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Theoretical study of the structure and position of the hydrogen phosphate anion intercalated between layers of the layered double hydroxide [Zn-Al-HPO_4], using the DFT B3LYP/6-311G method

Ibtissam Bouimadaghene, Habib El Alaoui El Abdallaoui, and Abdeslam El Hajbi

Chemistry Department, Faculty of Science,
Chouaïb Doukkali University,
El Jadida, Morocco

ABSTRACT: In this work, we carried out theoretical calculations to determine the structure of the hydrogen phosphate anion (HPO_4^{2-}) in the free state and its structure and position when intercalated between layers of the zinc and aluminum layered double hydroxide [Zn-Al-HPO_4]. We hypothesized that the anion might be intercalated either by forming strong bonds with zinc, or by means of hydrogen bonds with water molecules, and we performed a number of different calculations to determine which of the two hypotheses was correct. We used the DFT B3LYP/6-311G *ab initio* quantum method to calculate interatomic and interlayer distances, vibration frequencies and enthalpy of formation of the hydrogen phosphate anion in the free state and in the various models proposed, as well as the force constant of the Zn-O bond in the different chemical structures. Results obtained by DFT B3LYP/6-311G were compared to those obtained by experiment and by using the semi-empirical methods AM1 and PM3, and it was shown that results obtained by DFT B3LYP/6-311G correspond more closely to experimental results than those obtained by the two semi-empirical methods. Finally, we established that the hydrogen phosphate anion HPO_4^{2-} is intercalated between the two layers of the layered double hydroxide [Zn-Al-HPO_4] by means of hydrogen bonds with water molecules, while the phosphate anion PO_4^{3-} is bound to zinc atoms.

KEYWORDS: Interatomic distance; interlayer distance; vibration frequency; enthalpy of formation; intercalation.

1 INTRODUCTION

Layered double hydroxides (LDH) (also known as anionic clays, mixed metal layered double hydroxides, or hydrotalcite-type compounds) have been studied intensively in recent years because of their electrochemical properties and capacity for anionic exchange [1]. These two-dimensional materials show a high degree of anisotropy in their chemical bonds, which are strong within the hydroxyl layers and weak between the layers [2]. This makes it possible to intercalate a wide variety of anions, both organic and inorganic.

The general formula for LDH is $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[A^{m-}_{x/m}nH_2O]^{x-}$ [3]. This can be abbreviated to $[M^{II}M^{III}X]$ [4] where M^{II} represents the divalent cation (Ca_2^+, Mg_2^+, Zn_2^+, Co_2^+, Ni_2^+, Cu_2^+, Mn_2^+, etc.) and M^{III} the trivalent cation (Al_3^+, Cr_3^+, Fe_3^+, Co_3^+, Ni_3^+, Mn_3^+, etc.); $X = \frac{M^{II}}{M^{II}+M^{III}}$ is the rate of replacement of the divalent cation by the trivalent cation; and A^{m-} is the anion bound to the water molecules in the interlayer space. The main anions which have been intercalated are the inorganic anions F^-, Cl^-, ClO_3^-, NO_3^-, IO^-_3, SO_4^{2-}, CO_3^{2-}, HPO_4^{21-}, etc. and the complex anions $Fe(CN)_6^{3-}$, PCl_4^{2-}, etc.

The charge of the layer is $y = x$ when *M* is divalent, $y = 2x - 1$ when *M* is monovalent and $y = 2x$ when *M* is tetravalent. The structure of the layers is a coplanar association of *M*$(OH)_6$ octahedra forming brucite-type hydroxyl layers of the formula *M*$(OH)_2$. The coexistence of divalent and trivalent cations in these layers produces an excess positive charge which is counterbalanced by the intercalation of anionic species and water molecules in the interlayer space [2].

Study of the structural arrangement of the water molecules, anions and other molecular species within the interlayer space enables us to understand the reactions which take place in various technical, physical-chemical and biological procedures. The aim of the present study was to compare experimental results with results of theoretical calculations concerning the hydrogen phosphate anion in the free state, when bound to water molecules by means of hydrogen bonds, and intercalated between the layers of the LDH [Zn-Al-HPO_4].

The hydrogen phosphate anion is used among other things in agricultural fertilizers, but in the free state the anion dissolves rapidly in water and is dispersed in the soil. Intercalating the anion within a LDH enables it to remain useful for longer. In our study we attempted to determine the most stable configuration of the hydrogen phosphate anion intercalated in the layered double hydroxide [Zn-Al-HPO_4]. We used density functional theory (DFT) B3LYP/6-311G to calculate interatomic and interlayer distances, vibration frequencies and enthalpies of formation of the intercalation of the hydrogen phosphate anion [5] as well as the force constant of the Zn-O bond in the various chemical systems considered. We then compared our results with values calculated using the semi-empirical methods AM1 and PM3 [6].

2 METHODS OF THEORETICAL CALCULATION

Optimization of the geometric parameters of the molecules studied and calculation of interatomic and interlayer distances, vibration frequencies and enthalpies of formation of intercalation of the hydrogen phosphate anion as well as force constants of the Zn-O bond in the various chemical systems proposed were carried out using the DFT method B3LYP with the base 6-311G [7], using Gaussian 09 software [8].

In previous work we used the semi-empiric methods AM1 and PM3 [6] to determine the behavior of the hydrogen phosphate anion intercalated between layers of the LDH [Zn-Al-HPO_4] and compared the results with experimental results, in order to establish the relation between experimental results and theory. In the present study we applied DFT B3LYP to complete these studies, using a number of different bases (STO-3G, 3-21G, 6-31G, 6-311G, SDD), and found that only 6-311G gave results which corresponded to experimental results. In this paper therefore we shall limit our discussion to results obtained using B3LYP/6-311G.

3 RESULTS AND DISCUSSION

3.1 STRUCTURAL STUDY OF THE HPO_4^{2-} ANION IN THE FREE STATE

The hydrogen phosphate anion shown in Figure 1 possesses a number of structures which contribute to its stability by resonance. The geometric parameters (Table I) show that the distance P_1-O_5 is greater than the three others. The symmetry of the HPO_4^{2-} anion is therefore assimilated experimentally to a pseudo C_{3v} symmetry [9] and theoretically to a C_s symmetry.

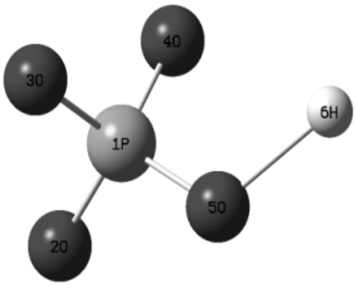


Fig. 1. HPO_4^{2-} (hydrogen phosphate) anion

NB. 1P in the above diagram corresponds to P_1 in the text and in Table 1, 2O corresponds to O_2 and so on.

Table 1. Optimized geometric parameters of the HPO_4^{2-} anion

	Distances (Å)				Absolute error (Å)		
	DFT B3LYP/ 6-311G	AM1	PM3	Experimental	DFT B3LYP/ 6-311G	AM1	PM3
P_1—O_4	1.624	1.515	1.584	1,53	0.094	0.015	0.054
P_1—O_2	1.597	1.509	1.574	1.522	0.075	0.013	0.052
P_1—O_3	1.597	1.509	1.574	1.519	0.078	0.01	0.055
P_1—O_5	1.796	1.702	1.823	1.587	0.209	0.115	0.236
O_5—H_6	1.018	0.948	0.943	-	-	-	-

	Angles θ (°)		
	DFT B3LYP/ 6-311G	AM1	PM3
$O_3P_1O_4$	115.295	115.316	114.453
$O_2P_1O_4$	115.316	115.765	114.453
$O_5P_1O_4$	92.018	97.0357	99.7515
$H_6O_5P_1$	86.3801	107.436	107.055

Interatomic distances calculated using DFT B3LYP/6-311G are close to those obtained by X-ray diffraction [10]. Absolute error is around 0.1% except for the distance P_1—O_5, for which it is around 0.2%.

Table 2 shows the vibration frequencies of the hydrogen phosphate anion in the free state, the PO_4^{3-} base matrix [11], the hydrogen phosphate anion bound to water molecules [12] and the same anion intercalated between layers of the LDH [Zn-Al-HPO4] [13].

Table 2. Vibration frequencies (cm^{-1})

	Vibration frequencies (cm^{-1})			
	$ν_1$	$ν_2$	$ν_3$	$ν_4$
HPO_4^{2-}	932	417	1059	557
PO_4^{3-}	940	420	1020	560
$Na_2HPO_4.2H_2O$	993 953	-	1135 1120 1070 1055	575 558 539 520
Na_2HPO_4	948	461	1150 1068	590 570 547 522
[Zn-Al-HPO_4]	780	-	1030	550

Table 2 shows that vibration modes $ν_1$, $ν_2$, $ν_3$ and $ν_4$ are active in infrared for the HPO_4^{2-} anion and for the anion of the base matrix PO_4^{3-} in the free state. However, the frequency corresponding to $ν_2$ is inactive for the HPO_4^{2-} anion when it is bound to water molecules and when it is intercalated in the LDH [Zn-Al-HPO_4], which might indicate that the C_s symmetry of the HPO_4^{2-} anion intercalated between the LDH layers is maintained (one anion bound to one or two zinc atoms) or transformed into D_{2h} (two anions bound to two zinc atoms), as described below. We hypothesized that the HPO_4^{2-} anion may be intercalated within the [Zn-Al-HPO_4] phase either by strong bonds with the zinc atoms, or by hydrogen bonds with the water molecules. In order to check these hypotheses, we calculated the vibration frequencies in each case.

3.2 STRUCTURAL STUDY OF THE PO_4^{3-} ANION IN THE INTERLAYER SPACE

The interaction between the intercalated anion and the hydroxyl layer depends upon the intrinsic characteristics of the anionic species. These characteristics also affect the maximum temperature at which the layered structure is maintained [14]. In the case under study here, the interlayer distance is considerably reduced, from 10.51Å to 6.98Å [15], by the departure of the water molecules when the hydrogen phosphate ions are intercalated in accordance with the following equation:

$$M - \mathrm{OH} + \mathrm{PO_3} - \mathrm{OH} \rightarrow M - \mathrm{O} - \mathrm{PO_3} + \mathrm{H_2O}$$

The anion intercalated in the interlayer space liberates one hydrogen atom when it binds to a metallic cation which itself liberates one hydroxyl group. When heated to 100°C so that the water molecules are driven off, a contracted phase is obtained in which the position of the anions is stable [16]. The theoretical distance *d* (Figure 2) is the sum of the height *h* of the phosphate anion PO_4^{3-} obtained using DFT B3LYP/6-311G, the distance between two hydroxyl groups along the *c* axis of the same layer (2Å) and the distance between the anion and the layer (2.80Å), i.e. a total of 4.80 Å.

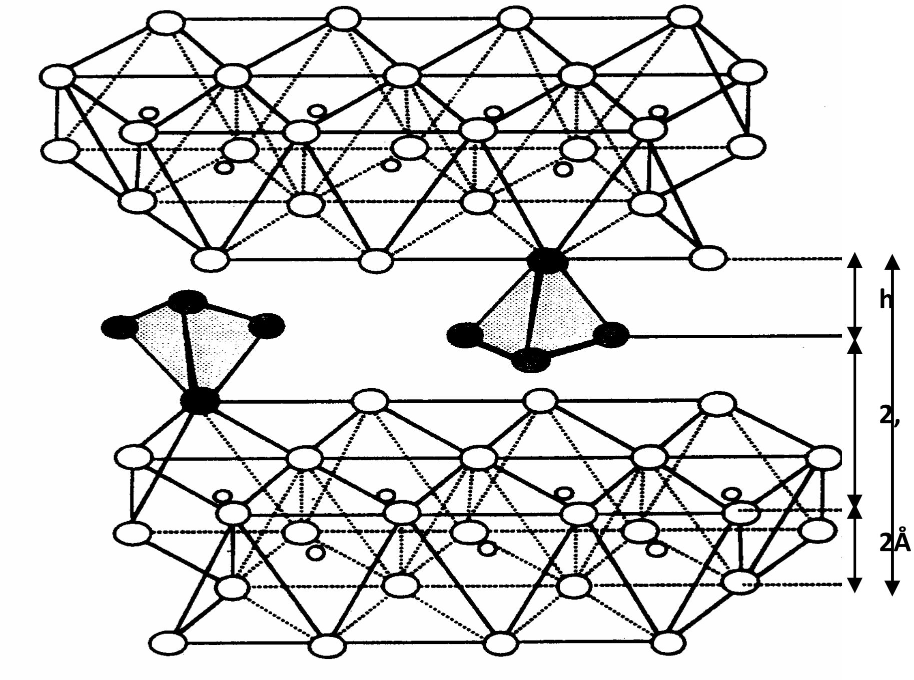


Fig. 2. Reconfiguration of the interlayer space following grafting of the PO_4^{3-} anion

The distance *h* can be determined by calculating the height of the regular pyramid of triangular base whose corners are hydrogen atoms. The PO_4^{3-} anion may be compared to a regular tetrahedron ABCD whose six edges are all the same length and whose four faces are equilateral triangles (Figure 3).

The height [AH] passes through the intersection of the median lines of the equilateral triangle forming the base. (M and N are the halfway points along the edges). Applying Pythagorus' theorem to the triangle BNC with a right angle at N, and then to the triangle AHN with a right angle at H, we obtain the following equation:

$$AH = \frac{\sqrt{6}}{3} AB$$

i.e.

$$h = \frac{\sqrt{6}}{3} O_i O_j$$

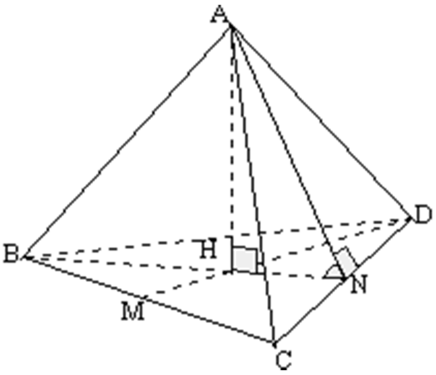


Fig. 3. PO_4^{3-} anion compared to a regular tetrahedron

The interatomic distances O_i–O_j as calculated [6] and the interlayer distance *d* calculated using the method DFT B3LYP/6-311G, AM1 and PM3 are shown in Table 3, together with the distance *d* obtained experimentally [15].

Table 3. Theoretical and experimental interlayer distances of intercalation of the PO_4^{3-} anion

	DFT B3LYP/ 6-311G	**AM1**	**PM3**
Interatomic distance O_i–O_j	2.68	2.54	2.71
Height *h* (Å)	2.18	2.07	2.21
Distance *d*: calculated (Å)	6.98	6.87	7.01
Distance *d*: experimental (Å)	6.98		
Absolute error (Å)	0	0.11	0.03
Relative error (%)	0	1.58	0.43

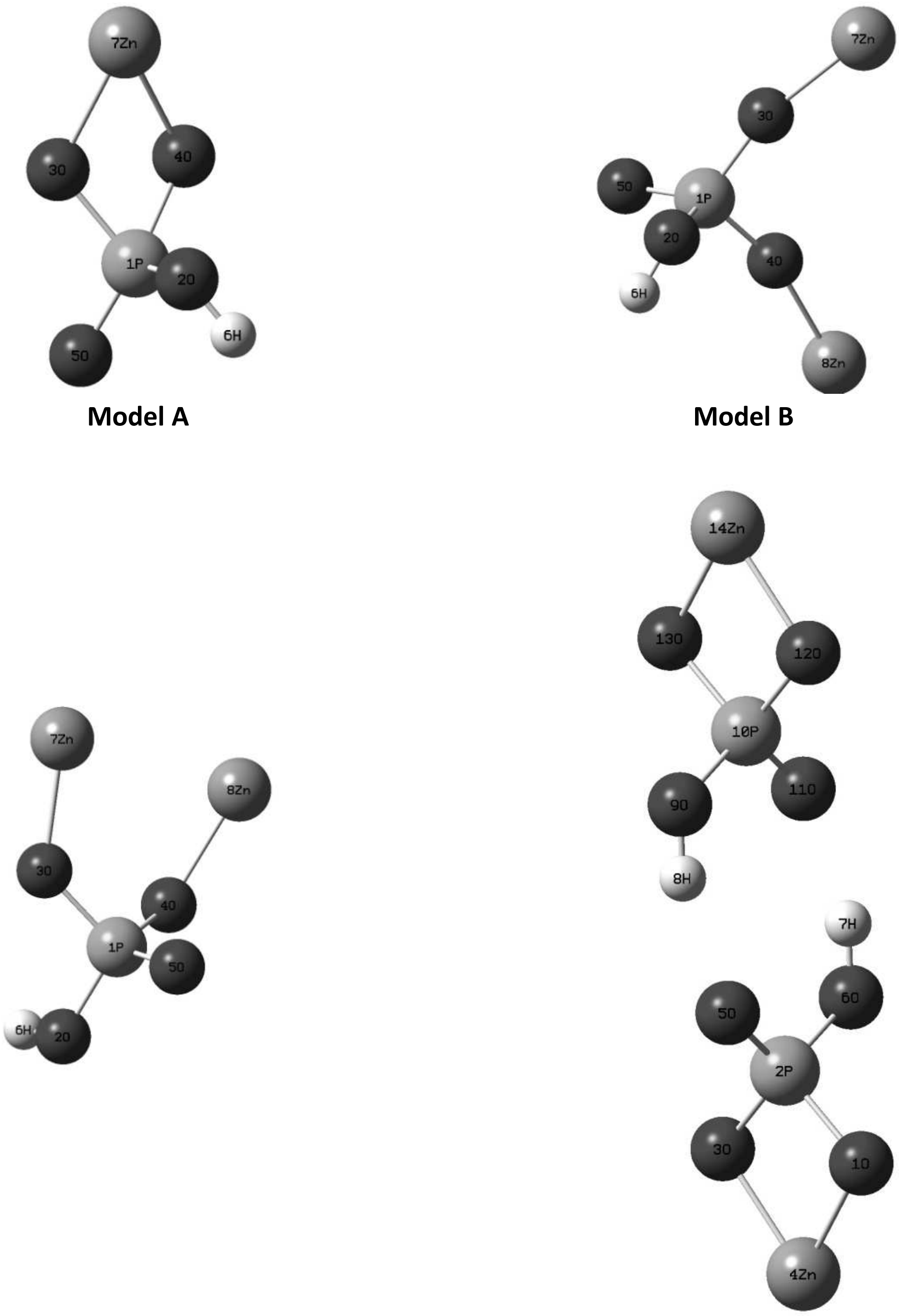
Calculation using DFT B3LYP/6-311G gave the same result as that obtained experimentally, namely 6.98 Å with 0% error (Table 3), showing that this is the most reliable method. These results show that the phosphate anion has indeed been grafted to the layers, with the formation of new Zn–O–PO_3 bonds.

3.3 THE HPO_4^{2-} ANION IN STRONG BONDS

A number of different models may be proposed for this structure. Strong bonds may form randomly between the HPO_4^{2-} anions and the two metals in the layer. The divalent metal is present in significantly greater quantity than the trivalent metal, which leads us to suggest four main models (Figure 4) for which the geometric parameters, theoretical interlayer distance, vibration frequencies, enthalpies of formation and force constants can be calculated.

Model A: One HPO_4^{2-} anion bound to one zinc atom with C_s symmetry.
Model B: One HPO_4^{2-} bound to two zinc atoms in the same layer with C_s symmetry.
Model C: One HPO_4^{2-} anion bound to two zinc atoms in the same layer with C_s symmetry.
Model D: Two HPO_4^{2-} anions bound to two zinc atoms in two successive layers with D_{2h} symmetry.

In order to determine which of the four models is the most stable, we calculated their geometric parameters using DFT B3LYP/6-311G (Tables 4 and 5), fundamental vibration frequencies (Table 6) and enthalpies of formation (Table 7). We also calculated the force constants of the Zn-O bonds in the models A, B, C and D (Table 8).



Model A

Model B

Model C

Model D

Fig. 4. Fig. 4. Models A, B, C and D

Table 4. Models A, B, C and DOptimized geometric parameters of the three models A, B and C

N.B. Values calculated by AM1 and PM3 are those we obtained in a previous study [6]. This study did not include values for Zn_7-Zn_8.

	Model A			Model B			Model C		
	DFT B3LYP/6-311G	AM1	PM3	DFT B3LYP/6-311G	AM1	PM3	DFT B3LYP/6-311G	AM1	PM3
	Distance (Å)								
P_1-O_3	1.739082	1.71712	1.60028	1.681749	1.71712	1.68504	1.656102	1.55495	1.64648
P_1-O_4	1.739091	1.71712	1.60028	1.681915	1.71712	1.68504	1.645126	1.55495	1.64648
P_1-O_5	1.571209	1.46123	1.4574	1.572174	1.46123	1.46807	1.585770	1.46441	1.47422
P_1-O_2	1.715401	1.68918	1.60285	1.699679	1.68918	1.69809	1.740920	1.6118	1.70424
O_2-H_6	0.972861	0.944321	0.95467	0.971949	0.944321	0.9444	0.971538	0.95291	0.94397
Zn_7-O_3	1.923754	1.84349	1.9427	1.893481	1.84349	1.82847	1.924056	1.93609	1.7973
Zn_8-O_4				1.893431	2.01384	1.82847	1.893571	1.93609	1.7973
Zn_7-Zn_8				2.546			6.282		

	Angle θ (°)								
$O_4P_1O_3$	90.6175	90.34999	92.0608	100.9515	96.78386	107.17484	99.2983	99.21509	99.43587
$O_5P_1O_3$	119.6429	121.95194	120.8876	114.6592	119.8831	116.37134	117.5566	118.99216	118.66946
$O_2P_1O_3$	103.0951	106.74618	105.07443	106.5414	106.15715	102.88384	105.4555	106.68648	104.89996
$H_6O_2P_1$	114.0639	114.47572	114.16848	114.11	113.81866	112.85571	112.9964	113.94299	113.40361
$Zn_7O_3P_1$	90.6175	99.08646	91.86913	115.6322	129.04174	118.08806	128.9707	163.63165	164.82321
$Zn_8O_4P_1$				115.606	129.04174	118.08806	131.9457	163.63165	164.82321

Table 5. Optimized geometric parameters of model D

	DFT B3LYP/6-311G	AM1	PM3
	Distance (Å)		
O_1—P_2	1.739188	1.60529	1.72149
O_3—P_2	1.739152	1.60438	1.71988
O_6—H_7	1.026065	0.96478	0.9655
O_5—H_8	1.516337	2.0662	1.7961
H_8—O_9	1.026065	0.96478	0.9655
O_3—Zn_4	1.922519	1.93966	1.84151
P_2—O_5	1.584394	1.46304	1.48042
P_2—O_6	1.656791	1.58503	1.66001
O_9—P_{10}	1.656791	1.58503	1.66001
P_{10}—O_{11}	1.584393	1.46304	1.48042
P_{10}—O_{12}	1.739167	1.60455	1.71915
P_{10}—O_{13}	1.739173	1.60529	1.72149
O_{12}—Zn_{14}	1.922520	1.93966	1.84151

	Angle θ (°)		
$O_3P_2O_1$	95.3073	90.21513	91.83932
$Zn_4O_3P_2$	90.3455	98.9677	91.90173
$O_5P_2O_1$	115.3053	119.41925	118.76831
$O_6P_2O_1$	106.7581	106.26565	106.61905
$H_7O_6P_2$	116.8274	117.39804	116.21191
$H_8O_5P_2$	135.8102	153.11287	138.09187
$O_9H_8O_5$	172.0896	156.73556	173.91434
$P_{10}O_9H_8$	116.8272	117.39804	116.21191
$O_{11}P_{10}O_9$	115.2729	112.58903	111.58168
$O_{12}P_{10}O_9$	106.7541	106.27571	106.76512
$O_{13}P_{10}O_9$	106.7538	106.27571	106.76512
$Zn_{14}O_{12}P_{10}$	90.3451	98.9677	91.90173

Table 6. Vibration frequencies of models A, B, C and D and of the LDH [Zn-Al-HPO_4] (cm^{-1})

	ν_1			ν_2			ν_3			ν_4		
	DFT	AM1	PM3	DFT	AM1	PM3	DFT	AM1	PM3	DFT	AM1	PM3
Model A	1004	923	215	390 373	406 431	357 380	1078	1049	961	726	865	722 728
Model B	808 964	909 947	808	400 358	394 431	362	1086	1054	948	528 691	563	689 770
Model C	832 979	817	841	293 375	412 443	367 422	1075	959	941	666 798	533	771
Model D	936 981	927 932	829 837	401 412 456	413 432 442	365 386 438 470	981	1069 1079	960 972	834 837 889	849 857	720 424 739
[Zn-Al-HPO_4]	780			-			1030			550		

Table 7. Enthalpy of formation of the HPO_4^{2-} anion and the four models A, B, C and D calculated by DFT B3LYP/6-311G (Kcal/mol)

	Enthalpy of formation
HPO_4^{2-}	- 403345.985
Model A	-1519880.819
Model B	-2636424.798
Model C	-2636419.571
Model D	-3039787.994

Table 8. Force constants of the Zn-O bond of the four models A, B, C and D calculated by DFT B3LYP/6-311G (mdyn/Å)

	DFT B3LYP/6-311G	AM1	PM3
Model A	0.8887	1.2291	1.3778
Model B	0.882	0.8325	1.3489
Model C	0.3551	0.5708	0.9013
Model D	1.292	1.2493	1.3985

The two bonds P_1-O_3 and P_1-O_4 are longer in models A, B and C than in the free HPO_4^{2-} anion. However the length of the P_1-O_5 bond remains almost constant in the free anion and in models A, B and C.

From Tables 7 and 8 we can draw two main observations. Firstly, the enthalpy of formation calculated using DFT B3LYP/6-311G shows that in absolute value the ΔH°f of model D is greater than that of model B, that of model B is greater than that of model C, that of model C is greater than that of model A, and that of model A is greater than that of the hydrogen phosphate anion HPO_4^{2-} in the free state. Secondly, the force constant of the Zn-O bond in model D is greater than that in model A, that in model A is greater than that in model B, and that in model B is greater than that in model C. We can see that the four models A, B, C and D do not have the same physico-chemical properties, even though models B and C in particular appear very similar in structure, and can be transformed into each other by rotation. The results show that model D is the most stable of the four, and that the hydrogen phosphate anion intercalated between the layers of the LDH [Zn-Al-HPO$_4$] is probably bound not to the zinc atoms but to water molecules by hydrogen bonds.

3.4 THE HPO_4^{2-} ANION IN HYDROGEN BONDS

The hydrogen bond forms between the hydrogen atoms of the water molecules and the oxygen atoms in non-shared doublets of the HPO_4^{2-} anion. The anion has eight free doublets and two negative charges, enabling it to bind to ten water molecules. In this study, we consider only the five most stable cases (Figure 5).

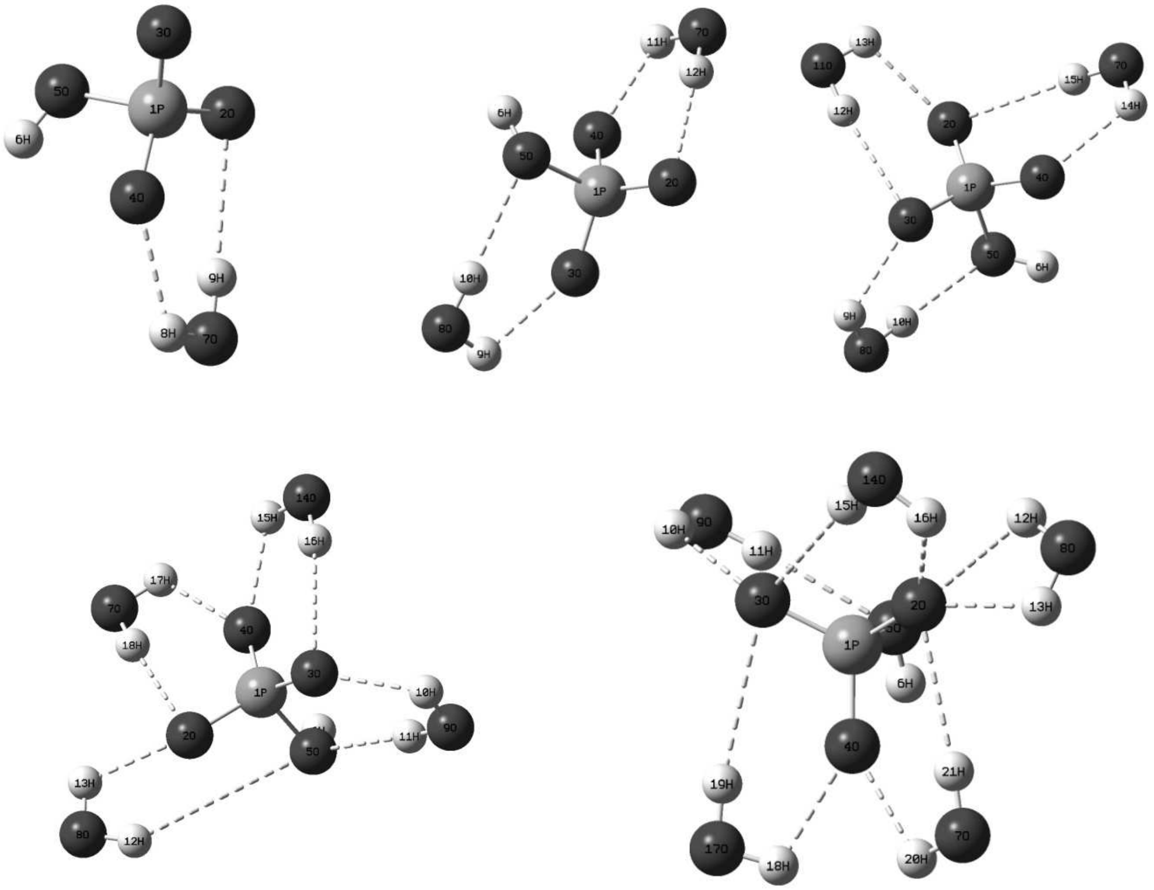


Fig. 5. The HPO_4^{2-} anion bound to water molecules by hydrogen bonds: the five most stable structures

In order to determine the most stable configuration, we determined the enthalpy of formation of each system as a function of a number of geometric parameters. The formation of the hydrogen bonds corresponds to the following reaction:

$$\mathrm{HP}_4^{2-} + n\mathrm{H_2O} \rightarrow (\mathrm{HPO_4}, n\mathrm{H_2O})^{2-}$$

$$\Delta \mathrm{H}°_r = \Delta \mathrm{H}°_f(\mathrm{HPO}_4^{2-}, n\mathrm{H_2O}) - \Delta \mathrm{H}°_\mathrm{f}(\mathrm{HPO}_4^{2-}) - n\Delta \mathrm{H}°_f(\mathrm{H_2O})$$

We calculated the values of enthalpy of formation (Table 9) and the enthalpy of the reaction as a function of the number of water molecules (Table 10) and plotted the variation in the enthalpy of reaction against the number of water molecules bound to the hydrogen phosphate anion (Figure 6).

Table 9. Enthalpy of formation calculated by DFT B3LYP/6-311 (ΔH°f, Kcal/mol).

Molecules	**$\Delta H°_f$, Kcal/mol DFT B3LYB/6-311G**
$(HPO_4, 1H_2O)^{2-}$	-451338.329
$(HPO_4, 2H_2O)^{2-}$	-499323.845
$(HPO_4, 3H_2O)^{2-}$	-547306.54
$(HPO_4, 4H_2O)^{2-}$	-595290.487
$(HPO_4, 5H_2O)^{2-}$	-643268.91
HPO_4^{2-}	-403247.62
H_2O	-47951.601

Table 10. Enthalpy of reaction calculated by DFT B3LYP/6-311 (ΔH°r, Kcal/mol)

Number of water molecules	**$\Delta H^{°}_r$ (Kcal/mol)**
1	-139.108009
2	-173.023582
3	-204.117308
4	-236.463856
5	-263.286061

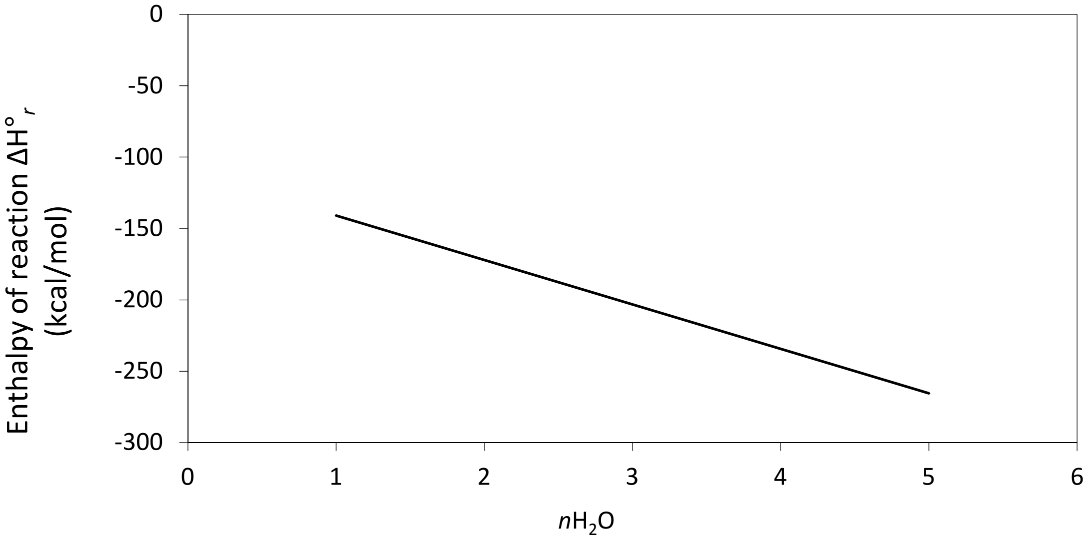


Fig. 6. Plot of ΔH°r as a function of the number of water molecules bound to the HPO_4^{2-} anion (R²=0.9985)

The plot of $\Delta H°_r$ (Figure 6) as a function of the number of water molecules bounds to the anion shows that the energy involved in the association between these chemical species is in inverse proportion to the number of water molecules. This decrease corresponds to the formation of increasingly stable structures, indicating that the HPO_4^{2-} anion is bound to five water molecules.

4 CONCLUSION

Comparison of theoretical and experimental results for interlayer and interatomic distances, vibration frequencies, force constants and enthalpies of formation of the hydrogen phosphate anion HPO_4^{2-} in the free state, the same anion bound to water molecules by hydrogen bonds, and intercalated between layers of the LDH [Zn-Al-HPO_4], together with calculation of the force constant for the Zn-O bond in the four models proposed has shown that the HPO_4^{2-} anions are linked to the layers in the LDH [Zn-Al-HPO_4] by hydrogen bonds rather than by strong bonds with the zinc atoms, with five molecules of water being bound to each HPO_4^{2-} anion, while the PO_4^{3-} anions form bonds with zinc. The results of these various calculations show that DFT B3LYP/6-311G provides results which correspond closely to experimental results.

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