1. Infrared bands (cm^{-1}) and assignments for Mn_2O_7

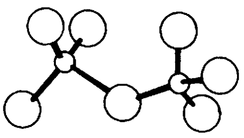
Annealed solid	Nitrogen matrix	Argon matrix	Assignment
	957.8	960.0	$\nu_{asym}(MnO_3)$
945	954.9	956.6	
	952.8	952.1	
		948.7	
	896.0	891.0	$\nu_{sym}(MnO_3)$
880	887.0	885.2	
		882.4	
	782.6	784.8	$\nu_{asym}(MnOMn)$
	779.5	782.8	
750	776.5	777.7	
	770.1	769.0	
	767.7	762.5	
(697)	(706)	—	(unassigned)
560	562.0	555.0	$\nu_{sym}(MnOMn)$
370	373	372	$\delta(MnO_3)$
350	360	358	
340	347	347	
320	325	325	



(I)



(II)



(III)

integrated i.r. intensity of the stretching mode, M_{Mn} and M_O are respective atomic masses, and 2θ is the bridge angle. This approach has been used elsewhere[8] to estimate bond angles in C_{2v} units, and has achieved moderate accuracy. From our nitrogen matrix spectra, it is evident that the components comprising ν_{asym} at *ca.* 775 cm^{-1} are together very much more intense than ν_{sym} at *ca.* 560 cm^{-1}, and their intensity ratio is estimated to lie between *ca.* 70 : 1 and *ca.* 200 : 1. Using these limiting values, equation (1) predicts a bridge angle lying between 150 and 160°.

For a bridged structure such as (I) the terminal stretching modes transform as $\Gamma_{Mn-O} = 2A_1 + A_2 + 2B_1 + B_2$, of which only the A_2 component is inactive. Five distinct features should therefore appear in the terminal stretching region, and it may further be shown that two of these ($A_1 + B_1$) are associated with 'ν_{sym}' (at *ca.* 890 cm^{-1}) and the remaining three with 'ν_{asym}' (at *ca.* 955 cm^{-1}). Our nitrogen matrix spectrum [Figure 1(*b*)] shows the appropriate number of components for these modes, but unfortunately the argon matrix spectrum does not. Furthermore, this extended analysis cannot provide any explanation for the even more complex structure associated with the bridge mode at *ca.* 775 cm^{-1}. The traditional rationalisation of this phenomenon is to invoke multiple site trapping,[9] but for a molecule such as Mn_2O_7 one can visualise that the presence of other conformers such as (II) and (III) might also complicate the spectrum.

In the crystalline forms of $SrCr_2O_7$ and $PbCr_2O_7$,[10] which contain discrete C_{2v} ions ($Cr_2O_7^{2-}$), conformers of types (I)

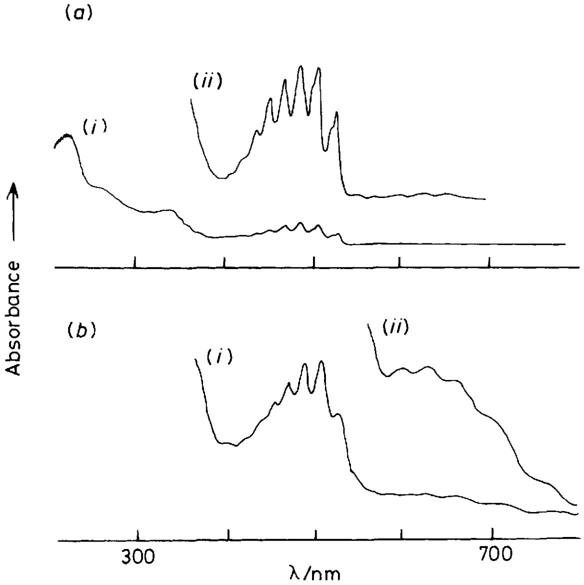


Figure 2. Ultraviolet–visible spectra of Mn$_2$O$_7$ (200—800 nm): (*a*) isolated in a nitrogen matrix, (*b*) solid. Spectra (*ii*) were recorded at a later stage in the deposition than spectra (*i*)

and (II) are both found in the lattice, and it is interesting to note that in our spectra of *solid* Mn$_2$O$_7$ this same mode is significantly broader than the other fundamentals.

On the basis of the i.r. studies the structure comprises two MnO$_3$ groups linked by an oxygen bridge with an angle Mn–O–Mn *ca.* 150—160°. In this respect, the shape of Mn$_2$O$_7$ is perhaps closer to that of Re$_2$O$_7$[11] and Tc$_2$O$_7$,[12] where the bridge angles are 165(±15) and 180° respectively, than to the isoelectronic ion Cr$_2$O$_7^{2-}$ in which[13] the bridge angle is *ca.* 126°. The occurrence of linear M–O–M bridges in 4*d* and 5*d* transition-metal compounds (*e.g.* Cl$_5$RuORuCl$_5^{4-}$ and Cl$_5$OsOOsCl$_5^{4-}$) has been rationalised in terms of d_π–p_π bonding involving the bridge atom.[14] We also note that for the isoelectronic ions Fe$_2$O$_7^{8-}$ and Co$_2$O$_7^{6-}$, the M–O–M angle widens from *ca.* 120 to *ca.* 180°,[15] and this may similarly be due to increased π bonding as a result of increased effective charge on the metal. The same trend would account for the rather wide angle indicated here for Mn$_2$O$_7$.

U.v.-Visible Spectroscopy.—Electronic spectra were recorded for solid Mn$_2$O$_7$ and for the monomer isolated in a nitrogen matrix. Figure 2(*a*) shows a typical survey spectrum obtained from the matrix-isolated sample, whilst Figure 2(*b*) shows part of the solid spectrum. Over the wavelength range 200—800 nm, five main features could be identified. These had maxima at *ca.* 220 (*ca.* 45 400), *ca.* 253 (*ca.* 39 500), *ca.* 332 (*ca.* 30 100), *ca.* 490 (*ca.* 20 400), and at *ca.* 630 nm (*ca.* 15 900 cm^{-1}) and vibrational structure was observed on the three longest-wavelength bands. These two sets of results were very similar, and also closely resembled the electronic spectrum of Mn$_2$O$_7$ in CCl$_4$ solution reported by Briggs.[16] Table 2 summarises our nitrogen matrix data in detail.

Table 2. Ultraviolet–visible absorptions * for matrix-isolated Mn$_2$O$_7$

Band I (*ca.* 630 nm)	Band II (*ca.* 490 nm)	Band III (*ca.* 332 nm)	Band IV (*ca.* 253 nm)	Band V (*ca.* 220 nm)
13 490	18 990	27 100		
13 750	19 190	27 850		
14 020	19 780	28 650	structureless feature centred at 39 500 cm^{-1}	structureless feature centred at *ca.* 45 400 cm^{-1}
14 300	19 960	29 410		
14 570	20 580			
14 860	20 750			
15 170	21 370			
15 380	21 550			
15 920	22 170			
16 720	22 940			
17 540	23 720			
17 980				

* Absorption positions converted into cm^{-1} from spectral data in nm. Estimated uncertainty ±50 cm^{-1}.

Our interpretation of these absorptions is based on the extensive information available on the electronic spectrum of the permanganate ion,[17] and also on studies of the related manganese(VII) oxo-species[18] MnO$_3$F and MnO$_3$Cl. For the MnO$_4^-$ ion five principal regions of absorption have been found,[16] at *ca.* 43 500, *ca.* 33 000, *ca.* 27 000, *ca.* 20 000, and *ca.* 15 000 cm^{-1}. For MnO$_3$F,[18] corresponding bands are observed at *ca.* 48 000, *ca.* 39 000, *ca.* 32 000, *ca.* 22 000, and *ca.* 15 000 cm^{-1}. It is evident that there is considerable similarity between our Mn$_2$O$_7$ features and both these species, and in addition the most prominent vibrational progression found in both MnO$_4^-$ and MnO$_3$F is in ν_{sym}(Mn=O) at 750—800 cm^{-1} whilst in Mn$_2$O$_7$ we observe progressions in *ca.* 780 cm^{-1} on at least two of the bands (Table 2).

However, although the main features of our spectrum can be interpreted as oxygen to manganese charge transfer by comparison with the MnO$_4^-$ and MnO$_3$F bands, the assignment of the vibrational structure is more difficult. The matrix i.r. data clearly indicate that we should regard the manganese environment as C_{3v}, and one might therefore anticipate a more complex spectrum than for MnO$_4^-$. For this (T_d) ion the five principal bands are assigned as either $^1T_1 \leftarrow {}^1A_1$ or $^1T_2 \leftarrow {}^1A_1$ transitions,[17] and if the symmetry is lowered to C_{3v} the T states will split, $^1T_1 \rightarrow {}^1A_2 + {}^1E$ and $^1T_2 \rightarrow {}^1A_1 + {}^1E$. This type of splitting has been observed[19] for MnO$_4^-$ in crystalline LiClO$_4$·3H$_2$O/LiMnO$_4$·3H$_2$O, where it is known to occupy a substitutional site of C_{3v} symmetry, and in particular, the band at *ca.* 20 000 cm^{-1} shows a site splitting of *ca.* 500 cm^{-1} in the (T_2) excited state. Transitions to both these $^1A_1$ and ^1E components are each accompanied by two vibrational progressions, and it was only by carrying out single-crystal polarisation studies that this band could be satisfactorily analysed.[19] The *unpolarised* spectrum, although showing some structure, does not obviously reveal either the site splitting or the frequencies of the vibrational progressions.

There is no reason to suppose that the site splitting in Mn$_2$O$_7$ should be significantly less than 500 cm^{-1} for the same transition, as the geometric distortion will almost certainly be greater. Although our matrix spectra *can* be interpreted (Table 2) in terms of progressions of *ca.* 780 and *ca.* 200 cm^{-1} for this band *without* invoking a site splitting, we believe that this is probably an oversimplification. In MnO$_3$F, where a C_{3v} site symmetry is again evident, the detailed analysis of this transition also involves excited-state splittings comparable in magnitude to the vibrational progressions.[18] Although the main electronic transitions in Mn$_2$O$_7$ can be assigned by comparison with MnO$_4^-$ and MnO$_3$F, we believe that a correct analysis of the vibrational structure will only be possible with the availability of polarisation data on oriented Mn$_2$O$_7$ molecules.

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