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Interpretation of the IR Spectrum of Manganese Cyclotetraphosphate $Mn_2P_4O_{12}$ and Vibrational Analysis of the Cycle $P_4O_{12}^{4-}$

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Abstract:*The X-ray diffraction structural study showed that the cyclotetraphosphate of manganese,* $Mn_2P_4O_{12}$ *crystallizes in the monoclinic system,* $Z = 4$, *with space group* $C_{2/c}$ (C^6_{2h}), *with the following lattice parameters:* $a = 11.883$ (1) Å - $b = 8.588$ (2) Å$c = 10.137$ (1) Å, $\beta = 119.21$ (2) °. *The crystal lattice contains 4 cycles* $P_4O_{12}^{4-}$ *with symmetry* C_i. *All the atoms occupy the sites " 8f " of symmetry* C_1 *except manganese Mn atoms, which are non equivalent, half occupy the 4 sites "e" of symmetry* C_i *and the other half occupy the 4 sites "d" of symmetry* C_2.

Keywords:*X-ray Diffraction, Cyclotetraphosphate, Condensed Phosphates, Infrared Vibration Spectrometry*

INTRODUCTION

G. Foumakoye and al. (1990) have studied a large number of cyclotetraphosphates of structures determined by X-ray diffraction by IR spectroscopy and Raman scattering and have adopted the same approach as that adopted by K. Sbai (1984) for a cycle of order 3. They confirmed and extended the findings of A. N.Lazarev (1974) and showed that it is possible to characterize the $P_4O_{12}^{4-}$ cyclic anion, particularly by its IR spectrum, and to some extent to forecast the symmetry of Cycle P_4O_{12}, as well as a P_3O_9 cycle, by exploiting the number, profile and position of the sPOP).υ Observed IR bands in the POP valence symmetric vibration domain the diagram of figure1 gives the bands observed in the IR spectra of cyclotetraphosphates as a function of the symmetry of the cycle of each class of isomorphic compounds.

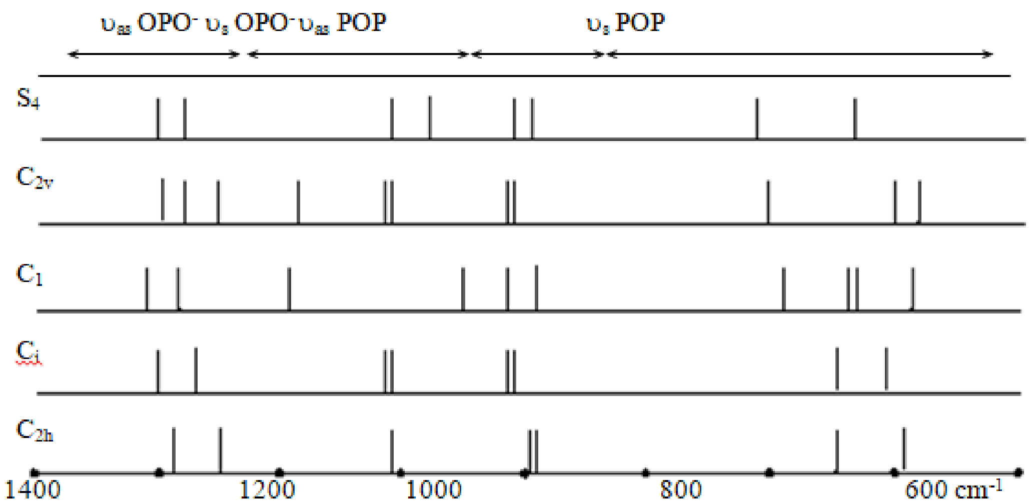


Figure 1: Diagram of the bands in the IR spectra of cyclotetraphosphates according to the symmetry of the cycle.

A detailed examination of the IR spectra of a series of cyclotetraphosphates of different symmetries: S_4, C_{2v}, C_1, C_{2h} and C_1 allowed G. Foumakoye and al. (1990) to reveal a general pattern characterized

From 1330 to 1180 cm-1: antisymmetric vibration of ν_{as} OPO-
From 1180 to 1080 cm-1: symmetrical vibration of ν_s OPO-
From 1060 to 960 cm-1: antisymmetric vibration of ν_{as} POP
From 850 to 660 cm-1: symmetrical vibration of ν_s POP
<660 cm-1: deformation of the cycle + translations and rotations.

Results and Discussion

The experimental IR spectra were in accordance with the theoretical predictions of Table 1. As a result, the authors revealed the spectral characteristics of each type of symmetry:

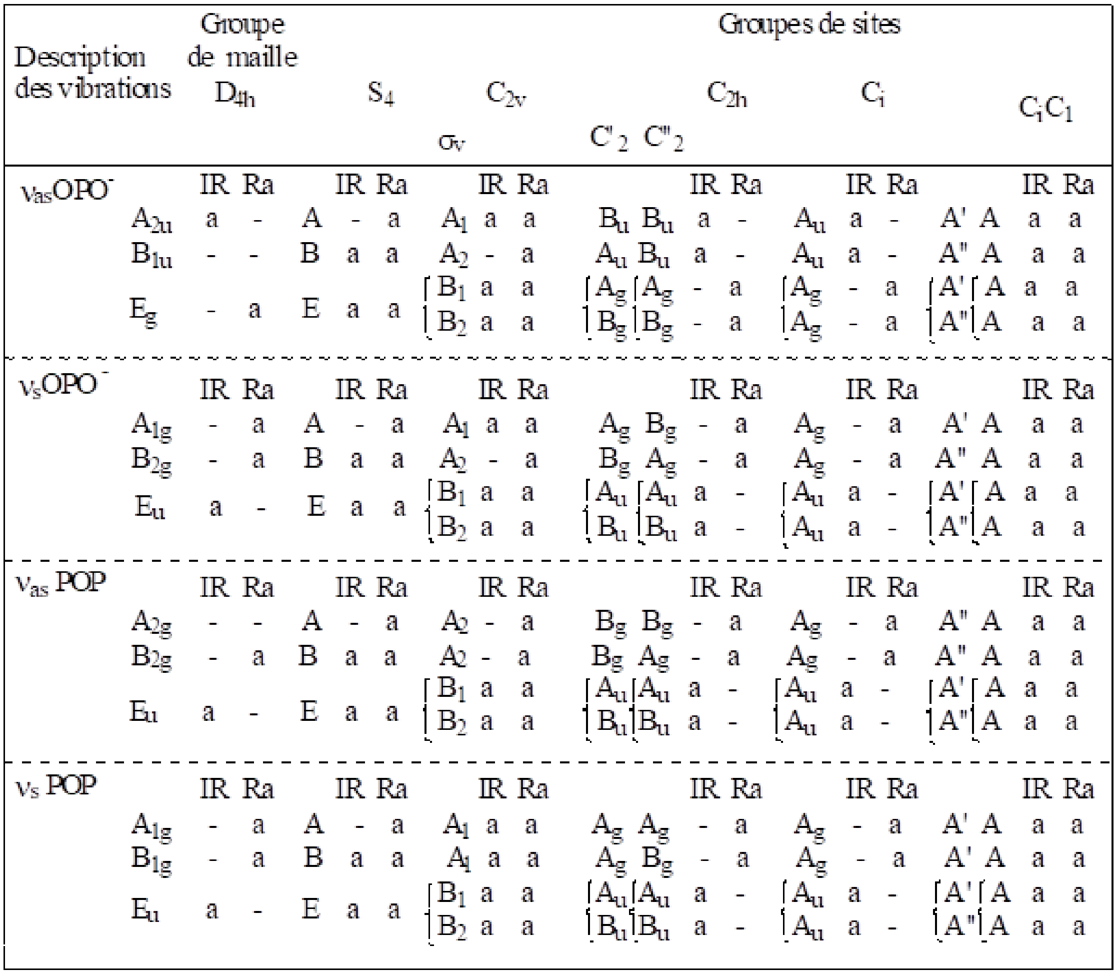
- The presence of two bands, in the area of ν_sPOP vibrations, of medium intensity, one towards 800 cm-1 accompanied by another (possibly split) around 700 cm -1, characterizes a cyclotetraphosphate with anion of symmetry S_4 . When these two bands are observed, a third band is observed of very low intensity situated between 690-660 cm -1, there is a cytotrophosphate anion of C_{2v} symmetry (theoretically, we can also expect the splitting of the Band at 700 cm-1);

  For symmetries C_i (or C_{2h}), we see the disappearance of the band located around 800 cm $^{-1}$, observed in the case of the symmetry S_4 and C_{2v}, and the splitting of that around 700 cm $^{-1}$;
- in the case of symmetry C_1, the known cases show that it is translated into IR by the presence of a band towards 800 cm $^{-1}$, accompanied by a doublet between 730-770 cm $^{-1}$ and a very Low band to 670 cm^{-1}.

1. Theoretical analysis of a $P_4O_{12}^{4-}$ cycle of molecular symmetry D_{4h}

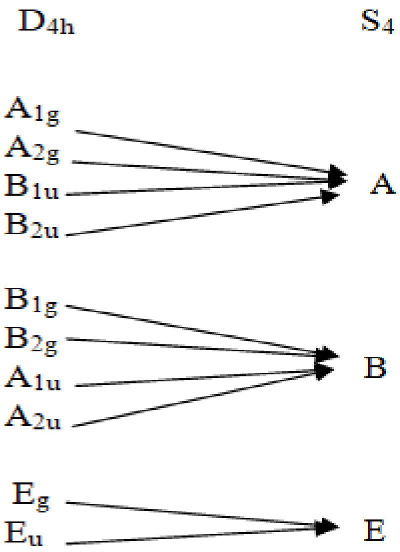
We have found all the results given by G. Foumakoye and al. (1990) for the various symmetries encountered in the $P_4O_{12}^{4-}$ anion. But K. Sbai (1984) detected an error on the way in which modes are transformed during the transition from the symmetry D_{4h} to the symmetry S4. Indeed, during the transition from symmetry D_{4h} to symmetry S4 the modes are transformed in the following way:

Table 1: Description of normal valence vibration modes of the P_4O_{12} cycle for the known symmetries.



Description des vibrations	Groupe de maille						Groupes de sites													
	D_{4h}			S_4			C_{2v}			C_{2h}				C_i			C_iC_1			
							σ_v			C'_2	C''_2									
$\nu_{as}OPO^-$		IR	Ra		IR	Ra		IR	Ra			IR	Ra		IR	Ra			IR	Ra
	A_{2u}	a	-	A	-	a	A_1	a	a	B_u	B_u	a	-	A_u	a	-	A'	A	a	a
	B_{1u}	-	-	B	a	a	A_2	-	a	A_u	B_u	a	-	A_u	a	-	A"	A	a	a
	E_g	-	a	E	a	a	B_1 B_2	a a	a a	A_g B_g	A_g B_g	- -	a a	A_g A_g	- -	a a	A' A"	A A	a a	a a
ν_sOPO^-		IR	Ra		IR	Ra		IR	Ra			IR	Ra		IR	Ra			IR	Ra
	A_{1g}	-	a	A	-	a	A_1	a	a	A_g	B_g	-	a	A_g	-	a	A'	A	a	a
	B_{2g}	-	a	B	a	a	A_2	-	a	B_g	A_g	-	a	A_g	-	a	A"	A	a	a
	E_u	a	-	E	a	a	B_1 B_2	a a	a a	A_u B_u	A_u B_u	a a	- -	A_u A_u	a a	- -	A' A"	A A	a a	a a
ν_{as} POP		IR	Ra		IR	Ra		IR	Ra			IR	Ra		IR	Ra			IR	Ra
	A_{2g}	-	-	A	-	a	A_2	-	a	B_g	B_g	-	a	A_g	-	a	A"	A	a	a
	B_{2g}	-	a	B	a	a	A_2	-	a	B_g	A_g	-	a	A_g	-	a	A"	A	a	a
	E_u	a	-	E	a	a	B_1 B_2	a a	a a	A_u B_u	A_u B_u	a a	- -	A_u A_u	a a	- -	A' A"	A A	a a	a a
ν_s POP		IR	Ra		IR	Ra		IR	Ra			IR	Ra		IR	Ra			IR	Ra
	A_{1g}	-	a	A	-	a	A_1	a	a	A_g	A_g	-	a	A_g	-	a	A'	A	a	a
	B_{1g}	-	a	B	a	a	A_1	a	a	A_g	B_g	-	a	A_g	-	a	A'	A	a	a
	E_u	a	-	E	a	a	B_1 B_2	a a	a a	A_u B_u	A_u B_u	a a	- -	A_u A_u	a a	- -	A' A"	A A	a a	a a

a = actif, - = inactif, { = doublet.



While for G. Foumakoye and al. (1990), the mode A2u of the symmetry D4h is transformed into A of the symmetry S4, which is incorrect.

2. Interpretation of the IR spectrum of manganese cyclotetraphosphate $Mn_2P_4O_{12}$

Vibrational analysis of the cycle $P_4O_{12}^{4-}$ isolated with local symmetry C_i

According to E. Steger and A. Simon (1957), the highest symmetry which the anion $P_4O_{12}^{4-}$ can possess is D_{4h}. For this idealized symmetry the reduced representation is: $\Gamma = 4A_{1g} + 2A_{2g} + 3B_{1g} + 4B_{2g} + 4E_g + A_{1u} + 3A_{2u} + 3B_{1u} + 2B_{2u} + 6E_u$. The separation of normal modes of vibration into stretching and bending modes, $\Gamma = \Gamma_{stretching} + \Gamma_{bending}$, of the cycle $P_4O_{12}^{4-}$was also given by the authors G. Foumakoye and al. (1990):

$\Gamma_{stretching} = 2A_{1g} + A_{2g} + B_{1g} + 2B_{2g} + E_g + A_{2u} + B_{1u} + 3E_u$.

$\Gamma_{bending} = 2A_{1g} + A_{2g} + 2B_{1g} + 2B_{2g} + 3E_g + A_{1u} + 2A_{2u} + 2B_{1u} + 2B_{2u} + 3E_u$.

In the case of the "isolated" cycle $P_4O_{12}^{4-}$ with symmetry C_i, The group theory predicts 42 normal modes : $\Gamma int = 21\ Au + 21\ Ag$. The mode Au is active only in IR and the mode Ag is active only in Raman. The separation of normal modes of vibration of the isolated cycle with symmetry C_i is given in Table 2.

It is clear from this analysis that the site symmetry of the $P_4O_{12}^{4-}$ cycle is C_i. The group theory predicts two IR observed frequencies (2_{Au}) and two Raman frequencies (2_{Ag}) in each of the four domains of stretching vibrations. The site group C_i is centrosymmetric, no IR / Raman coincidence is possible Table 3.

Table 2: Separation of the normal modes of vibration, IR and Raman activities of the cycle $P_4O_{12}^{4-}$ isolated with symmetry C_i (Steger and al., 1957)

	IR	Raman
Internal vibration modes of cycle with symmetry C_i	$21\ A_u$	$21\ A_g$
Stretching modes	$8\ A_u$	$8\ A_g$
Bending modes	$13\ A_u$	$13\ A_g$

The experimental IR spectrum of $Mn_2P_4O_{12}$ prepared by dry method and that obtained during the dehydration of $Mn(NH_4)_4(P_3O_9)_2.6H_2O$ between 320 and 970°C are the same. It shows, three very distinct spectral regions, in the domain of stretching vibrations of the cycle (1400-650 cm^{-1}) by S. zerraf and al. (2017):

From 1330 to 1180 cm^{-1}: in this vibrations domain ν_{as} OPO^-, 3 frequencies are observed (1315, 1301 and 1275 cm^{-1}),

From 1180 to 970 cm^{-1}: in these two vibrations domains $\nu_s OPO^-$ and $\nu_{as}POP$, 4 frequencies are observed (1116, 1101 cm^{-1}) and (1048, 1017 cm^{-1}),

From 850 to 700 cm^{-1}: vibrations domain of ν_s POP, three frequencies are observed at 733 cm^{-1}, 712 cm^{-1} and 669 cm^{-1}.

The position and the profile of the bands situated at 733 and 712 cm^{-1} for the stretching vibrations ν_s POP suggest that the ring $P_4O_{12}^{4-}$has the symmetry C_i or C_{2h}. In fact, all the other known symmetries S_4, C_{2v} and C_1, present in the domain of the stretching vibrations ν_s POP, in addition to the two bands at 733 and 712 cm^{-1}, a band around 800 cm^{-1}(Foumakoye et al., 1990). But for both the symmetries C_i and C_{2h} of an isolated $P_4O_{12}^{4-}$ring, two frequencies are predicted in each of the four domains of the stretching vibrations (ν_{as} OPO^-, ν_s OPO^-, ν_{as} POP, ν_s POP) of the ring $P_4O_{12}^{4-}$(Table 3). The IR spectrum of $Mn_2P_4O_{12}$shows three frequencies in the domain of the stretching vibrations ν_{as} OPO^- : 1330-1180 cm^{-1}. These frequencies are observed at 1315, 1301 and 1275 cm^{-1}. The site symmetry C_i doesn't allow the explanation of the three frequencies observed in the domain of the stretching vibrations ν_{as} OPO^-. Therefore, we make the analysis of the vibrations of the crystalline lattice in order to take into account the interaction between the four cycles of the crystalline lattice of $Mn_2P_4O_{12}$.

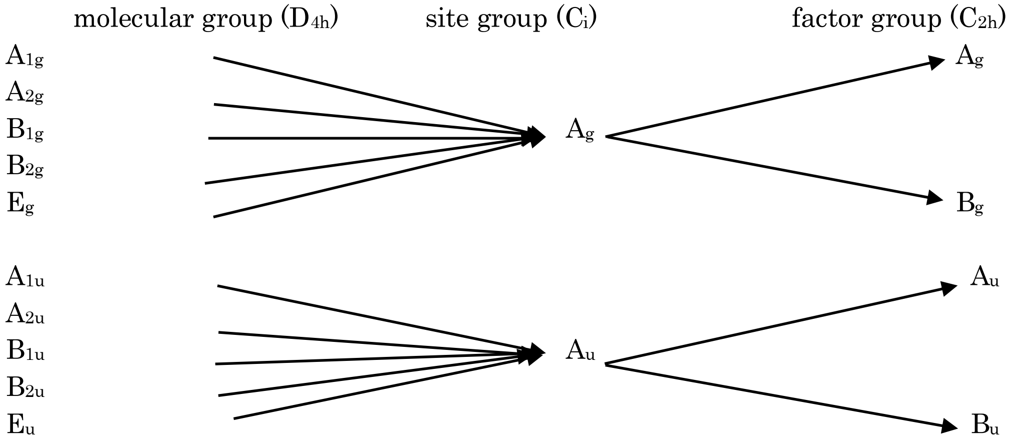
3. Analysis of the vibrations of the manganese cyclotetraphosphate $Mn_2P_4O_{12}$

The crystalline lattice of $Mn_2P_4O_{12}$ contains 4 cycles $P_4O_{12}^{4-}$ with symmetry C_i, Z = 4, while the primitive lattice contains only 2 cycles $P_4O_{12}^{4-}$. The analysis of the vibrations by the method of factor group (C_{2h}) leads to the results gathered in Table 4.

For the two cycles of the primitive lattice, the group theory leads to the existence of 42 IR active modes (21_{Au} + 21_{Bu}) and the same number of modes in Raman (21_{Ag} + 21_{Bg}). No IR / Raman coincidence is possible for the factor group (C_{2h}) centrosymmetric.

During the passage from the isolated cycle with symmetry C_i to the primitive lattice, each band with mode Au active in IR or mode Ag active in Raman should lead respectively to a doublet (Au + Bu) or (Ag + Bg) according to the correlation scheme as follows :

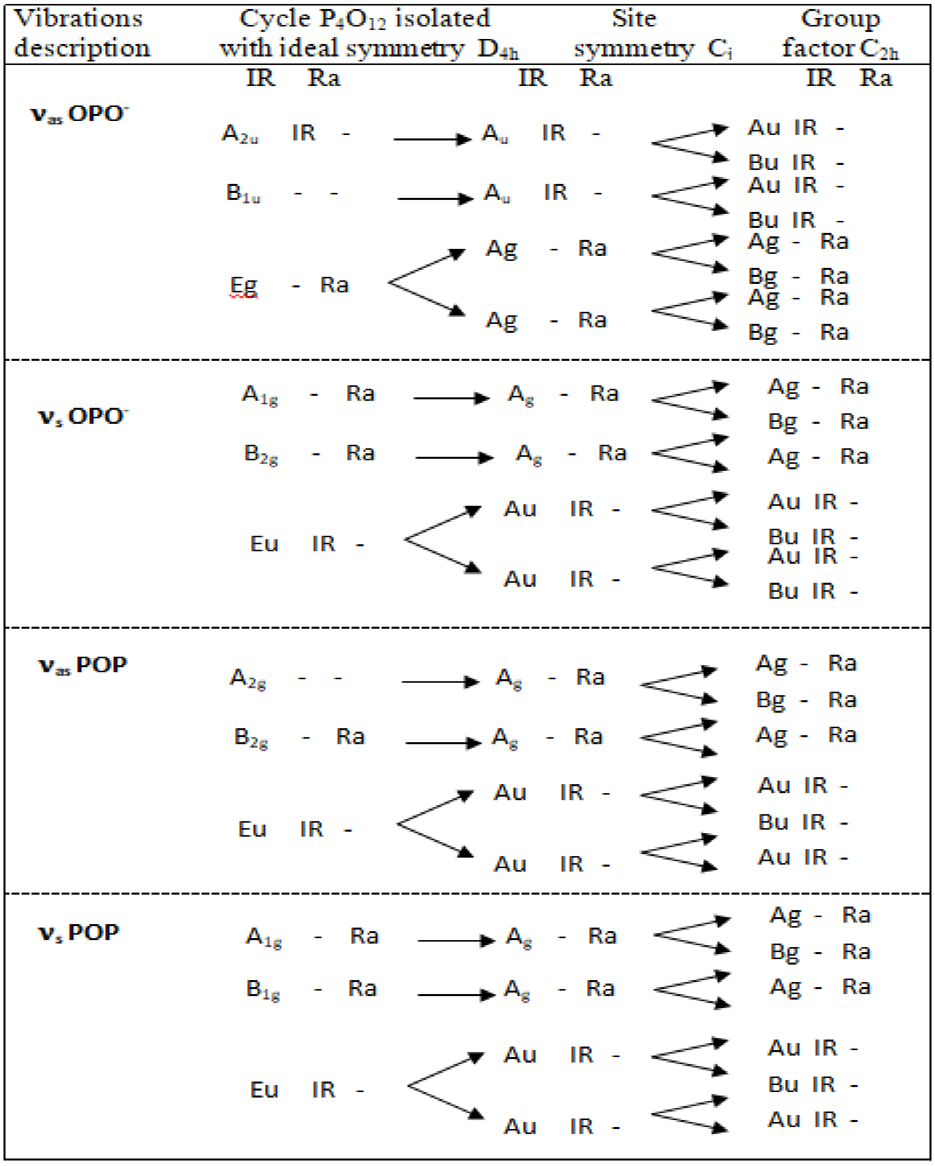
Correlation diagram: molecular group (D_{4h})
– Site group (C_i) – factor group (C_{2h})



It is useful to have a clear idea about the way the stretching vibration modes are corresponding for the idealized isolated cycle D_{4h} and the isolated cycle in the crystal with site symmetry C_i and then when the coupling is established, optionally, between the cycles in the crystal with space group $C_{2/c}$ (C^6_{2h})(Table 3).

The results of this theoretical analysis is that the possible interaction or vibrational couplings between the two cycles $P_4O_{12}^{4-}$ of the primitive lattice $Mn_2P_4O_{12}$ should occur on the IR spectrum and the Raman spectrum by the existence of four observed frequencies in each of the 4 domains of the stretching vibrations (v_{as} OPO^-, v_s OPO^-, v_{as} POP, v_s POP) of the $P_4O_{12}^{4-}$ ring.

Table 3: Comparison of the stretching vibration modes of the cycle P_4O_{12} «isolated" with local symmetry C_i with the two cycles of the primitive lattice interacting with each otherin $Mn_2P_4O_{12}$



Vibrations description	Cycle P_4O_{12} isolated with ideal symmetry D_{4h} IR Ra	Site symmetry C_i IR Ra	Group factor C_{2h} IR Ra
ν_{as} OPO$^-$	A_{2u} IR -	A_u IR -	Au IR - Bu IR -
	B_{1u} - -	A_u IR -	Au IR - Bu IR -
	Eg - Ra	Ag - Ra Ag - Ra	Ag - Ra Bg - Ra Ag - Ra Bg - Ra
ν_s OPO$^-$	A_{1g} - Ra	A_g - Ra	Ag - Ra Bg - Ra
	B_{2g} - Ra	A_g - Ra	Ag - Ra
	Eu IR -	Au IR - Au IR -	Au IR - Bu IR - Au IR - Bu IR -
ν_{as} POP	A_{2g} - -	A_g - Ra	Ag - Ra Bg - Ra
	B_{2g} - Ra	A_g - Ra	Ag - Ra
	Eu IR -	Au IR - Au IR -	Au IR - Bu IR - Au IR -
ν_s POP	A_{1g} - Ra	A_g - Ra	Ag - Ra Bg - Ra
	B_{1g} - Ra	A_g - Ra	Ag - Ra
	Eu IR -	Au IR - Au IR -	Au IR - Bu IR - Au IR -

Table 4: Separation of the normal modes of vibration, IR and Raman activities of the $P_4O_{12}^{4-}$ cycles in $Mn_2P_4O_{12}$

	IR	Raman
Active internal modes (total)	$27A_u + 27B_u$	$25\ A_g + 26B_g$
Lattice vibration modes	$6\ A_u + 6\ B_u$	$A_g + 2\ B_g$
Libration modes of the cycles	---	$3\ A_g + 3\ B_g$
Internal vibration modes of the cycles	$21\ A_u + 21\ B_u$	$21\ A_g + 21\ B_g$
Stretching modes	$8\ A_u + 8\ B_u$	$8\ A_g + 8\ B_g$
Bending modes	$13\ A_u + 13\ B_u$	$13\ A_g + 13\ B_g$

The experimental IR spectrum of $Mn_2P_4O_{12}$ shows two frequencies in each of the two fields of the stretching vibrations ν_s OPO^- (1116, 1101 cm^{-1}), ν_{as} POP (1048, 1017 cm^{-1}) and three frequencies in each of the two domains of the stretching vibrations ν_{as} OPO^- (1315, 1301 and 1275 cm^{-1}) and ν_s POP (733, 712 and 669 cm^{-1}). The assignment of the stretching frequencies of the $P_4O_{12}^{4-}$ cycles on the basis of factor group C_{2h} is given in Table 5. Vibrational couplings are therefore effective only for antisymmetric vibrations, ν_{as} OPO^-, involving external oxygen atoms of the ring which are the most susceptible to interact with a neighbor ring through bonds between cation and external oxygen atoms of the $P_4O_{12}^{4-}$ cycle. But, for the vibrations of the groups P-Oi-P, ν_{as} POP and ν_s POP, couplings are less important and can be observed as two bands instead of four theoretically expected. The results of the analysis of the IR spectrum related to the symmetry of the ring $P_4O_{12}^{4-}$ in the manganese cyclotetraphosphate, $Mn_2P_4O_{12}$, are in good agreement with the structural resolution (Hinsch and al., 1986).

Table 5: Assignments of the stretching vibrations of the $P_4O_{12}^{4-}$ cycles in $Mn_2P_4O_{12}$

Vibrations description	Cycle P_4O_{12} isolated with ideal symmtry D_{4h}			Site symmetry C_i			Group factor C_{2h}			Observed IR frequencies	Calculated frequencies S_4 [7]	
ν_{as} OPO^-		IR	Ra		IR	Ra		IR	Ra	IR	IR	Ra
	A_{2u}	IR	-	A_u	IR	-	Au	IR	-	1315	1275	-
							Bu	IR	-	1301		
	B_{1u}	-	-	A_u	IR	-	Au	IR	-		1261	-
							Bu	IR	-	1275		
				Ag	-	Ra	Ag	-	Ra			
	Eg	-	Ra									
							Ag	-	Ra			
							Bg	-	Ra			
ν_s OPO^-	A_{1g}	-	Ra	A_g	-	Ra	Ag	-	Ra		-	1128
							Bg	-	Ra			
	B_{2g}	-	Ra	A_g	-	Ra	Ag	-	Ra		-	-
				Au	IR	-	Au	IR	-	1116		
	Eu	IR	-				Bu	IR	-		1121	-
							Au	IR	-	1101		
							Bu	IR	-			
ν_{as} POP	A_{2g}	-	-	A_g	-	Ra	Ag	-	Ra			
							Bg	-	Ra			
	B_{2g}	-	Ra	A_g	-	Ra	Ag	-	Ra			
				Au	IR	-	Au	IR	-	1048	994	-
	Eu	IR	-				Bu	IR	-	1017		
							Au	IR	-			
ν_s POP							-			733		
				Au	IR	-	Au	IR	-	712	739	-
	Eu	IR	-				Bu	IR	-			
							Au	IR	-			
							Bu	IR	-	669		
	A_{1g}	-	Ra	A_g	-	Ra	Ag	-	Ra			
	B_{1g}	-	Ra	A_g	-	Ra	Bg	-	Ra			
							Ag	-	Ra			

Conclusion

With further increase in temperature, the latest amorphous phase is converted to a mixture of $Mn_2P_2O_7$ and $Mn_2P_4O_{12}$. Finally the mixture $Mn_2P_2O_7$ and $Mn_2P_4O_{12}$ leads by heating at higher temperature to $Mn_2P_4O_{12}$. So, the final product of the total thermal dehydration of $Mn_3 (P_3O_9)_2.10H_2O$ under atmospheric pressure is its corresponding anhydrous cyclotetraphosphate $Mn_2P_4O_{12}$. The vibrational spectra $Mn_2P_4O_{12}$ is examined and interpreted in the domain of the stretching vibrations of the P_4O_{12} rings.

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