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The Infrared Absorption of Crystalline Thorium Tetraformates. II. Detection of Polymorphic Transitions by Infrared Spectroscopy—Interpretation of the δ(OCO) Vibrational Mode Splitting in the Carboxylic Group of Thorium Tetraformates

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A new method applied to the investigation of polymorphic transitions in the solid state, by infrared spectroscopy is described. The reversibility of the $Th(HCOO)_4\alpha \rightleftharpoons Th(HCOO)_4\gamma$ allotropic transition has been checked, and it has been established that residual water molecules had a blocking effect on the $\gamma \rightarrow \alpha$ transition. The splitting of the δ(OCO) vibrational mode of the formate ion in the thorium tetraformates has been discussed in terms of a vibrational analysis under the factor group.

Introduction

The most widely used experimental method in detection of polymorphic transitions is differential thermal analysis. Unfortunately, the energy corresponding to a polymorphic transition is sometimes too weak to be easily detected by this method. We have recently established that under these circumstances, the use of infrared spectroscopy leads to better results (*1*).

It will first be shown how this method can be tested on a well-known example of allotropic transition. In a second step, this method will be applied to the study of the following reactions (*2*):

$$Th(HCOO)_4\lambda \xrightarrow{65^\circ C} Th(HCOO)_4\alpha \xrightarrow{125^\circ C} Th(HCOO)_4\gamma.$$

Finally, the splitting of the δ(OCO) vibrational mode of the carboxylic group in the thorium tetraformate will be discussed in terms of a vibrational analysis under the factor group.

The experimental methods used here have already been described in Ref. (*2*).

Polymorphic Transition of Phosphocristobalite $AlPO_4$

α-$AlPO_4$ exhibits a polymorphic transition at 222°C (*3*),

$$\alpha\text{-}AlPO_4 \rightleftharpoons \beta\text{-}AlPO_4.$$

The infrared spectrum of α-$AlPO_4$ presents at room temperature a doublet at 732 and 710 cm^{-1} corresponding to the splitting of the ν(Al–O) vibrational mode. In Table I some structural data of α- and β-$AlPO_4$ are mentioned. The profile of the above-mentioned absorption bands is sharp enough for the investigation of their shift throughout the heating of the crystalline sample.

Infrared spectra in the 900–625 cm^{-1} spectral range are drawn every 5 min, the temperature being increased each time by 5°C. If the spectra are

TABLE I

STRUCTURAL DATA FOR α-$AlPO_4$ AND β-$AlPO_4$

	α-$AlPO_4$	β-$AlPO_4$
Crystal system	Tetragonal	Cubic
Space group	D_4^2 or D_4^1	O_h^7
Unit cell	Primitive	Face-centered
Z (Number of molecules per unit cell)	2	4
(Number of molecules per elementary cell)	2	1
ν(Al–O) Absorption frequency	732 and 710 cm^{-1}	715 cm^{-1} (at 222°C)

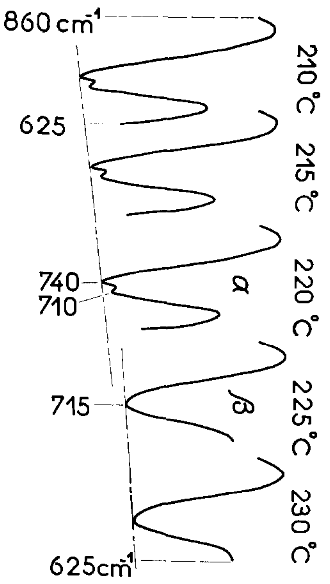


FIG. 1. Detection of the α-$AlPO_4$ → β-$AlPO_4$ allotropic transition by infrared spectroscopy.

displaced by a fixed distance, we get near the transition temperature the results shown in Fig. 1.

During the heating of α-$AlPO_4$ the following facts can be emphasized:

(a). The maxima of homologous absorption bands shift slightly towards the low frequencies. This is normal, since an increase in the interatomic distances provokes a decrease in the corresponding stretching force constants;

(b). Up to 220°C, the absorption maxima are located on a straight line, and the relative intensities of the bands decrease slightly. This is due to thermal effect, the result being a broadening of the bands; since the area under an absorption band is constant, its height must decrease;

(c). Above 225°C, the precedent doublet disappears and a single band is observed at 715 cm^{-1}. If the heating is carried on, the absorption maximum of this band is on a new straight line. Both the discontinuity of the straight line and the change in the shape of the ν(Al–O) absorption band, reveal that a modification has occurred in the crystalline structure of α-$AlPO_4$.

In order to discuss the splitting of any absorption band in a crystalline compound, the number of molecules in the primitive cell must be determined (*4*, *5*). α-$AlPO_4$ crystallizes in the tetragonal system with two molecules/unit cell; thus, there are two distinct Al–O bonds in the primitive cell. Therefore, two components are expected for the internal vibration ν(Al–O). These two components are indeed observed in the infrared spectrum of α-$AlPO_4$ (732 and 710 cm^{-1}), and they correspond to the two symmetrically different Al–O vibrations in the elementary volume. β-$AlPO_4$ presents a face-centered cubic structure, and its primitive cell (the rhombohedron) contains a single molecule; thus, the ν(Al–O) vibration in this crystal corresponds to a single infrared band (715 cm^{-1}).

Investigation of the Polymorphic Transitions $Th(HCOO)_4\lambda \rightarrow \alpha \rightarrow \gamma$

It has been mentioned in Ref. (*2*) that the infrared spectra of thorium tetraformates exhibit strong and sharp absorption bands corresponding to the δ(OCO) vibrational mode, and that the shape of these split bands were characteristic of the corresponding phase. Therefore, in order to detect any change in the structure of these crystalline compounds, the shift in δ(OCO) bands will be investigated throughout the heating of a sample.

According to the above-mentioned investigation method, the characterization of the polymorphic species issued from $Th(HCOO)_4\lambda$ leads to the following observations:

(a). The complex δ(OCO) band of $Th(HCOO)_4\lambda$, initially split into six components at 783, 778, 775, 770, 767, and 759 cm^{-1} is modified near 60°C;

(b). At 65°C the structure of $Th(HCOO)_4\alpha$ appears, and the previous six absorption peaks are replaced by three other peaks at 780, 771, and 765 cm^{-1};

(c). Above 125°C another polymorphic transition takes place, and the δ(OCO) band splits into two components at 783 and 764 cm^{-1};

(d). Throughout the heating, the line joining the absorption maxima of the strongest component of the δ(OCO) bands, presents two discontinuities corresponding to the two polymorphic transitions

$$Th(HCOO)_4\lambda \rightarrow Th(HCOO)_4\alpha \rightarrow Th(HCOO)_4\gamma.$$

Particular Effect of Residual Water on the $Th(HCOO)_4\alpha \rightleftharpoons \gamma$ Allotropy

It has been specified in Ref. (*2*) that the infrared spectrum of $Th(HCOO)_4\alpha$ exhibits a weak absorption band corresponding to the vibration of residual water.

The above described method has been used to check the reversibility of the following polymorphic transition,

$$\mathrm{Th(HCOO)_4}\alpha \rightleftharpoons \mathrm{Th(HCOO)_4}\gamma.$$

During a run performed on the α-anhydrous thorium tetraformate the following details can be observed:

(a). If $\mathrm{Th(HCOO)_4}\alpha$ is heated up to 135°C, the transition to $\mathrm{Th(HCOO)_4}\gamma$ takes place, but the weak water band at 3420 $\mathrm{cm^{-1}}$ still persists. After cooling, the reverse transition to the α species is not observed;

(b). If the same sample is heated up to 153°C, the absorption band at 3420 $\mathrm{cm^{-1}}$ vanishes, and after cooling the $\gamma \rightarrow \alpha$ transition is observed near 95°C;

(c). It is now possible to realize several runs in the temperature range 25–135°C and check for each run the reversibility of the $\alpha \rightleftharpoons \gamma$ allotropy;

(d). If the sample is then allowed to rest for 24 hr at room temperature, the infrared spectrum again exhibits the residual water band at 3420 $\mathrm{cm^{-1}}$, and it is possible to reproduce the observations described in sections (a)–(c).

According to these observations, it is possible to characterize the γ species below the $\gamma \rightarrow \alpha$ transition temperature, this particular effect being related with a blocking effect due to crystal water or to adsorbed water.

Interpretation of the Splitting of the δ(OCO) Vibration in Anhydrous Thorium Tetraformates

In the case of the thorium tetraformates, in order to discuss the splitting of the δ(OCO) vibrational mode, it is necessary to consider the individual vibrations of each formate ion included in the primitive cell. It has been shown that the free formate ion possesses six nondegenerated vibrations of species $3A_1 + 2B_1 + B_2$ (*2*). The δ(OCO) vibration belongs to the symmetry species A_1.

When the formate ions are coordinated on a thorium atom, they are most generally distorted; their site-symmetry in the crystal lessens until C_1, and in this case, the atoms all lie on general positions. Under these conditions, there are expected as many components for each internal vibration of the formate ion as there are symmetrically independent vibrators in the primitive cell. The fine structure of the absorption bands due to the formate ion internal vibrations are ascribed to crystal-field splitting. The symmetry of the δ(OCO) vibrations is related to the factor group of the unit cell. In most cases, for a given crystal, the point symmetry of the factor group is the same as the symmetry of the crystal class.

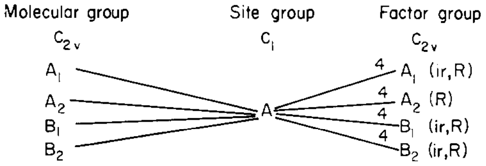
$\mathrm{Th(HCOO)_4}\lambda$

The X-ray data for this compound are as follows (*6*):

Space group:	C_{2v}^{7} or D_{2h}^{13}
System:	Orthorhombic
Z:	4 molecules/unit cell.

Thus, there are 16 formate ions in each primitive cell, and therefore, 16 components are expected for each internal vibration of the formate ion. None of the two space groups corresponds to a site symmetry of the formate ion higher than C_1; accordingly, the atoms all lie on general positions.

Factor Group C_{2v}. The correlation table is established as follows:



According to crystal-field effect, each internal vibration of the formate ion in the general position C_1 splits into 16 components:

$$4A_1 + 4A_2 + 4B_1 + 4B_2,$$

Raman active vibrations (R):

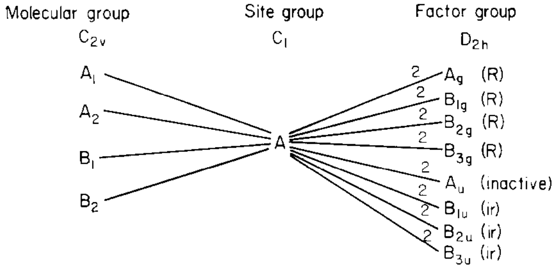
$$4A_1 + 4A_2 + 4B_1 + 4B_2,$$

Infrared active vibrations (ir):

$$4A_1 + 4B_1 + 4B_2.$$

Only vibrations of three symmetry species (A_1, B_1, B_2) are infrared active, and if completely resolved, the spectrum should reveal 12 components for the δ(OCO) vibrational mode. As mentioned in Ref. (*2*) only six components are observed, and the fine structure of the δ(OCO) absorption band corresponds to $4A_1 + 4B_1 + 4B_2$.

Factor Group D_{2h}. In a similar way the following correlation table is established:



Thus, we can expect six infrared active components,

$$2B_{1u} + 2B_{2u} + 2B_{3u}$$

and eight Raman active components,

$$2A_g + 2B_{1g} + 2B_{2g} + 2B_{3g}.$$

The two factor groups C_{2v} and D_{2h} are suitable, and only a study of Raman spectra would be of any assistance in the determination of the space group for the Th(HCOO)$_4\lambda$ crystal; as a matter of fact, if the observed frequencies are the same on infrared and Raman spectra, the space group will be C_{2v}^7, and in the opposite case D_{2h}^{13}.

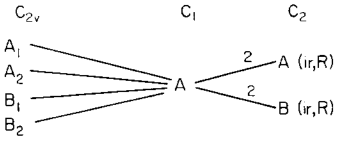
Th(HCOO)$_4\alpha$

X-ray data for this variety are (*6*):

Space group:	$C_2{}^3$, $C_s{}^3$ or C_{2h}^3 (end-centered unit cell)
System:	Monoclinic
Z:	2 for the doubly primitive unit cell

Three factor groups are available, and in each case the atoms all lie on general positions.

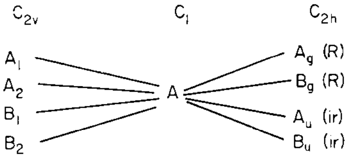
Factor Group C_2. The conventional unit cell being end-centered, the corresponding primitive cell contains only one molecule. Each internal vibration of the formate ion is expected to split into four components. In the case where the factor group is C_2, the following correlation table holds:



The three vibrations at 780, 771, and 765 cm^{-1} correspond to the symmetry species $2A + 2B$.

Factor Group C_s. In the same manner the splitting of the δ(OCO) vibration corresponds to the symmetry species $2A' + 2A''$, which are both Raman and infrared active.

Factor Group C_{2h}.



In this case the infrared spectrum is expected to exhibit at most two distinct components for the δ(OCO) vibration. Since three components are effectively observed, the factor group C_{2h} is not suitable.

Accordingly, the space group symmetry for the Th(HCOO)$_4\alpha$ can possibly be $C_2{}^3$ or $C_s{}^3$.

Th(HCOO)$_4\gamma$

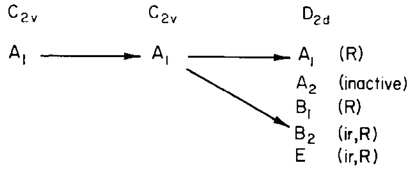
It has been established by X-ray diffraction that the diffraction symbol corresponding to the structure of tetragonal Th(HCOO)$_4\gamma$ is *I*..., the corresponding unit cell being body-centered (*6*). Eight possible space groups agree with this diffraction symbol, and the "International Tables for X-Ray Crystallography" (*9*) gives the number of positions and point symmetries corresponding to each space group. These are summarized as follows:

Space group	Site groups in the unit cell
$C_4{}^5$	$C_4(2)$, $C_2(4)$, $C_1(8)$
$S_4{}^2$	$4S_4(2)$, $2C_2(4)$, $C_1(8)$
C_{4h}^5	$2C_{4h}(2)$, $C_{2h}(4)$, $S_4(4)$, $C_1(4)$, $C_2(8)$, $C_s(8)$, $C_1(16)$
C_{4v}^9	$C_{4v}(2)$, $C_{2v}(4)$, $2C_s(8)$, $C_1(16)$
$D_4{}^9$	$2D_4(2)$, $2D_2(4)$, $C_4(4)$, $5C_2(8)$, $C_1(16)$
D_{2d}^9	$4D_{2d}(2)$, $2C_{2v}(4)$, $2C_2(8)$, $C_s(8)$, $C_1(16)$
D_{2d}^{11}	$2D_{2d}(2)$, $D_2(4)$, $S_4(4)$, $C_{2v}(4)$, $3C_2(8)$, $C_s(8)$, $C_1(16)$
D_{4h}^{17}	$2D_{4h}(2)$, $D_{2h}(4)$, $D_{2d}(4)$, $C_{4v}(4)$, $C_{2h}(8)$, $4C_{2v}(8)$, $C_2(16)$, $3C_s(16)$, $C_1(32)$

The $2C_{2v}(4)$ symbol means that the space group D_{2d}^9 contains two distinct sets of sites having point symmetry C_{2v} with four equivalent sites per set.

In a first step, it will be assumed that the formate ion in the crystal structure of Th(HCOO)$_4\gamma$ is on a site of point symmetry C_{2v}. In this case, only the two space groups D_{2d}^9 and D_{4h}^{17} are suitable, since they contain at least eight sites of point symmetry C_{2v} for the eight formate ions in the body-centered unit cell. For both factor groups D_{2d} and D_{4h}, each internal vibration of the formate ion is expected to split into four components, since the primitive cell of Th(HCOO)$_4\gamma$ contains a single molecule. Henceforth, only the splitting of the δ(OCO) vibration of the totally symmetric species A_1 will be considered.

Factor Group D_{2d}. The correlation tables given by Wilson et al. (*7*) lead to the following scheme:



The infrared spectrum is thus expected to exhibit a single absorption band corresponding to the δ(OCO) vibration. Now, two distinct absorption bands of the same relative intensity are observed at 783 and 764 cm^{-1}. Hence, the space group D_{2d}^9 is not valid.

This result could be foreseen, since the space group D_{2d}^9, which contains $2C_{2v}(4)$, supposes that the eight formate ions are on two crystallographically nonequivalent sets of point symmetry C_{2v} with four equivalent sites per set. This is not in agreement with the body-centered unit cell, which imposes that the two Th(HCOO)$_4\gamma$ molecules are symmetrically equivalent.

Factor Group D_{4h}. In this case, the eight formate ions of the body-centered unit cell are located on eight equivalent sites of point symmetry C_{2v} corresponding to one of the $4C_{2v}(8)$. According to the correlation tables, it is expected that the A_1 vibration splits into four components, and this, in four different ways:

(i) $A_1 \rightarrow A_{1g}(\mathrm{R}) + B_{1g}(\mathrm{R}) + A_{2u}(\mathrm{ir}) + B_{2u}(\mathrm{inactive})$

(ii) $A_1 \rightarrow A_{1g}(\mathrm{R}) + B_{2g}(\mathrm{R}) + A_{2u}(\mathrm{ir}) + B_{1u}(\mathrm{inactive})$

(iii) $A_1 \rightarrow A_{1g}(\mathrm{R}) + B_{1g}(\mathrm{R}) + E_u(\mathrm{ir})$

(iv) $A \rightarrow A_{1g}(\mathrm{R}) + B_{2g}(\mathrm{R}) + E_u(\mathrm{ir})$.

None of these four combinations is in agreement with the two distinct absorption bands observed on the infrared spectrum.

According to the above discussion, we can assert that the site symmetry of the formate ion in the Th(HCOO)$_4\gamma$ crystal is less than C_{2v}. Hence, the possible site groups of the formate ion are subgroups of the C_{2v} point group, i.e., C_2, C_s or C_1. The different possibilities available for the localization of eight formate ions on eight equivalent sites, and the corresponding splittings of the A_1 species into more than four components, have been precluded.

TABLE II

δ(OCO) SPLITTING IN Th(HCOO)$_4\gamma$

Space group	Site group	Splitting of the A_1 δ(OCO) mode[a]
$C_4{}^5$	$C_1(8)$	$A(\mathrm{ir, R}) + B(\mathrm{R}) + E(\mathrm{ir, R})$
$S_4{}^2$	$C_1(8)$	$A(\mathrm{R}) + B(\mathrm{ir, R}) + E(\mathrm{ir, R})$
C_{4h}^5	$C_2(8)$	$A_g(\mathrm{R}) + B_g(\mathrm{R}) + A_u(\mathrm{ir}) + B_u(\mathrm{i})$
	$C_s(8)$	$A_g(\mathrm{R}) + B_g(\mathrm{R}) + E_u(\mathrm{ir})$
$D_4{}^9$	$5C_2(8)$	$A_1(\mathrm{R}) + A_2(\mathrm{ir}) + B_1(\mathrm{R}) + B_2(\mathrm{R})$
		$A_1(\mathrm{R}) + B_1(\mathrm{R}) + E(\mathrm{ir, R})$
		$A_1(\mathrm{R}) + B_2(\mathrm{R}) + E(\mathrm{ir, R})$
C_{4v}^9	$2C_s(8)$	$A_1(\mathrm{ir, R}) + B_2(\mathrm{R}) + E(\mathrm{ir, R})$
D_{2d}^{11}, D_{2d}^9	$3C_2(8)$	$A_1(\mathrm{R}) + A_2(\mathrm{i}) + B_1(\mathrm{R}) + B_2(\mathrm{ir, R})$
		$A_1(\mathrm{R}) + B_1(\mathrm{R}) + E(\mathrm{ir, R})$
	$C_s(8)$	$A_1(\mathrm{R}) + B_2(\mathrm{ir, R}) + E(\mathrm{ir, R})$

[a] ir, Infrared active; R, Raman active; i, Inactive.

Among the several theoretical possibilities mentioned in Table II, only four of them can be retained:

Space group	Site group for the formate ion	Assignment of the δ(OCO) doublet (ir active only)
$C_4{}^5$	C_1	$A + E$
C_{4v}^9	C_s	$A_1 + E$
$S_4{}^2$	C_1	$B + E$
D_{2d}^{11} or D_{2d}^9	C_s	$B_2 + E$

Thus, the 783–764 cm^{-1} doublet presents in each case a doubly degenerated component of symmetry species E. On the other hand, the A_1 vibration being totally symmetric, its splitting leads to at least one totally symmetric component A or A_1. The corresponding space groups which are finally available are $C_4{}^5$ or C_{4v}^9.

The point symmetry of the Archimedean antiprism is D_{4d}. This point group is not suitable for a crystal class, and if we assume that the coordination polyhedron of the thorium atom in Th(HCOO)$_4\gamma$ is the antiprism, the factor groups available for the crystal structure of this compound are the subgroups of D_{4d}, i.e., D_4, C_{4v}, S_8, C_4, C_{2v}, C_2, or C_s. Among these factor groups, the two factor groups which have been retained above are met again. Since the site symmetry of the formate ion in the crystal structure of the investigated tetraformate is C_1 or C_s, it can reasonably be concluded that the coordination polyhedron of the thorium atom in this compound is a distorted Archimedean antiprism. This latter statement is in accordance with the results established in the previous work (Ref. 2).

Splitting of the δ(OCO) Vibrational Mode in the Thorium Tetraformate Hydrates

Up to this day, solely the crystal lattices of the trihydrate and the L-intermediate formate have been established (*6*, *8*). For the latter, the splitting of the δ(OCO) vibration has already been investigated, since this compound presents the same crystal lattice as the λ-anhydrous thorium tetraformate.

X-ray data for $Th(HCOO)_4$, $3H_2O$ are as follows:

Space group:	$C_2{}^2$ or C_{2h}^2 Primitive unit-cell
System:	Monoclinic
Z:	2

There are eight formate ions in the primitive cell, and for both space groups $C_2{}^2$ and C_{2h}^2, the atoms all lie on general positions.

Factor Group C_2.

$$\begin{tikzcd}
C_{2v} & C_1 & C_2 \\
A_1 \arrow[r] & A \arrow[r, "4"] \arrow[dr, "4"] & A\ (\mathrm{ir,R}) \\
& & B\ (\mathrm{ir,R})
\end{tikzcd}$$

Factor Group C_{2h}.

$$\begin{tikzcd}
C_{2v} & C_1 & C_{2h} \\
A_1 \arrow[r] & A \arrow[r, "2"] \arrow[dr, "2"] \arrow[ddr, "2"] \arrow[dddr, "2"] & A_g\ (\mathrm{R}) \\
& & B_g\ (\mathrm{R}) \\
& & A_u\ (\mathrm{ir}) \\
& & B_u\ (\mathrm{ir})
\end{tikzcd}$$

The infrared spectrum of $Th(HCOO)_4$, $3H_2O$ exhibits three components at 798, 793, and 781 cm^{-1} corresponding to the δ(OCO) vibrations, and in this case, only a study of Raman spectra can establish whether the δ(OCO) vibration splits into $4A + 4B$ (space group $C_2{}^2$) or $2A_g + 2B_g + 2A_u + 2B_u$ (space group C_{2h}^2).

Conclusion

According to the above discussion, it has been established that the investigation of the crystal-field splitting of the δ(OCO) vibrational mode in terms of a vibrational analysis under the factor group, succeeds in stating more precisely some crystallographical data of the thorium tetraformates, especially in the case of $Th(HCOO)_4\gamma$,

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