Vibrational studies of molybdates, tungstates and related compounds—I. New infrared data and assignments for the scheelite-type compounds $X^{II}MoO_4$ and $X^{II}WO_4$

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Abstract—New experimental data lead to revised assignments for the i.r. frequencies of molybdates and tungstates of the scheelite family. The investigation of isotopic species reveals non-negligible interactions between the internal bending modes and the external translational modes, and allows an easy discrimination between translational and rotational modes. As a consequence, the low-frequency band of these compounds must be assigned to a rotation, and not to a translation as previously assumed.

Introduction

THE VIBRATIONAL spectrum of molybdates and tungstates with the scheelite structure has been investigated and discussed by numerous authors [1–11]. Nevertheless, the agreement between these papers is not as good as it should be. Some of the observed frequencies exhibit discrepancies which are well outside the experimental error of the actual spectroscopic equipment; and the assignment of some of the low-frequency modes is still uncertain.

This paper will be restricted to a re-examination of the i.r. data. The much more complicated case of the Raman spectra will be discussed in a forthcoming paper.

Experimental

Infrared spectra of powders have been obtained in the 1000–50 cm^{-1} region with a Beckman IR 12 (1000–200 cm^{-1}) and a Cameca SI 36 (200–50 cm^{-1}) spectrometer. The pressed disc technique has been used throughout (KI or polythene discs according to the spectral region). The compounds have been synthesized by conventional solid state reaction techniques. Their purity was checked by X-ray diffractometry.

Results

The i.r. frequencies of pure compounds are collected in Table 1. Before discussing their assignment, it is useful to briefly comment on some discrepancies in the

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[4] R. K. Khanna and E. R. Lippincott, *Spectrochim. Acta* **24A**, 905 (1968).
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[10] J. P. Russell and R. Loudon, *Proc. Phys. Soc. (London)* **85**, 1029 (1965).
[11] M. Nicol and J. F. Durana, *J. Chem. Phys.* **54**, 1436 (1971).

Table 1. Infrared frequencies of pure compounds

CaMoO$_4$	CaWO$_4$	SrMoO$_4$	SrWO$_4$	BaMoO$_4$	BaWO$_4$	PbMoO$_4$	PbWO$_4$	CdMoO$_4$	Assignment
813	813	830	833	830	828	786	792	777	$\nu_3(A_u) + \nu_3(E_u)$
431	440	404	410	371	379	374	377	437	$\nu_2 A_u$
329	326	327	320	324	313	307	301	310	$\nu_4 E_u$
284	286	282	278	292	283	272	262	245	$\nu_4 A_u$
237	229	181	168	154	142	125	116	165	transl. E_u
200	177	166	~150?		129				transl. A_u
153	147	137	140	105	109	110	94	138	rot. E_u

published experimental data, CaWO$_4$ and CaMoO$_4$ (the most widely investigated compounds) being taken as an example (Tables 2 and 3). It will be noticed that significant discrepancies (as high as 20 cm^{-1} for the strong band in the 820 cm^{-1} region) appear in the i.r. spectrum. The reason for this may be sought in the i.r. reflexion data published by Barker [1]: for some of the i.r. active vibrations, the frequency difference between the longitudinal optic and the transversal optic modes is rather large, and the 'absorption' maximum of powders must be observed somewhere between these extreme frequencies, depending on the granulometry of the sample. For the high-frequency, very strong band near 820 cm^{-1}, the situation is

Table 2. Literature data on the i.r. frequencies of CaWO$_4$

Ref. [2]	[4]	[9]	This work	[1] L.O.	[1] T.O.
1120					
1020					
	870				
825	805	823	813	{893	778
	769			{905	793
440	429	428	440	448	435
		408			
325	320	330	326	363	309
285	292	290	286	327	237
	220	230	229	248	202
			177	182	180
	150	148	147	147·5	143

Table 3. Literature data on the i.r. frequencies of CaMoO$_4$

Ref. [2]	[4]	[9]	This work	[1] L.O.	[1] T.O.
1080					
	873				
830	802	819	813	{897	775
				{913	802
430	436	404	431	434	425
325	324	332	329	358	318
	272	282	284	319	245
	218	234	237	261	208
		204	200	197	196
	150	150	153	156	150

further complicated by the overlapping, in the same spectral region, of the 2 i.r. active components of ν_3.

Data on the longitudinal and transversal optic frequencies are not available for the other scheelite compounds, but it is very probable that the same explanation holds for the other compounds of this family.

ASSIGNMENT OF THE FUNDAMENTAL FREQUENCIES

The group theoretical analysis [1, 3, 4, 7, 10] leads to the irreducible representation: $\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$. The $3B_u$ modes are Raman and i.r. inactive; moreover, $1A_u$ and $1E_u$ mode correspond to translations and should be subtracted. Now, if the separation of the vibrations into internal and external modes is accepted as a good approximation, the i.r. active normal modes may be described as follows:

5 internal modes: stretching—$\nu_3 A_u$ and $\nu_3 E_u$;

bending—$\nu_2 A_u$, $\nu_4 A_u$ and $\nu_4 E_u$.

3 external modes: 1 rotation E_u; 2 translations $1A_u$ and $1E_u$.

A fairly detailed interpretation of the spectra implies the solution of the following problems:

(i) The assignment of the bands to the various classes of symmetry. This is a more or less easy task as far as monocrystals are available. Such data have already been published for the i.r. spectra of $CaWO_4$ and $CaMoO_4$ [1]. For compounds which have been investigated as powders only, the assignment may be attempted by comparison. This procedure is probably reliable for the internal frequencies, which are expected to occur in the same succession in the spectra. This is no longer true, however, for the external modes, whose frequency strongly depends on the type of motion (translation or rotation) and on the nature of the cation.

(ii) The assignment of the bands to the different types of vibrations. For several reasons, this assignment may be a matter of difficulty:

(1) the 2 types of bending motions ν_2 and ν_4 may occur in the same frequency range and thus may be confused;

(2) likewise, the discrimination between a translational and a rotational mode is very difficult, and in fact nearly impossible without further experimental data. As a matter of fact, our own data will show that the previous assignments must be revised;

(3) Finally, the labeling into internal, external, translational and rotational modes is necessarily an approximation, since all vibrations belonging to the same representation are liable to be more or less mixed up. The possibility of significant vibrational interactions is probably very remote for the stretching frequencies, which are much higher than the bending and external frequencies. But such interactions are likely to occur between rotational, translational and low-lying internal modes.

Since a detailed comparison of the various assignments has already been published

[9], we shall restrict here to the modes for which controversial assignments have been proposed. 2 main points are open to discussion:

(1) The proper assignment of the 2 medium-frequency bands of the A_u class to the ν_2 and ν_4 modes;

(2) the assignment of the low-frequency bands to either rotational or translational modes.

These assignment problems will be discussed and solved by the combined investigation of pure compounds and isotopic species [12].

Calcium molybdate

We shall first discuss the case of $CaMoO_4$, for which numerous data have been published. The assignments to be discussed are collected in Table 4. Most of KHANNA and LIPPINCOTT's assignments [4] are in contradiction with the symmetry assignments deduced from BARKER's single crystal data [1] (e.g. the 150 cm^{-1} band is assigned to an A_u mode, whereas this band clearly appears as an E_u mode in Barker's spectra). Such assignments are expected to be erroneous and will not be further discussed.

Table 4. Controversial assignments for $CaMoO_4$ i.r. frequencies

	Ref. [3]	[4]	[5]	[9]	This work*
$\nu_2(A_u)$	245†	324	425	404	431
$\nu_4(A_u)$	425	436	245†	282†	284†
$\nu_4(E_u)$	318	436	318	332	329
Rot. (E_u)	208	272	208	204	153
Transl. (E_u)	150	218	150	234	237
Transl. (A_u)	196	150	196	150	200

* More refined assignments in Table 5.

† Despite the very large difference, these figures refer to the same band. This comes from the fact that the 245 figure quoted by PORTO [3] and SCOTT [5] is the transversal optic frequency calculated by BARKER [1], whereas the 282 or 284 figures are the experimental values observed in 'absorption': these values are likely to be an average between the T.O. and L.O. values calculated by BARKER.

Thus, as far as the internal modes are concerned, our problem is restricted to the assignment of the 400 and 280 cm^{-1} bands to the $\nu_2(A_u)$ and $\nu_4(A_u)$ modes. It has been argued that the assignment of the high-frequency (near 400 cm^{-1}) band to $\nu_2(A_u)$ and of the low-frequency (near 280 cm^{-1}) band to $\nu_4(A_u)$, together with adequate assignments of the Raman frequencies, leads to averaged values of ν_2 and of ν_4 which compare favourably with the values observed for the molybdate ion in solution (405 and 318 cm^{-1} respectively) [5, 6, 9].

Since, however, in the scheelite structure, the tetrahedron is rather flattened with respect to a regular tetrahedron, our feeling is that this argument is not by itself a sufficient proof of the proposed assignment.

Likewise, the assignment problem of the lattice modes will be restricted to the

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[12] P. TARTE and J. PREUDHOMME, *Spectrochim. Acta* **26A**, 2207 (1970).

discrimination between the rotational and the translational modes of the E_u type, the assignment of the translational A_u mode being necessarily unequivocal. The problem is thus reduced to the assignment of the 150 cm^{-1} band to either a translation or a rotation.*

In Porto and Scott's paper [3], this band is assigned to the translational mode. But no proof or even argument is given to support this interpretation. And in fact, the problem cannot be solved with the existing experimental data.

Two types of experimental methods have been developed in this laboratory with the purpose of solving such assignment problems: the investigation of solid solutions (method of isomorphic substitution) [13, 14], and the investigation of isotopic species including medium-weight isotopes [12]. From a brief discussion of the respective possibilities and drawbacks of the two methods, it appears that whenever applicable the isotopic method is the most simple one.

From this point of view, CaMoO$_4$ is a very favourable case, since convenient isotopes are available for both cations (^{40}Ca and ^{44}Ca; ^{92}Mo and ^{100}Mo). The low-frequency region of the spectrum is represented in Fig. 1. The observed i.r. frequencies of the various isotope species are collected in Table 5.
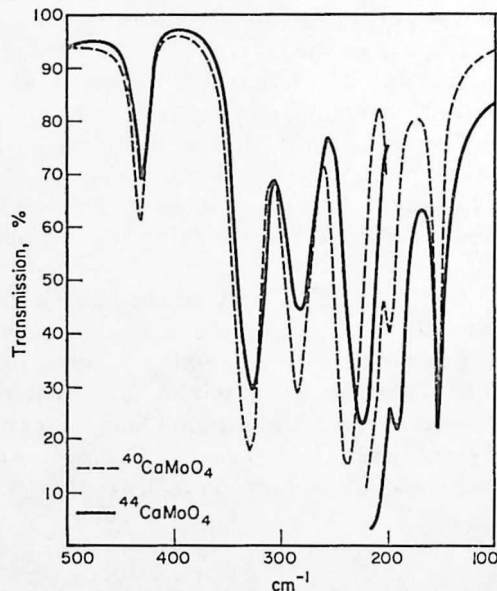

Fig. 1. Medium- and low-frequency region of the i.r. spectrum of CaMoO$_4$, showing the ^{40}Ca–^{44}Ca isotopic shifts.

* Despite previous Barker's work, and quite unexpectedly, the lowest-lying band (near 150 cm^{-1} for CaMoO$_4$ and CaWO$_4$) is assigned by Khanna and Lippincott [4] and by Brown et al. [9] to the unique lattice A_u mode. Since Barker's single crystal data bring the definite proof that the low-lying frequency is one of the $2E_u$ lattice modes, this latter assignment will be considered without further discussion. Indeed, our own results (see Table 5) prove that this frequency correspond to the unique i.r. active *rotational* mode, which necessarily belongs to the E_u class.

[13] P. Tarte, *Spectrochim. Acta* **18**, 467 (1962).
[14] P. Tarte, *Mém. Acad. Roy. Belg.* **35**, 4a and 4b (1965).

Table 5. I.r. frequencies (in cm^{-1}) of the isotopic species of CaMoO$_4$

^{40}CaMoO$_4$	^{44}CaMoO$_4$	$\Delta\nu$ cm^{-1}	%	Ca^{92}MoO$_4$	Ca^{100}MoO$_4$	$\Delta\nu$ cm^{-1}	%	Assignments
813	812	(−1)		812	804	−8	∼1·0	$\nu_3(A_u)$ and $\nu_3(E_u)$
431	431	0		432	431	(−1)		$\nu_2(A_u)$*
329	327	−2	0·60	327	324	−3	0·91	Essentially $\nu_4(E_u)$, but small contribution from a translation
284	282	−2	0·71	281	280	(−1)		Essentially $\nu_4(A_u)$* but small contribution from a translation
237	224	−13	5·6	232	225	−7	3·0	Translation (E_u)
200	193	−7	3·5	199	196	−3	1·5	Translation (A_u)
153	153	0		153	153	0		Rotation (E_u)

* These data do not allow a discrimination between the 2 $(\nu_2$ and $\nu_4)A_u$ modes. The actual assignments result from the comparison between the corresponding molybdates and tungstates.

Internal frequencies

The ^{92}Mo–^{100}Mo isotopic shifts are those expected for the ν_3 (near 810 cm^{-1}) and the $\nu_4(E_u)$ modes. These shifts are of the same order of magnitude that those already found for spinel molybdates [15]. But the results do not allow a clear-cut discrimination between the $2A_u$ modes, namely ν_2 and ν_4. For both bands, the shift (1 cm^{-1}) is hardly significant, and it is impossible to choose between the following hypotheses: either the shift is zero for ν_2, and say 2 cm^{-1} for ν_4, but the difference is lost into the experimental errors; or the shift is really 1 cm^{-1} for both bands, a result which would imply the occurrence of vibrational interactions between these modes which belong to the same class of symmetry. A comparison between the corresponding molybdates and tungstates will bring more information about this point (see below).

There should be no ^{40}Ca–^{44}Ca isotopic shift on the internal frequencies. But in fact, we find a small, but real calcium mass effect on the lowest-lying internal modes near 325 and 280 cm^{-1}. This points to some mixing between these internal modes and the external, translational modes. This mixing is not completely unexpected, since the frequency difference between the internal and the external modes of the same symmetry is not so great (less than 100 cm^{-1}). But the isotopic method brings the unequivocal proof that these interactions do really occur.

External frequencies

Definite assignments may be deduced from the isotopic frequencies (Table 5). It is now evident that the lowest-lying band, which was previously assigned to a translation [3], necessarily corresponds to the E_u rotation. Moreover, the lack of any mass effect strongly suggests that this mode is essentially free from significant interaction with the E_u translational mode near 230 cm^{-1}.

The 2 bands near 230 and 200 cm^{-1} are immediately assigned to the 2 translational modes, with a simultaneous contribution from both calcium and molybdenum cations.

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[15] J. PREUDHOMME and P. TARTE, *Spectrochim. Acta* **28A**, 69 (1972).

Calcium tungstate

The ^{40}Ca–^{44}Ca isotopic behaviour is so closely related to that already observed for $CaMoO_4$ that the interpretation of the results is evident (Table 6).

Table 6. I.r. frequencies of $^{40}CaWO_4$ and $^{44}CaWO_4$

$^{40}CaWO_4$	$^{44}CaWO_4$	$\Delta\nu$ cm^{-1}	%	Assignment
813	813	0		$\nu_3(A_u)$ and $\nu_3(E_u)$
440	441	(+1)		$\nu_2(A_u)$
326	324	−2	0·6	Essentially $\nu_4(E_u)$ but small contribution from a translation
286	283	−3	1·05	Essentially $\nu_4(A_u)$ but small contribution from a translation
229	219	−10	4·4	Translation E_u
177	175	−2	1·1	Translation A_u
147	146·5	(−0·5)		Rotation E_u

Extension of the assignments to the other molybdates and tungstates

The previous assignments may be immediately extended to the other molybdates and tungstates of the scheelite family (Table 1). And conversely, the investigation of the whole family brings a further confirmation of the proposed assignments.

The following comments can be made on the values quoted in Table 1.

ν_3. The strong band corresponding to ν_3 is observed at practically the same frequency for the corresponding molybdates and tungstates ($CaMoO_4$ and $CaWO_4$, $SrMoO_4$ and $SrWO_4$, . . .). Since tungsten is roughly twice as heavy as molybdenum, it may be concluded that, for this vibration, the mass effect is exactly compensated by the higher restoring force in the WO_4 group (which appears very clearly in the behaviour of ν_1: see Raman data).

ν_2. If Scott's assignment is correct, there will be no mass effect, and, in view of the higher restoring force in the tungstate group, the WO_4 frequencies should be higher than the MoO_4 frequencies in corresponding compounds. This is indeed the case, although the difference is small.

$\nu_4(E_u)$ *and* $\nu_4(A_u)$. The preceding effect is reversed ($\nu_{MoO_4} > \nu_{WO_4}$), suggesting a mass effect of the central cation. This is in agreement with the assignment of these bands to ν_4.

Translation E_u. Since this band exhibits a fairly large ^{40}Ca–^{44}Ca frequency shift, it is expected to be rather sensitive to the mass of the bivalent cation. Figure 2 shows that, apart from the calcium compounds, the relation between this frequency and the square root of the cationic mass is practically linear. This behaviour may be considered as an independent proof of the translational origin of this band.

Translation A_u. This band is fairly weak in the spectrum of $CaMoO_4$, and it was not observed for all compounds.

Rotation E_u. The corresponding frequency will depend on the nature of the bivalent cation (cation–oxygen distance and bonding force), but not on its mass. This lack of a significant mass effect is evident from the comparison of the values observed for $SrMoO_4$ and $CdMoO_4$, or $BaMoO_4$ and $PbMoO_4$. On the other hand,
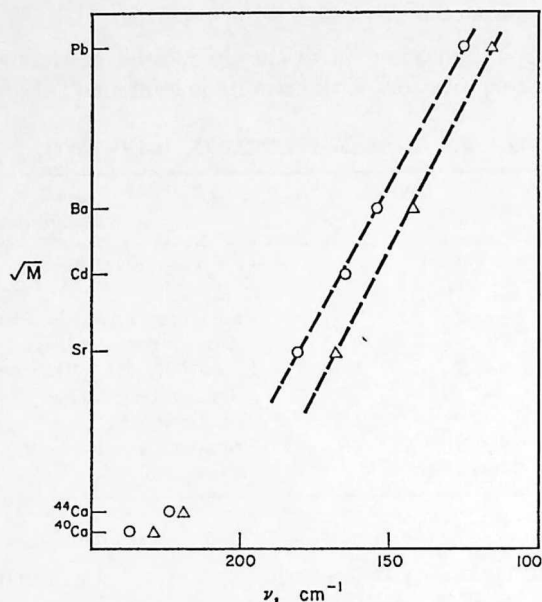
Fig. 2. Relationship between the frequency and the square root of the cationic mass for the band assigned to the E_u translation. Circles: molybdates; triangles: tungstates.

since the other external E_u mode is a translation and thus is mass-sensitive, the frequency difference between these 2 external E_u modes, which was moderately large for the calcium compounds (about 80 cm^{-1}), is much reduced for the lead compounds (10 to 20 cm^{-1}). It is thus quite possible that vibrational interactions, which could not be detected for the calcium compounds, are present in the case of the lead compounds. Finally, no simple relationship has been found between this rotational frequency and the ionic radius of the cation. Thus, the lack of any isotopic mass effect remains the best proof of the rotational origin of this mode.