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Infrared spectrum of whewellite

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Abstract—The infrared spectra of whewellite (calcium oxalate monohydrate), $CaC_2O_4 \cdot H_2O$ and its deuterated analogue have been recorded (4000–300 cm^{-1}) and an empirical assignment of the observed bands is given. The most striking feature of the investigated spectra is the appearance of five bands in the OH stretching region which are interpreted (after one of them has been assigned to an overtone reinforced by Fermi resonance) as due to the vibrations of four dissimilar hydrogen-bounded OH groups of two kinds of water molecules. Pairs of bands are observed for each water librational mode, thus confirming the existence of two non-equivalent types of water molecules in the unit cell of whewellite. Not all oxalate vibrations could be assigned with certainty.

INTRODUCTION

DESPITE the fact that calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$ is one of the most common analytical precipitates, is frequently found in plants [1–3], urinary calculi (cf. e.g. [4–6] and the references given therein) and other biological objects and, even, as a mineral deposit [7–10] (the mineral is called whewellite), its infrared spectrum has received surprisingly little attention. DOUVILLÉ *et al.* [11] have reported the infrared spectrum of solid calcium oxalate (the water content is not given) and have made some assignments. Although their frequencies coincide only roughly to ours and some of them could not be confirmed by us, it is apparent that the species they have examined was indeed $CaC_20_4 \cdot H_2O$. SCHMELZ *et al.* [12] also listed the frequencies of the main bands observed in crystalline $CaC_2O_4 \cdot H_2O$ and gave explicit assignments only for the three of the most prominent bands, although some additional bands could be interpreted on the basis of their proposed assignment (based on a normal coordinate treatment) of the vibrations of the "free" oxalate ion. FREEBERG *et al.* [13], in connection with their study of the kinetics of the calcium oxalate pyrolisis, list the frequencies of the bands in the $CaC_2O_4 \cdot H_2O$

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[11] F. DOUVILLÉ, C. DUVAL and J. LECOMTE, *Bull. Soc. Chim. Fr.* **9**, 548 (1942).
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spectrum and assign most of them, but do not discuss the spectrum in detail and leave several bands without interpretation. Stojanova *et al.* [5] simply list the frequencies and give the tracing of the spectrum of whewellite, but offer no interpretation whatsoever. It, thus, seemed desirable to look more closely into the spectrum of $CaC_2O_4 \cdot H_2O$ and attempt to give a more detailed interpretation of its spectral features. Our continuous interest in the spectra of crystallohydrates [14–16] was a further reason to undertake the present investigation.

Experimental

Calcium oxalate monohydrate was prepared by the standard analytical procedure [17]. Partially deuterated samples were prepared similarily, except that D_2O solutions were used throughout. The infrared spectra were recorded of KBr pellets on a Perkin–Elmer 521 infrared spectrophotometer.

Results and Discussion

The infrared spectra of protonated and partially deuterated calcium oxalate monohydrate are presented in Fig. 1. The frequencies of the observed bands, together with a qualitative estimate of their intensities and a tentative assignment are given in Table 1.

Group-theoretical considerations

Calcium oxalate monohydrate crystalizes in the monoclinic system, its space group being variously referred to as either $P2_1/c$ [3, 18, 19] or $P2_1/n$ [10, 20]. The

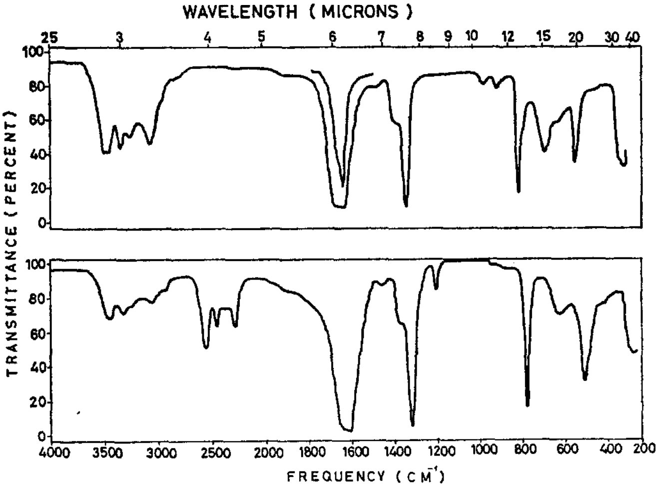

Fig. 1. Infrared spectra of $CaC_2O_4 \cdot H_2O$ and its partially deuterated analogue.

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Table 1. Infrared spectrum of calcium oxalate monohydrate and calcium oxalate monodeuterate

$CaC_2O_4 \cdot H_2O$[a]	$CaC_2O_4 \cdot D_2O$[a]	Approximate description[b]
3495 ms	2570 m	ν(OH)
3440 ms	2560 m	ν(OH)
3340 ms	2425 m	ν(OH)
3250 m	2390 w	2δ(HOH)
3060 ms	2290 m	ν(OH)
1645 sh (?)	1208 w	δ(HOH)
1620 vs	1610 vs	ν_9(ox): $\nu_a(CO_2)$
1483 vvw	~1450 w	ν_1(ox) (?): $\nu_s(CO_2)$ and δ(HOD)
1460 vvw		
1380 sh	1385 sh	ν_1(ox) (?): $\nu_s(CO_2)$ and/or combinations
1365 sh	~1370 sh	
1316 vs	1317 vs	ν_{11}(ox): $\nu_s(CO_2)$
943 w	~670 sh	ν_R' (H_2O)
880 w	~620 sh	
782 s	782 vs	ν_{12}(ox): δ(OCO)
765 sh		
656 m	550 sh	$\nu_R''(H_2O)$
625 sh	~630 m	ν_8(ox): $\omega(CO_2)$
600 sh	~495 sh	$\nu_R''(H_2O)$
513 s	512 s	ν_7(ox): $\omega(CO_2)$
~450 sh	~445 sh	ν_3(ox) (?): δ(OCO)
415 sh	~415 sh	
~300 sh	~300 sh	ν_{10}(ox): $\rho(CO_2)$; ν_6(ox): $\rho(CO_2)$ and/or $\nu(Ca–O_W)$
~280 ms (?)	~280 ms (?)	

[a] w—weak, m—medium, s—strong, v—very, sh—shoulder. [b] ν—stretching, δ—in-plane bending, ω—wagging, ρ—rocking; ox—oxalate band; ν_R—water libration band; s—symmetric, a—antisymmetric.

crystal structure of whewellite has been determined in some detail only by Cocco [18] and refined by Cocco and Sabelli [19]. The accuracy of their data has been questioned [21], however.

According to Cocco's investigations [18, 19] in the structure of whewellite there are two types of crystallographically non-equivalent types of oxalate ions, one approximating the ideal, D_{2h} symmetry of the free oxalate ions, the other having symmetry lower than that (close to C_{2h} according to Sterling [21]). In fact, the sites occupied by both types of oxalate ions in the structure of whewellite have only the trivial C_1 symmetry, so that, strictly speaking, all 12 vibrations of the oxalate ion, which, under the D_{2h} symmetry are of the following species*: $3A_g + A_u + 2B_{1g} + B_{1u} + B_{2g} + 2B_{2u} + 2B_{3u}$, should become active for both

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* Using Herzberg's [22] choice of axes. If the plane of the molecule is taken as *yz* (the *z* axis coinciding with the C—C line) the distribution becomes $3A_g + A_u + B_{2g} + 2B_{1u} + 2B_{2u} +$ $+ 2B_{3g} + B_{3u}$.

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types of oxalate ions (only the B_{1u} (ν_7), B_{2u} (ν_9 and ν_{10}) and B_{3u} (ν_{11} and ν_{12}) are i.r. active under the D_{2h} symmetry). In view of the rather high geometrical symmetry of at least one of the two types of oxalate ions, however, the intensity of the bands corresponding to vibrations which are infrared inactive under the D_{2h} symmetry is expected to be, in general, low. Furthermore the mutual-exclusion principle, valid strictly for the idealized ion, should probably still hold approximately and relatively strong Raman lines should correspond to the weakest infrared bands. Owing to the fact that there are eight formula units of whewellite per unit cell (whose factor group is C_{2h}), each of the vibrations should be further split to eight components, two of each A_g, A_u, B_g and B_u (only the *ungerade* vibrations being infrared active) as a result of the correlation-field splitting effects.

According to COCCO [18, 19] in the unit cell of whewellite there are also two types of non-equivalent water molecules, denoted $H_2O(1)$ and $H_2O(2)$, both of which have one shorter and one significantly longer $O \cdots O$ contact. The corresponding values are 2·57 and 3·22 Å for $H_2O(1)$ and 2·54 and 3·36 Å for $H_2O(2)$ [19]. As with the case of the oxalate ions, the sites of both types of H_2O molecules are of C_1 symmetry, so that, in principle, not only all internal vibrations, but also those of rotational origin (librations) could be expected to appear in the investigated by us spectral region. The fact that both the geometry and the environment of the two types of water molecules are somewhat different, at least two bands corresponding to each of the vibrational modes (internal or external) could be expected to appear in the spectrum (the same is, of course, true for the oxalate modes as well) and the correlation-field splitting could further increase the number of bands.

The comparison of the spectra of the protonated and deuterated compounds permits, in general, a clear-cut differentiation between the bands due to vibrations of the oxalate ions and those originating from motions of the water molecules and they will be discussed in the above order.

Oxalate vibraions

As mentioned before, despite the low site symmetry of the oxalate ions, the most prominent bands in the spectrum should still be due to the i.r. active under the D_{2h} symmetry modes ν_7, ν_9, ν_{10}, ν_{11} and ν_{12}. Of these, the CO_2 rocking mode ν_{10} could possibly fall beyond the region accessible to our instrument, whereas the bands at 1620, 1316 and 782 cm^{-1} undoubtedly correspond to ν_9 (antisymmetric CO_2 stretching), ν_{11} (symmetric CO_2 stretching) and ν_{12} (in-plane deformation) modes, as already pointed out by SCHMELZ *et al.* [12]. FREEBERG *et al.* [13] assign the last of the above modes to a CO_2 wagging mode (probably ν_7), placing the in-plane bending mode at around 510 cm^{-1}, contrary to most recent investigators, e.g. TOMAR *et al.* [23] or FUKUSHIMA [24, 25] both of which, in the case of $K_2C_2O_4 \cdot H_2O$, explain their band at around 520 cm^{-1} as due to the CO_2 wagging mode, an

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assignment which seems more plausible, since it is supported by a normal coordinate treatment [25]. Our 513 cm^{-1} band is, consequently, assigned to the ν_7, CO_2 wagging mode. The remaining mode, infrared active under the D_{2h} symmetry, ν_{10} (a CO_2 rocking mode, as mentioned before) was placed around 222 cm^{-1} by SCHMELZ *et al.* [12], around 295 cm^{-1} by MURATA and KAWAI [26] and, for the case of $K_2C_2O_4 \cdot H_2O$, at 353 cm^{-1} by TOMAR *et al.* [23]. The only band which could be due to this vibration is found, in our spectra, just below 300 cm^{-1}. The bands in this region, however, are rather uncertain because of the strong absorption of light by the atmospheric water vapour and, moreover, another CO_2 rocking mode (ν_6) as well as the M—O_w stretching frequencies (H_2O "translations") may appear in the same region. It is, thus, difficult to be certain about either the exact location of the band maximum or its unequivocal interpretation.

The remaining seven frequencies, infrared inactive under the D_{2h} symmetry, are somewhat more difficult to assign since, as pointed out earlier, the rather small physical distortion of the oxalate ion should probably make these vibrations only slightly i.r. active and the corresponding bands are expected to appear weakly in the infrared spectrum.

Of these modes, ν_5 (another antisymmetric CO_2 stretching) is probably overlapped by the intense and rather broad band at around 1615 cm^{-1} and the other rocking CO_2 vibration, if visible at all, would participate, as pointed out earlier—in discussing the origin of the band below 300 cm^{-1}, in the formation of this band. The inactive (both in the infrared and Raman spectra) ν_4 vibration (an essentially C—C torsion, using here and throughout the description of SCHMELZ *et al.* [12]) is probably undetectable in our spectra too. Thus, in fact, only four frequencies should be located in the 1500—400 cm^{-1} region. One of these corresponds, almost certainly, to the band which is seen only as a shoulder in the spectrum of the protonated compound (at around 630 cm^{-1}) but appears as a medium and well defined band in the spectrum of the deuterated analogue, after the neighbouring bands (due to water librations) have been shifted downwards.* Neither SCHMELZ, *et al.* [12] nor MURATA and KAWAI [26] give a calculated frequency in this region but TOMAR *et al.* [23] have assigned a band at 612 cm^{-1} in their $K_2C_2O_4 \cdot H_2O$ spectrum to the CO_2 wagging, ν_8 vibration and our 630 cm^{-1} band is probably due to the same mode.

The assignment of the three remaining frequencies: ν_1 (a symmetric CO_2 stretching), ν_2 (a C—C stretching) and ν_3 (an in-plane deformation) would have been greatly facilitated if Raman spectra of solid whewellite were in hand, since all three of these modes are of the A_g species and would, therefore, be expected to give rise to relatively strong Raman lines. In the absence of such spectra, however, one should rely on the published Raman spectra of oxalate ions in solutions (e.g. [27, 28]) and the assignments made for other solid oxalates (e.g. [23–25]).

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* In fact, in this region of the spectrum of the deuterated compound the appearance of the other two D_2O librational bands (vide infra) is expected. However the low intensity of their counterparts in the spectrum of the protonated compound (where they are located around 943 and 880 cm^{-1}) suggests that the 630 cm^{-1} band can not be made up entirely of them.

[26] H. MURATA and K. KAWAI, *J. Chem. Phys.* **25**, 589 (1956).

[27] K. ITO and H. J. BERNSTEIN, *Can. J. Chem.* **34**, 170 (1956).

[28] G. M. BEGUN and W. H. FLETCHER, *Spectrochim. Acta* **19**, 1343 (1963).

On the basis of the published data, one would expect to find these modes around 1490, 900 and 450 cm^{-1} respectively. An extremely weak band seems to be indeed present around 450 cm^{-1} and if so it should correspond to the ν_3 mode. The ν_2 mode could not be located even tentatively: in the region where it is expected to appear the two already mentioned weak bands, due to water librations, are present and the incomplete deuteration still leaves some traces of them in the spectrum of the deuterated compound. Thus it is not clear whether or not a weak band, corresponding to the ν_2 mode, is also present around 900 cm^{-1}. As for the assignment of the ν_1 mode two possibilities exist. One is to assign to this mode the very weak band observed around 1450 cm^{-1} in the spectra of both the protonated and the deuterated compound (particularly clearly in the latter case), while the other is to locate this mode somewhat lower, around 1380–1360 cm^{-1} where, on the high-frequency side of the 1320 cm^{-1} band, two weak bands are observed, only one of which could be interpreted as binary combination. The latter alternative seems more attractive since this would also explain the appearance of two distinct, almost equally intense, bands in the same region of the spectra of some $MC_2O_4{\cdot}2H_2O$ type compounds (M is a divalent transition metal or Mg) [29]. Furthermore, the band, clearly visible in the spectrum of the deuterated compound may not be identical with the one observed in the spectrum of the protonated analogue, since the deformation HOD frequency is expected to appear in exactly the same region. It is, of course, possible that more than one band is observed in the 1400–1300 cm^{-1} region as a result of the existence of two types of oxalate ions in the unit cell and the fact that it contains four ions of each type. This latter interpretation would then be in line with the existence of a clearly visible shoulder at the low-frequency side of the 780 cm^{-1} band (which, however, is not noticeable in the spectrum of the deuterated compound, as discussed below) and the fact that the low-frequency side of the 520 cm^{-1} band is also broadened, although no clearly resolved band or shoulder could be observed. As mentioned before, the analysis of the Raman spectra would help to clear up these points.

Water vibrations

The bands shifted on deuteration must be, in one way or other, related to vibrations (internal and external) of the water molecules. Of these, the easiest to notice is the complex of at least five bands found, in the spectrum of the protonated compound, between 3500 and 3000 cm^{-1} and shifted, on deuteration, to the 2600–2200 cm^{-1} region. The appearance of five bands in the OH stretching region is rather unexpected. One would, namely, expect to find four, rather than five, bands (possibly split further as a result of correlation-field-splitting effects) if, as suggested by SEIDL *et al.* [30] or HOLZBECHER *et al.* [31], each non-equivalent OH group of crystalline water gives rise to a distinct OH stretching band. Since both types of water molecules have one of their OH groups involved in a much

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[29] I. PETROV, B. ŠOPTRAJANOV and P. NANE (to be published).
[30] V. SEIDL, O. KNOP and M. FALK, *Can. J. Chem.* **47**, 1361 (1969).
[31] M. HOLZBECHER, O. KNOP and M. FALK, *Can. J. Chem.* **49**, 1413 (1971).

stronger hydrogen bond than the other [19], four bands are expected to appear—the ones lying highest and lowest corresponding to vibrations of $H_2O(2)$ and the intermediate ones to vibrations of $H_2O(1)$. The situation is greatly simplified, however, if one considers the weakest of the five bands (that at around 3250 cm^{-1}) as arising from the overtone of the HOH bending mode reinforced by Fermi resonance with one of the neighbouring fundamental bands (it is difficult to decide which one, since the fundamental HOH bending band is hidden under the intense oxalate band at around 1620 cm^{-1}). The whewellite spectrum would then serve as an independent experimental confirmation of the essential correctness of Cocco's determination of the geometry of the two types of water molecules [18, 19] as well as another example of the applicability of the interpretation of the OH stretching region in the spectra of crystallohydrates to predicting the number and the approximate geometry of different types of water molecules (or, maybe more correctly, of types of environments around the water molecules), as suggested by Falk and his collaborators [30, 31].

As mentioned earlier, the exact location of the HOH deformation mode (or modes) is not known. The fact that, in the spectrum of the deuterated compound, only one DOD deformation frequency appears (as a rather sharp band around 1210 cm^{-1}) suggests that, despite the differences in the geometry and environment of the two types of water molecules, only one HOH deformation frequency exists too. It should be mentioned, however, that a part of the very weak band around 1480 cm^{-1} seems also to disappear on deuteration, but this, as already discussed, may simply be a consequence of the fact that the HOD deformation band has appeared in the same region and the very weak bands, observed in the spectrum of the protonated compound, are hidden under this band.

In the region below 1000 cm^{-1} several bands are sensitive to deuteration, some of which have been already mentioned. Thus two weak bands, at around 943 and 880 cm^{-1}, as well as the intense band at 656 cm^{-1} and the shoulder at around 600 cm^{-1} are clearly shifted to lower frequencies and are, thus, characterized as due to water librations. It is, however, difficult to decide which librational mode (rocking, wagging or, possibly, twisting) is responsible for a given pair of bands (the appearance of two bands corresponding to a given mode is, of course, consistent with the existence of two types of water molecules in the unit cell) and also which bands should be assigned to librations of $H_2O(1)$ and which to those of $H_2O(2)$.

Some additional changes in the spectra are noticed on deuteration. Of these, one has already been mentioned: the apparent disappearance of the bands at around 1480 cm^{-1}, which, however, may not be real but due to the appearance of the HOD bending vibration. The other such change has also been mentioned briefly. Namely, whereas in the spectrum of the protonated compound there is a clearly visible shoulder at 765 cm^{-1}, in the spectrum of the deuterated compound the 782 cm^{-1} band is almost symmetrical and no shoulder is visible on its low-frequency side. The region where the 765 cm^{-1} band would be shifted if it were due to some kind of water libration (around 550 cm^{-1}) contains a complex feature composed of the ν_7 oxalate band and the D_2O librational bands (shifted here from the 660–600 cm^{-1} region), so that it is difficult to decide whether or not an additional band is present here also. It is quite possible, however, that the bands at around 782 and 765 cm^{-1} originate from the same type of vibration of the two different types of oxalate ions or are, even, due to correlation-field splitting.

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