VIBRATIONAL SPECTRA OF HgMoO₄ AND HgWO₄

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Abstract—The i.r. and Raman spectra of mercury molybdate and tungstate ($HgMoO_4$ and $HgWO_4$) are reported. They can be interpreted assuming an effectively tetrahedral Mo(W) coordination, although the crystallographic coordination is sixfold (with two long distances). The same model seems to work for the tungstates with wolframite structures, e.g. $CdWO_4$.

INTRODUCTION

THE CRYSTAL structure of the isomorphous compounds $HgMoO_4$ and $HgWO_4$ has been reported recently[1]. In the course of our studies on the vibrational and electronic spectra of mixed metal oxides containing highly-charged transition-metal ions (like Nb^{5+}, W^{6+}) it seemed interesting to study these compounds in more detail for two reasons. In the first place, the octahedral coordination of Mo(W) in HgMo(W)O₄ is very irregular with two long Mo(W)–O distances. In the second place the mercury ions with a linear two-coordination by oxygen might influence the properties of the molybdate or tungstate group in an unexpected way. In this paper the vibrational spectra of $HgMoO_4$ and $HgWO_4$ are reported. Their luminescent properties will be discussed elsewhere using the present results.

EXPERIMENTAL

Samples were prepared by firing an intimate mixture of HgO and MoO_3 or WO_3 at 600°C using a 50 per cent excess of HgO. The reaction products were near-white. They were checked by X-ray analysis using CuKα radiation. The vibrational spectra were measured at room temperature. Raman spectra were obtained using a Spectra Physics 700 Raman spectrometer with an argon ion laser (courtesy Dr. J. H. van der Maas of this University). I.R. spectra were measured in KBr and CsI pellets and in paraffin using a Hitachi EPI-G3 grating spectrometer (down to 400 cm⁻¹) and a Grubb Parsons DM4 spectrometer with a CsI prism (down to 200 cm⁻¹). Samples of $MgWO_4$, $ZnWO_4$ and $CdWO_4$ were prepared by usual ceramic techniques with firing temperatures between 1100 and 1200°C.

RESULTS

In Table 1 the vibrational spectra of $HgMoO_4$ and $HgWO_4$ are tabulated. In Table 3 we have given the same data for $CdWO_4$. Results for $MgWO_4$ and $ZnWO_4$ are similar to those for $CdWO_4$. Our i.r. spectra of $MgWO_4$ and $ZnWO_4$ differ in some details

Table 1. Vibrational spectra of HgMoO₄ and HgWO₄

HgMoO₄		HgWO₄	
I.R.	Raman	I.R.	Raman
890 (s)	912 (s)	915 (m)	930 (s)
∼860 (m)	855 (m)	880 (s)	850 (m)
820 (w)	825 (m)	855 (m, sh)	815 (m)
665 (s)	694 (m)	660 (br)	705 (br)
∼620 (w, sh)	∼670 (w, sh)		
540 (m)	522 (m)	535 (m)	540 (m)
490 (m)	500 (w)	490 (m)	515 (w)
365 (w)	377 (m)	380 (w)	380 (m)
335 (m)	345 (w)	330 (m)	335 (w)
320 (s)	315 (m)	315 (s)	300 (m)
305 (s)	290 (w)	300 (s)	285 (m)
270 (m)	270 (m)	285 (w)	235 (w)
220 (w)	220 (s)	250 (m)	200 (s)

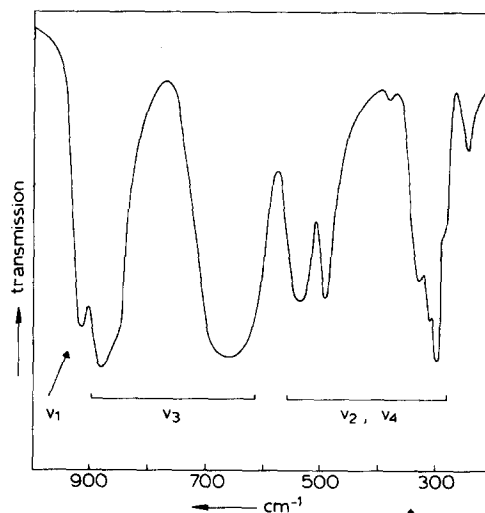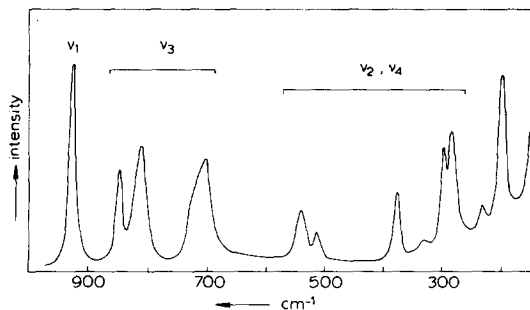All values in cm⁻¹. Abbreviations—s: strong, m: medium, w: weak, sh: shoulder, br: broad.

Fig. 1. Infrared spectrum of HgWO₄.

Fig. 2. Raman spectrum of HgWO$_4$.

Table 3. Vibrational spectra of CdWO$_4$

I.R.	Raman
875 (m)	900 (s)
805 (s)	775 (m)
~680 (m, sh)	710 (w)
600 (s)	690 (w)
510 (m)	550 (m)
445 (m)	520 (w)
405 (w)	390 (m)
350 (w)	355 (w)
320 (s, br)	310 (m)
270 (w)	272 (w)
230 (m)	235 (w)
	180 (w)

from those given by Clark and Doyle[2], our i.r. spectrum of CdWO$_4$ equals the spectrum given by Nyquist and Kagel[3]. Figures 1 and 2 present the vibrational spectra of HgWO$_4$.

DISCUSSION

As in previous papers we will try to assign the observed bands to the tungstate or molybdate internals. At first sight this seems to be a rather complicated problem, since the structure consists of edge-sharing tungstate (molybdate) octahedra, which would involve the absence of isolated molecular groups. The six Mo–O distances, however, are strongly different, viz. 1·722Å (2x), 1·944Å (2x) and 2·228 Å (2x)[1]. In view of this we tried to analyse the vibrational spectra by considering the crystal structure as a packing of Mo(W)O$_4$ groups and Hg^{2+} ions, i.e. we only consider the four nearest oxygen ions to belong to the molecular Mo(W)O$_4$ group. These groups do not have oxygen ions in common. The site symmetry of these groups is C_2 and there are two such groups per primitive unit cell. The space group symmetry is $C_{2h}(C2/c)$. For such a configuration the number of internals to be expected can be derived easily as indicated in Table 2.

First we note that the exclusion principle to be obeyed under C_{2h} symmetry is observed experimentally (Table 1). This, by the way, does not depend on our simplified structure consideration. The predictions of Table 2 are nicely realized by the experimental

Table 2. Correlation diagram for the vibrational modes of HgMoO$_4$ and HgWO$_4$ assuming tetrahedral Mo(W)O$_4$ groups with site symmetry C_2

T_d symmetry[a]	Site symmetry C_2[b]	Two groups under C_{2h} space group symmetry[c]
ν_1 A_1(R)	A	$A_g + A_u$
ν_2 E(R)	$2A$	$2A_g + 2A_u$
ν_3, ν_4 T_2(i.r., R)	$\begin{cases} A \\ 2B \end{cases}$	$\begin{matrix} A_g + A_u \\ 2B_g + 2B_u \end{matrix}$

[a] (R): Raman-active, (i.r.): i.r.-active. [b] No selection rules. [c] g modes Raman-active, u modes i.r.-active.

results of Table 1. The strong line in the Raman spectrum of HgWO$_4$ at 930 cm^{-1} is assigned to the A_g component of ν_1. Its A_u component is found in the i.r. spectrum at 915 cm^{-1}. Note that the value for ν_1 in the case of HgWO$_4$ is very close to values observed normally for the tetrahedral tungstate group. A comparison is given in Table 4, where values are given for Na$_2$WO$_4$ with WO$_4$ groups in the spinel structure [4] and CaWO$_4$ and BaWO$_4$ with WO$_4$ groups in the scheelite structure[5]. For the octahedral tungstate group the ν_1 mode is situated some hundred wave-numbers lower as is substantiated by the value for the WO$_6$ group in Ba$_2$CaWO$_6$ with ordered perovskite structure[6]. Note that the value of ν_1 is not largely influenced by the way in which the octahedra are condensed (corner-, edge- or face-sharing)[7]. The position of the ν_1 mode in HgWO$_4$ and HgMoO$_4$ is in our opinion strong evidence for the structural simplification proposed.

For the asymmetric stretching mode ν_3 we expect three components in the Raman as well as in the i.r. spectrum. This is observed experimentally, e.g. 850, 815 and 705 cm^{-1} in the i.r. and 880, 855 and 660 cm^{-1} in the Raman spectrum of HgWO$_4$. It should be realized, however, that the lower-frequency band of these three seems to contain another band (see Fig. 1). In the case of HgMoO$_4$ this is not the case, but there is a weak extra band present in this frequency range. This might be due either to a second harmonic or combination band or to the incompleteness of our structural description.

In the lower frequency range down to 250 cm^{-1} we find always five bands of at least medium intensity in both spectra for both compounds. These are assigned to the expected five components of the ν_2 and ν_4 modes. Bands at still lower energies are then due to external vibrations.

It is interesting to compare the averaged values for the ν_3 mode in the case of HgWO$_4$ with similar results for other tungstates (see Table 4). For molybdates the situation is analogous. We see that the values for HgWO$_4$ are only slightly lower than for Na$_2$WO$_4$, BaWO$_4$ and CaWO$_4$ with tungstate tetrahedra and

Table 4. Comparison of the averaged value of v_1 and v_3 for several tungstates

Compound	Crystal structure	v_1		v_3		References
		Raman	I.R.	Raman	I.R.	
$HgWO_4$	$HgWO_4$	930	915	785	$\sim$790	this work
$MgWO_4$	wolframite	925	910	740	730	this work
$ZnWO_4$	wolframite	915	880	730	700	this work
$CdWO_4$	wolframite	900	875	725	695	this work
Na_2WO_4	spinel	930	—	814	840	4
$BaWO_4$	scheelite	922	—	$\simeq$805	828	5
$CaWO_4$	scheelite	910	—	$\simeq$810	813	5
Ba_2CaWO_6	ordered perovskite	818	—	—	620	6

All values in cm^{-1}.

very much higher than for Ba_2CaWO_6 with tungstate octahedra. The latter comparison, however, is not fair, since the v_3 mode shifts to higher frequencies upon edge sharing[7, 8].

We, therefore, conclude that the vibrational spectra of $HgMo(W)O_4$ can be analyzed satisfactorily by assuming tetrahedral $Mo(W)O_4$ groups in the crystal structure, although the $Mo^{6+}(W^{6+})$ ion is formally coordinated by six oxygen anions. This is also substantiated by e.g. the Mo–O distances. The ionic radii for four- and six-coordinated Mo^{6+} and three-coordinated O^{2-} are 0·42, 0·60 and 1·36 Å, respectively [9]. The average of the six Mo–O distances in $HgMoO_4$ (1·965 Å) agrees with the distance calculated for six-coordinated Mo^{6+} (1·96 Å). The average of the four shorter Mo–O distances in $HgMoO_4$ (1·833 Å) is only a little longer than the distance calculated for four-coordinated Mo^{6+} (1·78 Å).

It is realized that this assignment may be less appropriate due to the occurrence of extensive mixing of internal vibrations, since many of them have the same symmetry species. Furthermore HgO shows strong i.r. absorption up to 600 cm^{-1}[3]. The structure of HgO contains Hg–O chains with linearly coordinated Hg (Hg–O distance 2·03 Å)[10]. In $HgMo(W)O_4$ the Hg^{2+} ion is also linearly coordinated with Hg–O distances equal to 2·03 Å, so that it is not excluded that the lower-frequency stretching vibrations contain considerable Hg–O character.

Finally we wish to report that similar considerations are also valid for the tungstate wolframites. Of these we studied $MgWO_4$, $ZnWO_4$ and $CdWO_4$. Usually the structure of these compounds is considered to contain zig-zag chains of edge-sharing octahedra. Two of the six W–O distances are, however, much longer than the other four. For the isomorphous $NiWO_4$ the following values have been found: 1·79 Å $(4x)$ and 2·19 Å $(2x)$[11]. Although the space group $(P2/c)$ is different from that of $HgMo(W)O_4$, the relevant symmetries are the same as in the case of the mercury compounds. As a consequence Table 2 predicts also the number of bands to be expected for the wolframites containing W^{6+} ions. A comparison between Table 2 and Table 3, where we have given our experimental results for $CdWO_4$, shows a satisfactory agreement. The strong Raman line at 900 cm^{-1} is the A_g com-

ponent of v_1, whereas the i.r. spectrum shows the A_u component at 875 cm^{-1}. The three components of the v_3 mode are found at 775, 710 and 690 cm^{-1} in the Raman and at 805, 680 and 600 cm^{-1} in the i.r. spectrum. The v_2 and v_4 modes are found in the lower-frequency range.

These results are also given in Table 4. The position of v_1 clearly points to an effectively tetrahedral co-ordination. The average values of v_3 are lower than the values observed for the tungstate tetrahedron and also for $HgWO_4$. This may be an indication that the simplification of effectively tetrahedral coordination of $W^{6+}(Mo^{6+})$ is more justified for the mercury compounds than for the tungstates with wolframite structure.

In a forthcoming paper we will show that the luminescence properties of these mercury compounds can also be described starting from a tetrahedral co-ordination and that the correlation between the luminescence of tungstates (molybdates) can be described in this way.

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