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Structural, Potential Surface and Vibrational Spectroscopy Studies of Hypophosphorous Acid in the Gas Phase and Chain Conformation. A Theoretical Study

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요 약. Hypophosphorous acid (HPA) 분자의 구조와 진동 위치에너지 표면을 HF, MP2, DFT-B3LYP 등의 이론적인 계산 방법을 이용하여 연구하였다. HPA 분자의 체인 수를 증가시켰을 때, 계산된 진동 frequency가 실험값에 보다 근접하게 되는 현상을 관측하였다. P-O 결합에 수직인 O=P-O-H 각도의 함수로 나타낸 위치에너지 표면은 O=P-O 평면의 ±42.5°에서 최소 에너지를 나타내며, saddle point와 복잡한 형태의 에너지 장벽을 보여준다. P-O-H의 비평면 진동운동에 대한 위치에너지 함수에 따르면 전자 바닥 함수에서는 284.87 cm^{-1}의 위치에너지 장벽을 보여주지만, 전자 들뜬 상태에서는 위치에너지 장벽이 나타나지 않았다.

주제어: DFT, IR, VCD, Vibrational Spectra, Isomeric Pathway, Hypo Phosphorous Acid

ABSTRACT. The potential energy surfaces (PES), molecular and vibrational structure of hypophosphours acid (HPA) were investigated by HF, MP2 and DFT-B3LYP level of theory using 6-31G** basis set. In order to approach solid state spectra we optimized mono-, di-, tri-, tetra- and penta-mer structures and computed frequencies and intensities of the vibrational modes of VCD and IR. It is found that by increasing the number of HPA molecules in the chain, some of calculated vibrational frequencies approach to the experimental solid state values. The potential energy surfaces of HPA are calculated in a wide range on the plane perpendicular to the P-O bond where the hydrogen can rotate 360 degree through O=P-O-H dihedral angle. A circular valley is found going up and down on the plane, the valley is centered to the continuation of P-O bond. There are two minima at angles ±42.5° to the O=P-O plane giving two mirror conformers and one saddle point in between with a height of 284.87 cm^{-1} at the angles 0° and a complex barrier with a height of 2089.40 cm^{-1} at the angle 180° to the same plane. On top of the complex barrier, there is a small well with depth of 15.65 cm^{-1}. To study the tunneling effect and pathway between the two conformers, the molecule is considered to have C_s symmetry and a symmetric double minimum potential energy well with a barrier of 284.87 cm^{-1} height in the middle. With the constructed potential, the torsional motion of P-O-H (Hindered Rotation) of the monomer, using variation method and harmonic oscillator wave functions is studied and IR frequencies and relative intensities of vibrational modes are calculated. Due to the width of the well and the trigonometric shape of the barrier, tunneling can occur at the ground state

and the next excited state does not feel the barrier at all.

Keywords: DFT; IR, VCD, Vibrational Spectra, Isomeric Pathway, Hypo Phosphorous Acid

INTRODUCTION

In spite of extensive experimental studies of molecules containing phosphate moieties,[1] only sporadic data exist for small organophosphates. In addition, few theoretical studies, most of which involve low-level calculations with small basis sets, are available for these molecules.

Ab initio calculations usually are carried out in order to obtain conformational, vibrational and other molecular information for a set of small oxygen-containing phosphorus compounds. Many of these molecules are fundamentally important since they are analogous to macrostructures that play a central role in biological processes. It is anticipated that the chemical and physical properties of these phosphorus compounds will provide valuable insight into problems in structural biology.[2] In the present work, our attention will be focused on the conformational and vibrational analyses of HPA and its deuterated analogous in the gas phase.

The structure of HPA crystals features chain association of the acid molecules connected by very short hydrogen bonds with symmetric potential wells. Diffraction work[3] has left the problem of the "true" symmetry of these bonds. Previous IR investigations of HPA were handicapped by the lack of both crystal structure data and experience with very short hydrogen bonds.[4-7]

Crystalline structure of HPA is determined by diffraction method,[8] it is orthorhombic with space symmetry group $P2_12_12$ or $D_2^3(z-2)$ with melting point 26.5°C. The molecule aggregates in zig-zag chains through hydrogen bonds. The O···O distance is 2.44 Å parallel to the crystallographic a axis. The symmetry of a single molecule in the lattice is C_1, *Fig.* 1. The HPA molecules have only one hydrogen atom bonded to oxygen thus it is a mono protonic oxy acid. This compound is a weak acid and forms only one series of hypophosphate salts.[9] In the liquid state, it is expected that chains of molecules resume their structures as a polymer, *Fig.* 2. Unfortunately, in the gas phase the molecule is unstable and regroups to phosphoric acid and phosphorus tri hydrogen, therefore, its IR and Raman spectra have not been reported.[2]

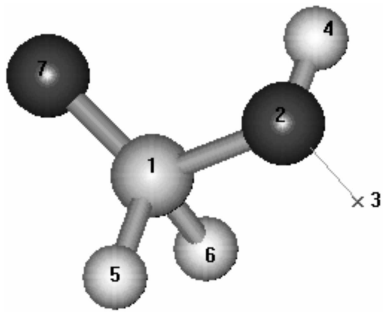

Fig. 1. Optimized structure of the H_3PO_2 molecule with Gaussian and displayed by Hyperchem. Atom No 1 is the Phosphorus atom, dark colored atoms are Oxygen atoms and white colored atoms are Hydrogen atom.

COMPUTATIONAL METHOD

The ab initio calculations were carried out with the GAUSSIAN 98W A.6 system of program.[10] Full geometry optimizations were done at the HF/6-31G**,[11] MP2/6-31G**,[12] and B3LYP/6-31G**[13] levels of theory. The theoretical harmonic vibrational fre-

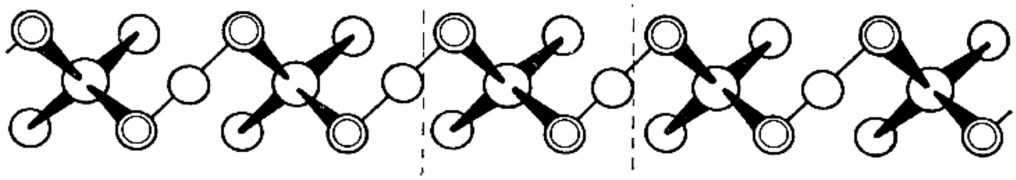

Fig. 2. Proposed liquid state chain conformation of HPA.

quencies and IR and VCD intensities were also calculated analytically at the same levels.

In order to approach the solid state IR spectra, conformations of one-, two-, three-, four- and five-molecules in a chain were optimized using B3LYP/6-31G**.

To obtain the potential surfaces a plane perpendicular to P-O bond is chosen and the hydrogen atom in an area of 2.6×2.6 Å by step of 0.1 Å is scanned. Next the O-H bond was rotated about P-O direction so the H-O-P=O dihedral angle was changed from 0° to 360° and scanned by step of 1° while all other structural parameters kept constant at their equilibrium position. From which double minimum potential energy profile is constructed. Finally the O-H bond is scanned from 0.1 to 1.7 Å by step of 0.01 Å.

RESULTS AND DISCUSSION

A. HPA (Monomer)

The defined bond angles and bond lengths of the HPA are shown in *Fig.* 1. The optimized structural parameters of single molecule calculated by different theoretical approaches are listed in Table 1.

In spite of the calculated free HPA geometry parameters are compared to the solid state HPA results; the parameters at MP2/6-31G** and B3LYP/6-31G** levels are close to the each other values while those obtained at HF/6-31G** level are a little different. For example the calculated O-H bond length for a free HPA at B3LYP, MP2, and HF levels are 0.9689, 0.9671, 0.947 Å, respectively.

Frequency assignments are done by animating vibrational modes using Gauss View2.1 and Hyper Chem7.[14] Inspection of Table 2 shows that calculated frequencies obtained by B3LYP and MP2 levels are in good agreement with the experimental data but markedly different from those obtained by HF approach and demonstrating the effect of electron correlation corrections. The calculated values by MP2 at low frequencies and B3LYP at high frequencies are more close to the experimental values. However, it must be pointed out that in Table 2 gas phase frequencies are compared to those of solid state.

The IR absorption spectrum of the acid and its deuterated analogous are constructed from calculated intensities and fixed full bandwidth of 20 cm^{-1} and presented in the *Fig.* 3a and *Fig.* 3c using Gaussian band shape functions.

The optical activity of dissymmetric molecules is explained when a plane polarized radiation passes through an active medium. The plane of the emergent plane polarized radiation rotates by an angle. The plane polarized beam can be considered as a superposition of two oppositely rotating circularly polarized component. The absorbance coefficient is defined[15] $\Delta\varepsilon=\varepsilon_l-\varepsilon_R$ and the line shape is nearly Gaussian. The absorbance coefficient of the VCDis given by

$$\Delta\varepsilon = \frac{2\sqrt{\ln 2}R\bar{\nu}}{2.296\times10^{-39}\sqrt{\pi}\Gamma_{1/2}}\exp\left[4\ln(2)\left(\frac{\bar{\nu}-\bar{\nu}_0}{\Gamma_{1/2}}\right)\right] \quad (1)$$

Table 1. The optimized geometrical parameters of the HPA (in Angstroms and Degrees)

Expt. Solid[18]	HF/6-31G**	MP2/6-31G**	B3LYP/6-31G**	Structural Parameter
1.512	1.596	1.628	1.628	R(P-O)
1.392	1.388	1.399	1.416	R(P-H)
1.392	1.388	1.393	1.410	R(P-H)
1.512	1.457	1.488	1.485	R(P=O)
1.22	0.947	0.967	0.969	R(O-H)
-	102.0	103.4	103.7	A(H-P-O)
-	102.0	96.8	97.0	A(H-P-O)
114.9	115.4	118.2	117.9	A(O=P-O)
106.3	103.5	103.7	103.6	A(H-P-H)
-	115.9	118.0	117.9	A(H-P=O)
-	113.1	111.9	111.9	A(P-O-H)

Table 2. Assignments of the calculated frequencies (Cm^{-1}) of the HPA and HPA_d with used methods and comparison of them with the solid state spectra

HPA_d		HPA				
Expt.[8]	B3LYP/6-31G**	Expt.[8]	B3LYP/6-31G**	MP2/6-31G**	HF/6-31G**	Assignment
238	182.6	232	237.5	238.1	83.7	OPOH torsion
-	385.6	394	413.3	422.4	408.2	OP (OH)bend+OH torsion
635	610.3	805	785.1	811.0	910.5	PH_2 rock+POH bend
982	661.0	1015	859.7	878.7	958.7	P-(OH) stretch
765	777.2	928	898.2	935.1	990.0	PH2 twist
1145	805.5	1130	1028.1	1049.7	1071.1	POH bend−HPO bend
718	860.2	1098	1117.1	1162.0	1243.3	PH_2 wag+POH bend
805	872.9	1122	1165.0	1212.8	1296.6	PH_2 scissor−P=O stretch
930	1271.6	1260	1296.6	1327.9	1408.4	PH2 scissor+P=H stretch
1772	1745.9	2442	2427.1	2562.2	2670.7	PH asymm. stretch
1798	1780.5	2465	2474.2	2611.3	2690.1	PH sym. stretch
1100	2777.1	1100	3817.1	3888.3	4157.5	OH stretch

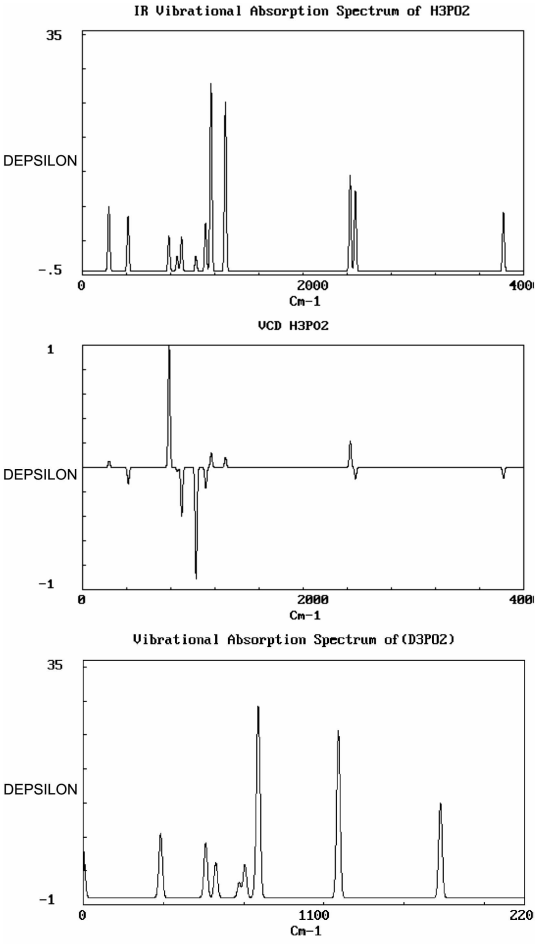

Fig. 3. a- IR, b- VCD and c- deutrated absorption spectrum of the H_3PO_2.

Where R is the rotational strength and $\Gamma_{1/2}$ is the full width at the half height. Using the full line width 20 cm^{-1} similar to IR absorbance spectra, the VCD spectra are shown in *Fig.* 3b. As shown in *Fig.* 3b PH_2 rock (ν=784 cm^{-1}) is strongly left polarized and PH_2 twist (ν=898 Cm^{-1}) is strong right polarized.

To obtain the potential surfaces a plane perpendicular to P-O bond is chosen and the hydrogen atom in an area of 2.6×2.6 Å by step of 0.1 Å is scanned. Three presentations which are prepared by using Surfer[16] soft ware are shown in *Figs.* (4 and 5). All of the numerical values of the potential energy of scanned area are inspected and a valley found whose deepest points going up and down on the

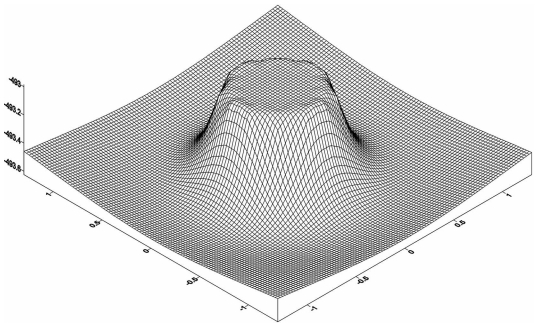

Fig. 4. The truncated and net presentation of the PES displayed by Surfer. The O=P-O plane is perpendicular and crossing through right hand side 0. From (-1, -1) corner the minimum can be clearly detected.

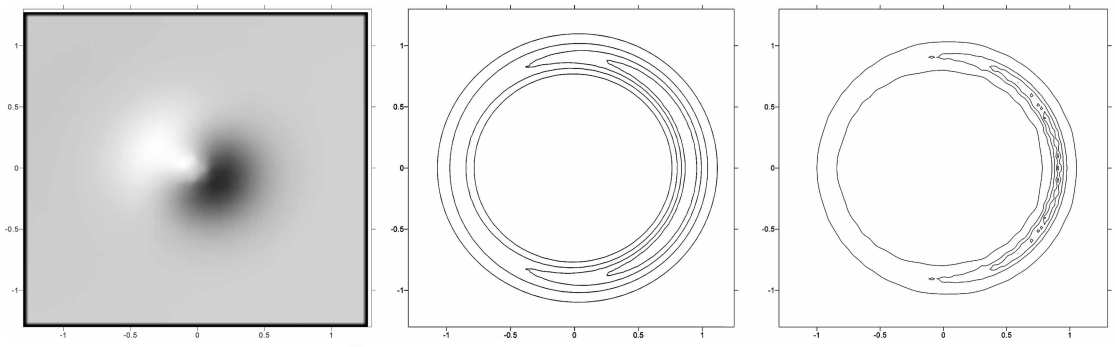

Fig. 5. a- the smooth and complete surface presentation, b and c- contour (iso-potential) map presentations of the PES displayed by Surfer.

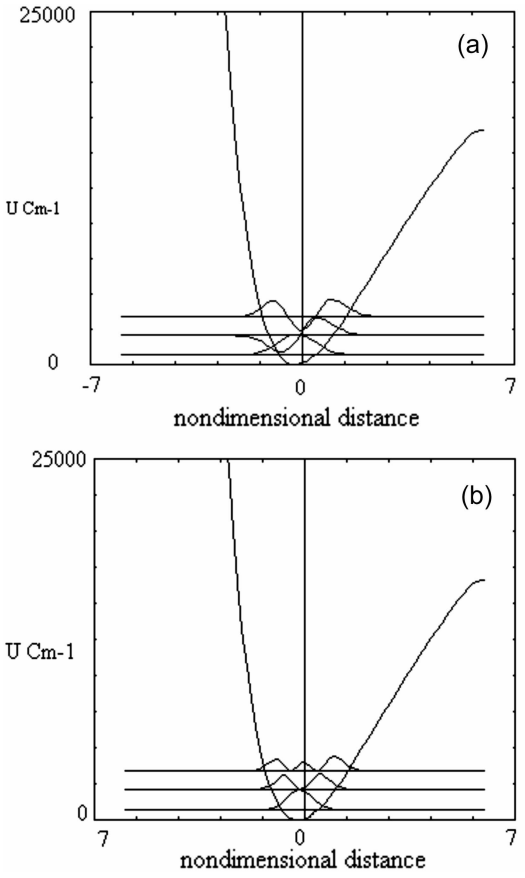

Fig. 6. The OH potential energy and a few vibrational energy levels: (a) wave functions and (b) probability distributions.

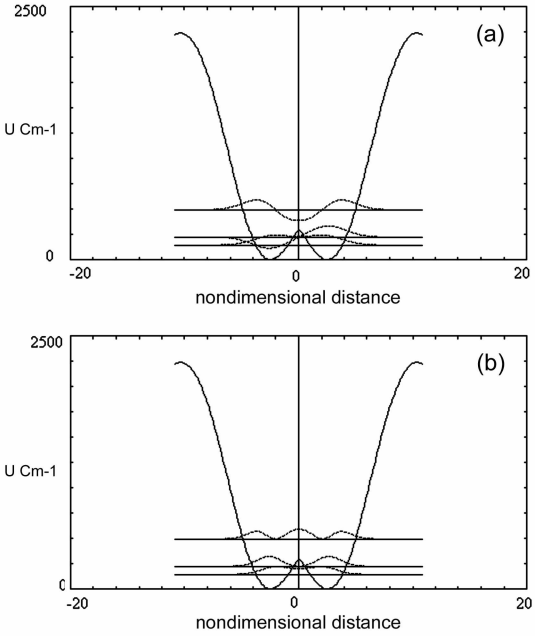

Fig. 7. Spatial isomeric pathway, barrier height and tunneling effect between them a: energy levels and wave functions, b: energy levels and probabilities distributions.

locations of hydrogen atom if O-H bond precess, *Fig.* 5b. In another and more involved scan, the O-H precession is carried out and isomeric path way, double minimum potential energy, is generated and opened up for tunneling studies, *Fig.* 7. There are two minima at ±42.5° and a saddle point in between (0°) with a height of 284.87 cm^{-1} and a complex barrier at 180° with the 2089.40 cm^{-1} height to the O=P-O plane. On the top of the complex barrier, there is a small well with the depth 15.65 cm^{-1}.

The free O-H stretch (C_1, to check our own generated computer program) and P-O-H torsion (C_s) of the HPA can be seen in the gas phase spectrum of the acid if it would be available, unfortunately

the acid in gas phase immediately disintegrate to PH_3 and H_3PO_4. Therefore, the gas phase spectrum has not been reported.[2] The dynamics of a microscopic particle such as stretching can be appropriately described with one-dimensional Schrödinger Equation.[17]

For the present case $V(R)$ of the stretching vibrational mode, which is produced by scanning the O-H bond length from 0.1 Å-1.75 Å and for the spatial isomeric pathway potential (torsional motion) a scanning of the torsional angle 360° with fixed bond length and using the Gaussian 98 computer program, *Figs.* 6 and 7. Wide double well potential curve of the pathway with a sharp and small barrier resulted. The net effect would be lowering the torsional frequency.

Introducing the dimensionless variable[17] $\xi=(\mu\omega_e/\eta)^2R$ to the Schrödinger Equation and by using the variation method and harmonic oscillator wave functions as basis sets:

$$\Psi(\xi) = \sum_{i=0}^{N} C_i G_i(\xi) \qquad (2)$$

We define matrix elements H_{jk}, as:

$$H_{jk} = HK_{jk} + HU_{jk} \qquad (3)$$

Where

$$HK_{jk} = \int \Phi_j^*(\xi) \frac{d^2}{d\xi^2} \Phi_k(\xi) d\xi$$

$$HU_{jk} = \int \Phi_j^*(\xi) \frac{2\mu V(R)}{\eta\omega_e} \Phi_k(\xi) d\xi \qquad (4)$$

The matrix elements HK_{jk} and HU_{jk} are computed analytically and numerically respectively. By using Eq. (2) wave functions are generated and after computational performances the results of the both computations for three energy levels and wave functions are reflected in *Figs.* 6 and 7.

As it is clear from the Fig. 7; due to the width (minima to minima 85°, about 2.0 Å) and height (284.87 cm^{-1}) of the well and also to the trigonometric shape of the barrier, tunneling occurred at the ground state and the next vibrational excited state does not felt the barrier at all. Therefore conformational transition energy is not required.

B. two, three, four and five unit chain of the HPA

Vibrational spectra of crystalline HPA and its deuterated analogous have been studied with both IR and Raman techniques.[8] The structural optimization of two, three, four and five molecules in chains are performed using DFT with B3LYP/6-31G** level. The optimized structures *Fig.* 8(a, b, c, d) clearly show that the chain in free space is screwing.

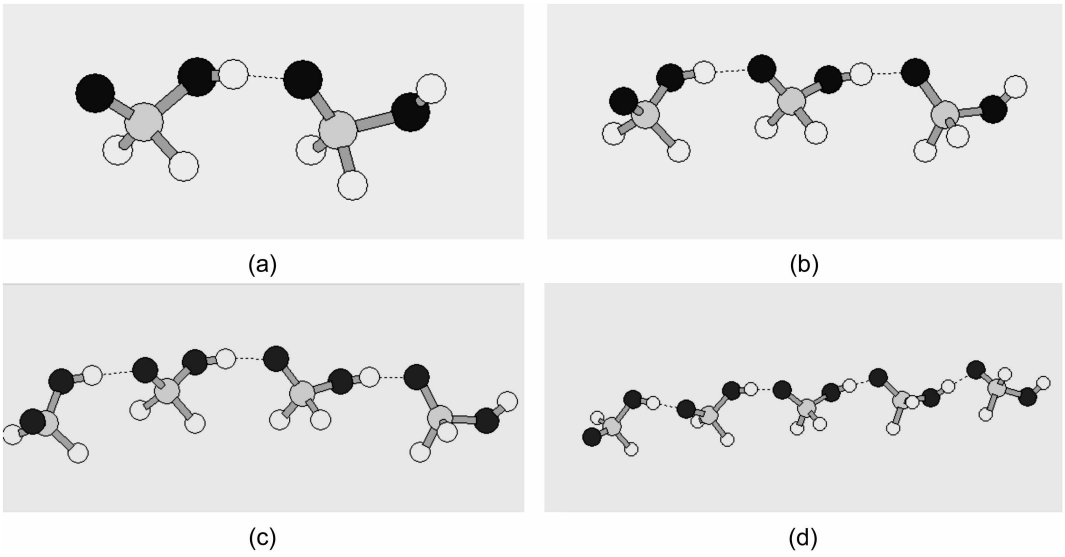

Fig. 8. The optimized structures of two, three, four and five member chain of the HPA.

Table 3 Optimized Parameters for central HPA unit (in Angstroms and Degrees)B3LYP/6-31G**

Name	Mono-mer(H_3PO_2)	Tri-mer ($H_6P_4O_6$)	Penta-mer ($H_7P_5O_8$)	Exp. Solid[18]
R(P-OH)	1.628	1.597	1.586	1.512
R(O-H)	0.969	0.994	1.004	1.22
R(P-H)	1.410	1.408	1.409	1.392
R(P-H)	1.416	1.417	1.415	1.392
R(P=O)	1.485	1.498	1.499	1.512
R(O-H...O)		2.66	2.601	2.44
A(POH)	111.9	117.2	118.9	-
A(HPO)	97.0	99.1	100.1	-
A(HPO)	103.6	104.6	104.9	-
A(OPO)	117.9	119.6	119.7	114.9
A(O-H...O)		172.7	175.0	-

The effects of increasing HPA chain units are reflected in *Table* 3. The dihedral angle, which is responsible for chain screwing changing about 10° (dimmer -128.83, trimer and -119.5, tetramer -108.5 and pentamer -101.3 degrees) P=O bond length, as expected, it is elongated about 0.013 Å from monomer to trimer but the change from trimer to pentamer is small and equal to 0.001 Å *Table* 3. The reported bond length[18] for both of the P-O bonds in the crystalline environment are the same and equal to the 1.512 Å (which is close to the calculated P=O bond length in free space) and the hydrogen bond is almost linear with a single minimum potential. The crystalline environment mainly is imposes on the P-OH and O-H bond lengths and equalizes them with related ones but the gas phase calculations predicts the HPA units keeping almost their monomer structure and connected to each other through a long hydrogen bonds.

The vibrational frequencies are calculated for

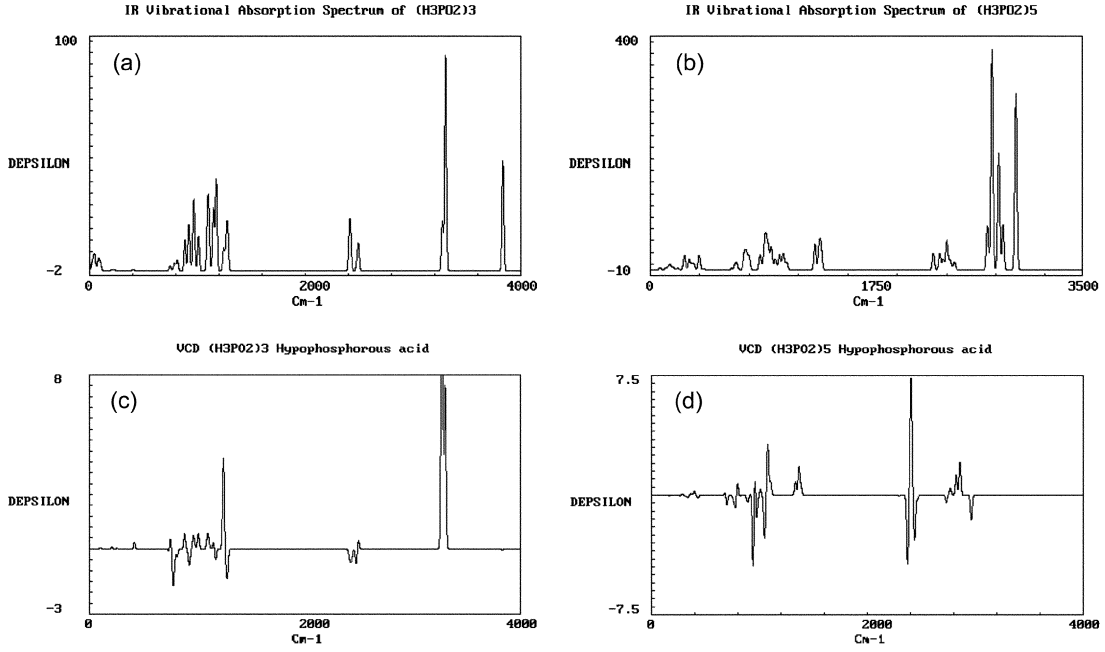

Fig. 9. IR (a, b) and VCD (c, d) absorption spectra of tri-and pentamers of the HPA.

HPA chains using the B3LYP/6-31G** approach. Then the IR and VCD modeled spectra of these molecules are constructed and presented in *Figs.* (9-a, b, c, d). The superiority of VCD to IR is its analytical applications.

CONCLUSION

A DFT/B3LYP/6-31G** calculation is preformed to optimize a series of HPA compounds in chains, determination of the potential energy surfaces, finding spatial isomeric pathway, computation of single bond potential energy, calculations of IR, and vibrational circular dichroism spectra using Gaussian 98w package.

Our PES calculations confirm two mirror stable conformations of the HPA with C_1 symmetry. The PES can be considered to consist of the many Morse type potentials with varying depth separated on a three dimensional space whose approaching to infinity sides are aligned to the P-O bond axis. The variation method calculations, which are generated by us, used to determine tunneling between two isomeric conformations, vibrational energy levels, transitions and probabilities are done with it.

The HPA chain in free space screw itself by about 10° for each unit. IR and VCD spectra are constructed for mono-, tri- and penta-mer of the HPA to approach to the solid state spectra. And it is found that by increasing number HPA units in the chain it is possible to approach to the solid state spectra, *Table* 4 and *Fig.* 10. In *Fig.* 10 the variation of the OP(OH) bend (ν_2=394 cm^{-1}) and P-(OH) stretch (ν_4=1015 cm^{-1}) with the number of HPA unites are shown and clearly supporting our theoretical calculations.

Table 4 Assignments of the calculated frequencies (with B3LYP/6-311G** in cm^{-1}) of Mono-, Tri- , Penta-mers of the HPA, which are compared with solid state spectra.

Expt.[8]	Penta	Tri	Mono	Assignment
232	231.5	226.7	237.5	OPOH torsion
394	398.3	406.9	413.3	OP (OH)bend+OH torsion
805	784.8	775.3	785.1	PH_2 rock+POH bend
1015	955.3	929.3	859.7	P-(OH) stretch
928	929.3	922.0	898.2	PH2 twist
11300	1011.7	971.0	1028.1	POH bend+HPO bend
1098	1105.8	1106.6	1117.1	PH_2 wag+POH bend
1122	1145.4	1148.0	1165.0	PH_2 scissor+P=O stretch
1260	1260.6	1265.6	1296.6	PH_2 scissor+P=H stretch
2442	2435.0	2421.4	2427.1	PH asym. stretch
2465	2484.4	2487.0	2474.2	PH sym. stretch
1100	3092.4	3273.0	3817.1	OH stretch

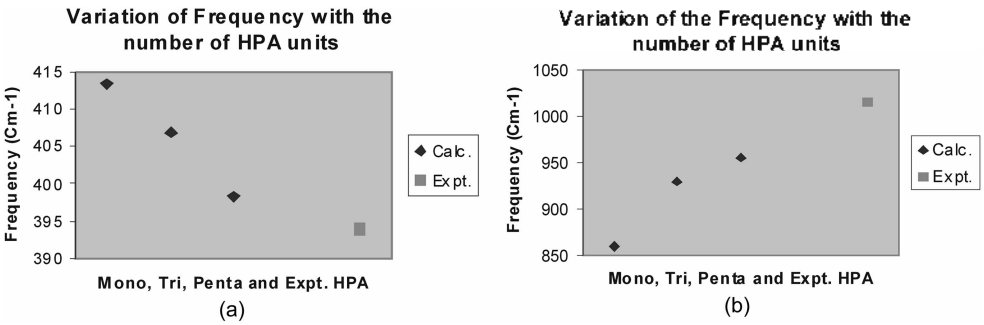

Fig. 10: a; the variation of the OP(OH) bend (ν_2=394 cm^{-1}) and b; P-(OH) stretch (ν_4=1015 cm^{-1}) with the number of HPA unites in the chain with corresponding experimental values.

Inspection of the *Table* 4 more closely indicate that, in general, the vibrational frequencies with increasing of the HPA units except for POH bend at 11300 cm^{-1} and OH stretch at 1100 cm^{-1} are improved. The reason may be arises from the point that we let the chain to optimize freely in the space. The crystalline environment imposes to the HPA units to appear in different optimization.

To show the trends of frequncy optimization ν_2 and ν_4 as an examples are ploted in *Fig.* 10 for visual demonstration.

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