

REINVESTIGATION OF THE INFRARED SPECTRA OF CALCIUM OXALATE MONOHYDRATE AND ITS PARTIALLY DEUTERATED ANALOGUES – AN EXPERIMENTAL AND THEORETICAL STUDY –

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The infrared spectra of calcium oxalate monohydrate studied earlier by us [1] have been reinvestigated using the Fourier transform technique and supplemented by quantum mechanical calculations aimed to create a firm basis for the assignment of oxalate vibrations. The Fourier transform infrared (FTIR) spectra of the protiated species and of partially deuterated analogues of the examined compound were studied both at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) in the 4000–400 cm^{–1} region.

Keywords: calcium oxalate monohydrate; whewellite; FT IR spectra

INTRODUCTION

Calcium oxalate monohydrate is a common analytical precipitate formed during the gravimetric determination of calcium with oxalates or vice versa. With reduced use of gravimetric methods of analysis, the analytical importance of calcium oxalate monohydrate has diminished. However, it is still an important compound worth studying since it is one of the most common constituents of urinary calculi (Fig. 1). In fact, among the patients from Macedonia $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and the corresponding dihydrate are by far the most often found constituents [2]. Rather rarely, it occurs in nature also as a mineral named *whewellite*, the same name being often used to denote *synthetic* calcium oxalate monohydrate as well.

Our interest in the infrared spectra of whewellite has always been twofold. On the one hand, it stemmed from the fact that it is a *crystalline hydrate*, i.e. it belongs to the large class of compounds which have been in the center of our scientific activities for a very long time. On the other hand, the studies of uroliths by infrared spectroscopy [2, 3] led us to the more detailed investigation

of one of their most important constituents. As a result, a rather detailed study of the infrared spectra of synthetic whewellite has been published [1]. It could also be mentioned that not so long ago we started a chemometric study of the composition of urinary and other stones which contain calcium oxalate monohydrate [4]. The infrared spectral data obtained by using the Fourier transform technique was the basis of these studies.

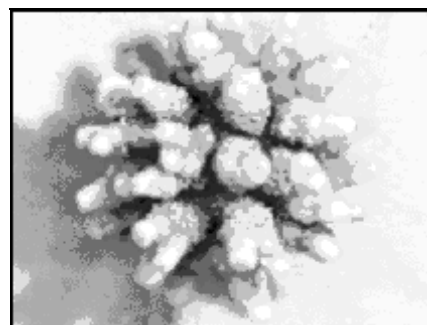


Fig. 1. Urinary calculus composed of whewellite

The availability of superior instrumentation (compared to that used to obtain the results reported in [1]) and of other experimental and theoretical opportunities (such as the possibility to study the spectra at low temperatures and to carry out quantum chemical calculations) were the two main factors which provoked the present study of the Fourier transform infrared spectra of whewellite and of some of its deuterated analogues. As it is obvious from the title, the study is complemented by a quantum chemical study of the vibrations of the oxalate anion. It should be mentioned that the infrared and Raman spectra of calcium oxalate monohydrate were studied, among others, by Shippey [5] whose results are in full agreement with those presented in our earlier study [1]. A less extensive study, limited to the 4000–2000 cm^{-1} region only but with the use of the isotopic dilution technique was reported by Carmona [6].

The crystal structure of whewellite has been determined several times. Apparently Cocco and Sabelli [7, 8] were the first to report the data on the structure, while more detailed analyses were done by Tazzoli and Domeneghetti [9], Deganello and Piro [10] and Deganello [11] (this latest work con-

cerns the structure determined at 328 K). At 328 K whewellite was found to be monoclinic (space group $I2/m$, $Z = 4$) [9] but below 318 K the structure changes to space group $P2_1/n$ [13]. Tazzoli and Domeneghetti [9] report the space group of whewellite as $P2_1/c$, actually, the same space group (C_{2h}^5) as $P2_1/n$ but with a different choice of axes. According to these authors, two independent water molecules (exhibiting disorder) were found. On the other hand, according to Deganello [11] only one type of water molecules exists in the structure at 328 K. Other reports on the structure of whewellite also exist (e.g. [10]) but no data are reported for low temperatures, e.g. at ≈ 80 K, the temperature at which our LNT spectra were recorded. Thus it may not be advisable to draw structural and spectroscopic conclusions taking into account the RT crystal structure on the one hand and the spectroscopic data obtained at LNT, on the other.

It should perhaps be mentioned that in addition to the monohydrate, calcium oxalate forms also a dihydrate (the mineralogical name is weddellite) and a trihydrate (the natural analogue of the synthetic compound was recently found [11] and is named caoxite).

EXPERIMENTAL

Well formed crystals of calcium oxalate monohydrate were obtained using standard analytical procedures. The partially deuterated analogues were prepared in an analogous manner, only using H_2O – D_2O mixtures of appropriate composition.

The Fourier transform infrared (FT IR) spectra were recorded at room temperature (RT) and at the boiling temperature of liquid nitrogen (LNT) on the Perkin Elmer 2000 Fourier transform system. Typically 64 scans were collected and averaged at LNT, while 32 were sufficient at RT. For acquisition of the spectra the GRAMS ANALYST [12] package was used, whereas the manipulation of the spectra was done using GRAMS/32 piece of software [13].

The quantum chemical calculations were carried out with the aid of the Gaussian 98 package [14]. The potential energy hypersurface (PEHS) of the oxalate anion was explored at gradient-corrected density functional level of theory, employing a combination of Becke's three-parameter adiabatic connection exchange functional (B3) with the Lee–Yang–Parr correlation functional (LYP) – B3LYP. The Dunning's correlation consistent basis set of TZ quality, augmented with diffuse functions for a better description of the anionic wavefunction (aug-cc-pVTZ) was used for orbital expansion in solving the Kohn–Sham SCF equations.

RESULTS AND DISCUSSION

The FT IR spectra of whewellite recorded at RT and LNT are shown in Fig. 2, the RT spectrum being essentially identical to that given in Ref. [1] with the important difference that the Fourier

transform spectra (recorded numerically) can be easily manipulated – expanded, compressed, presented with either transmittance or absorbance values on the ordinate axis etc.

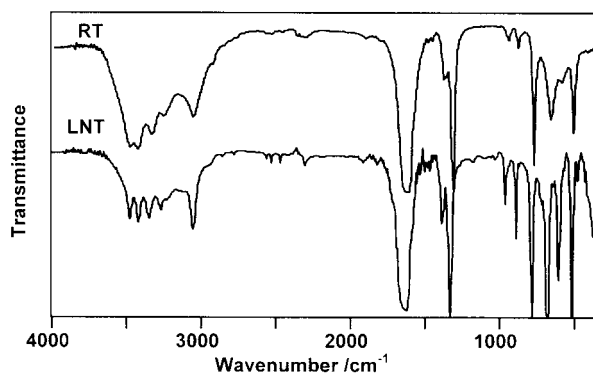


Fig. 2. FT IR spectra of calcium oxalate monohydrate: RT spectrum (upper curve) and LNT spectrum (lower curve)

Water bands

Even without reverting to the published results, it is easy to assign to water stretching vibrations the bands which appear above 3000 cm^{-1} and such an assignment was already made in Refs. 1 and 7–8. What is a little bothersome is the fact that at RT *five* bands are present in this region of the RT spectrum (the number of bands in the LNT spectrum is higher) while only four would, in the first approximation, be expected if two types of water molecules exist in the structure. Both Petrov and Šoptrajanov [1] and Shippey [7] have concluded that the fifth band is due to some sort of vibrational coupling between one of the water fundamentals and a second-order transition, the most likely candidate for such an interaction being the combination of two of the factor-group components of the H–O–H bending vibration (for the factor group isomorphous with the space group no true overtone could be infrared active).

To check the correctness of such an interpretation, the spectrum shown in Fig. 3 was produced. This is a difference spectrum obtained by subtracting the properly normalized spectrum of the protiated compound from the spectrum of the sample containing a small amount of deuterium. In this way the bands are expected to be the result of decoupled O–D vibrations of the isotopically isolated HOD molecules and be indicative of the strength of the hydrogen bonds in which the water hydrons take part.

As seen, in the O–D stretching region four strong bands are indeed seen, but it is clear that there is a fifth one and some other weak bands too. The interpretation of such a spectral appearance

may be twofold. On the one hand, it may be that there is more deuterium in the sample than expected so that the O–D oscillators are not completely isotopically isolated and vibrational interactions are still possible. On the other hand, the presence of the weak bands may be an indication that the results of Tazzoli and Domeneghetti [9] are correct and that the water molecules are indeed disordered. If the latter is true, then the assignment of the bands in the O–H stretching region of the protiated compound should follow a similar line of reasoning.

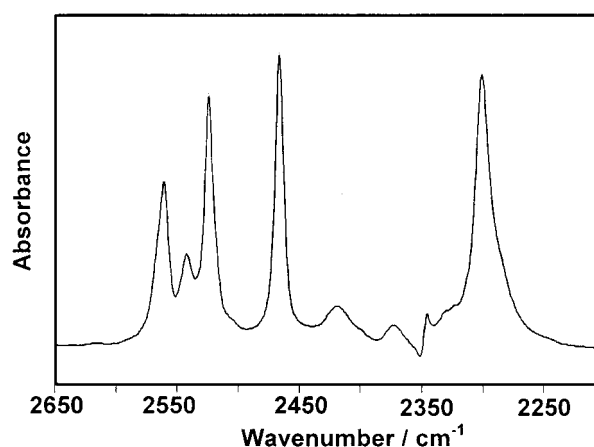


Fig. 3. Difference spectrum of isotopically isolated HOD molecules in the O–D stretching region

What is clear, however, is that the hydrogen bonds formed by the water molecules differ in strength, one of them being appreciably stronger than the other three.

The location of the H–O–H bending bands is practically impossible due to the fact that they should fall in the region where the very strong oxalate bands appear. The situation is not much better in the case of the H–O–D bending bands, whereas in the region where the D–O–D bendings are expected, there is a single band at 1214 cm^{-1} at RT and 1217 cm^{-1} at LNT. The attempts to either self deconvolute this band or represent it as a superposition of several components were unsuccessful. We were thus unable to verify the finding of Carmona [6] who claims that a shoulder exists around 1210 cm^{-1} . Similarly, we could not confirm the existence of bands at 1470 , 1460 and 1452 cm^{-1} which are attributed [6] to the H–O–D bending modes.

The availability of the LNT spectra is beneficial for the location of the bands due to the water librations. As seen in Fig. 4, a number of bands in the 1000–500 cm^{-1} region gain in intensity and shift towards higher wavenumber values – a behavior characteristic for the hindered water rotations (librations). The LNT values for these bands are 960, 891, 720, 680, 607 and 478 cm^{-1} . What is perhaps surprising is not only the number of such bands (if the fact that for each type of water molecules only three librational modes are expected under the site-group selection rules is taken into account) and even more so the broad range of frequencies. It should be pointed out that for water molecules whose symmetry is, apparently, quite reduced in comparison with that of free H_2O molecule the librations could not be easily classified as rocking, wagging and twisting. Appreciable mixing is, namely, expected (at least for the two out-of-plane modes – wagging and twisting – for each type of water molecules).

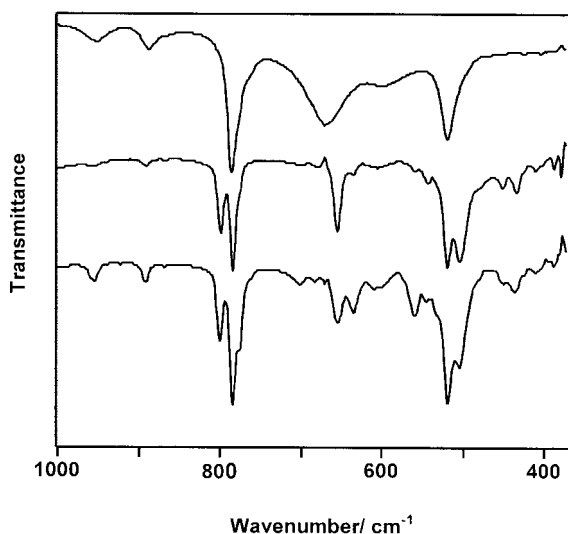


Fig. 4. The region of the water librations in the RT spectrum of whewellite (upper curve) and in the LNT spectrum (lower curve)

Quantum chemical results

The first task of the quantum chemical computations was to determine the molecular structure

of the idealized “free” oxalate anion and to calculate the harmonic frequencies of such an ion.

According to the employed level of theory, the stationary point with D_{2h} symmetry (on the B3LYP/aug-cc-pVTZ PEHS of oxalate anion corresponds to a first-order saddle point (such a geometry would correspond to a transition state) while the stationary point with D_{2d} symmetry corresponds to a minimum. This, it should be noted, is opposite to what has been found in the whewellite crystals where the oxalate anions are *planar*, i.e. their highest possible symmetry is D_{2h} . Such a change of the symmetry results, apparently, as a consequence of the bonding (coordinative and hydrogen) of the oxalate ions in the crystal.

The most relevant results from the harmonic vibrational analysis for both the true minimum and the first-order saddle point on the explored PEHS are given in Table 1 (for the transition state the imaginary frequency with negative sign corresponds to the COO-COO torsional motion).

As seen, the major differences between the two sets of data are found in the low-frequency region and for the mode number 3 for which the calculations showed that it contains contributions from the symmetric COO stretch and the CC stretch.

There is little doubt that the strongest band in the spectrum (its apparent maximum is at 1634 cm^{-1} at LNT) is the result of an overlap of the components of the antisymmetric COO stretches and of the HOH bendings. It should be noted, however, that the frequency of the maximum is *higher* than the calculated values for the “free” oxalate anion. The experimental frequency of 1320 cm^{-1} which by all means corresponds to the $\nu_{\text{sym}}(\text{COO})_{\text{out-of-phase}}$ mode is also higher than the calculated values. The relatively weak bands on its high-frequency side could then be attributed to the mode having $\nu_{\text{sym}}(\text{COO})_{\text{in-phase}} + \nu(\text{CC})$ character although the possibility that bands due to second-order transitions (as suggested in Ref. [1]) could not be ruled out entirely.

The experimental frequency of 515 cm^{-1} is in a very good agreement with the calculated values of 520.3/518.9 cm^{-1} for the planar ion and far greater than the frequency of 394.0 cm^{-1} calculated for the twisted ion.

Table 1

Harmonic vibrational analysis of oxalate anion at B3LYP/aug-cc-pVTZ level of theory

Mode	Wavenumber / cm ⁻¹		Approximate description	Wavenumber / cm ⁻¹
	<i>D</i> _{2h}	<i>D</i> _{2d}		Experiment
1	1595.3	1543.3	$\nu_{as}(\text{COO})_{\text{in-phase}}$	1634 vvs
2	1567.6		$\nu_{as}(\text{COO})_{\text{out-of-phase}}$	
3	1328.2	1394.1	$\nu_{\text{sym}}(\text{COO})_{\text{in-phase}} + \nu(\text{CC})$	1387/1378
4	1289.6	1291.3	$\nu_{\text{sym}}(\text{COO})_{\text{out-of-phase}}$	1320 vs
5	864.7	853.1	$\delta_{\text{out-of-plane}}$	865
6	806.9	831.8	$\nu(\text{CC})$?
7	750.1	741.0	$\delta(\text{OCO})_{\text{out-of-phase}}$	784 s
8	520.3		$\delta_{\text{out-of-plane}}$	515 s
9	518.9	394.0	$\delta_{\text{out-of-plane}}$	
10	391.8	279.8	$\delta_{\text{out-of-plane}}$	
11	291.0		$\delta_{\text{out-of-plane}}$	
12	-77.6	85.6	τ	

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Резиме

**ПОВТОРНО ИСПИТУВАЊЕ НА ИНФРАЦРВЕНИТЕ СПЕКТРИ НА КАЛЦИУМ ОКСАЛАТ
МОНОХИДРАТ И НА НЕГОВИТЕ ПАРЦИЈАЛНО ДЕУТЕРИРАНИ АНАЛОЗИ
– ЕКСПЕРИМЕНТАЛНА И ТЕОРИСКА СТУДИЈА –****Мира Трпковска¹, Бојан Шоптрајанов^{1,2}, Љупчо Пејов¹**¹*Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“,
ул. фах 162, МК-1001 Скопје, Република Македонија*²*Македонска академија на науките и уметностите, МК-1000 Скопје, Република Македонија***Клучни зборови:** калциум оксалат монохидрат; вевелит; Фурие трансформни инфрацрвени спектри

Инфрацрвените спектри на калциум оксалат монохидрат, претходно изучувани од нас [1], се преиспитани (техниката на Фуриеова трансформација на експериментално добиените интерферограми) и поткрепени со квантно механички пресметки насочени кон создавање посигурна основа за асигнација на оксалат-

ните вибрации. Фурие трансформните инфрацрвени спектри од протираното соединение и од неговите парцијално деутерирани аналози се испитувани на собна температура и на температурата на вриење на течен азот, во подрачјето од 4000 до 400 cm⁻¹.