Cumhuriyet Science Journal
e-ISSN: 2587-246X
ISSN: 2587-2680
Cumhuriyet Sci. J., 41(3) (2020) 659-664
http://dx.doi.org/10.17776/csj.721438

Computational study on molecular structure, vibrational spectrum analysis and acidity strength of P_4O_n (n = 6-10) phosphorus oxides with cage structure

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Abstract

In this study, molecular structure, IR spectra and acidity strength of P_4O_n (n = 6-10) type phosphorus oxides with cage structure were investigated at the PBE1PBE/6-311+G(2d) level. Structural parameters and IR spectra of oxides were obtained from optimized structures. From the structural parameters and IR spectra, P_4O_6 and P_4O_{10} molecules were found in T_d symmetry, P_4O_7 and P_4O_9 molecules in C_{3v} symmetry and P_4O_8 molecule in C_{2v} symmetry. Symmetry labeling of the peaks in the IR spectra of oxides was performed.
To predict the acidity strength of the oxides in the gas phase, the protonated species were optimized at the PBE1PBE/6-311+G(2d) level. Proton affinity values were calculated using the total energies of neutral and protonated species. Acidity strength ranking according to proton affinity values was obtained as $P_4O_6 < P_4O_7 < P_4O_8 < P_4O_9 < P_4O_{10}$.

Article info

History:
Received:16.04.2020
Accepted:06.08.2020
Keywords:
Computational study,
phosphorus oxides,
molecular structures,
acidity strength.

1. Introduction

Tetraphosphorus hexaoxide (P_4O_6) is obtained from the reaction of white phosphorus (P_4) in tetrahedral geometry with a limited amount of oxygen, and tetrophosphorus decoxide (P_4O_{10}) from its reaction with excessive oxygen. It has been reported that intermediate compounds such as P_4O_7, P_4O_8 and P_4O_9 can also be synthesized under controlled conditions [1,2].

The molecular structures of P_4O_6 and P_4O_{10} compounds have been determined in previous studies and have been found to have a white phosphorus structure [3,4]. P_4O_6 molecule is formed by the introduction of oxygen atoms between adjacent phosphor atoms in the white phosphorus structure. The difference of P_4O_{10} molecule from P_4O_6 is that each phosphorus atom contains a terminal oxygen atom. In P_4O_7, P_4O_8 and P_4O_9 compounds, one, two, and three of the phosphorus atoms have terminal oxygen atoms, respectively [5].

Phosphorus compounds and oxygen atoms give chemiluminescence reactions and form the basis of laser systems [6,7]. Therefore, P_4O_{10} is used in the development of high energy laser lenses [8]. Also, since these compounds contain cages, they are used as host materials for the vitrification of nuclear waste [9]. P_4O_{10} is a powerful dehydrating agent and is used in desiccators as desiccant. H_3PO_4 is formed as a result of the hydrolysis reaction of P_4O_{10}. Phosphoric acid is used in the pharmaceutical industry, oil industry, insecticide production and for various cleaning purposes. It is used in cola and baking powders in the food industry. It participates in the structure of DNA and RNA. It is found in the structure of all nucleotides. Phosphoric acid, an inorganic compound, is the group that imparts acidic properties to nucleic acids [10].

The acidity strength of a chemical species depends on two main factors: itself and its environment. The acidity force arising from the species itself is obtained from the proton affinity values measured in the gas phase. The higher the value of the proton affinity, the higher the basicity of the species, the weaker the conjugate acid [11].

Molecular orbital theory can also be used to predict acidity or basicity of chemical species. According to the molecular orbital theory, the acidity of a molecule depends on LUMO energy and its basicity depends on HOMO energy. The species with low LUMO energy are acidic. The species with high HOMO energy and with non-binding molecular orbitals act as bases [12].
In this study, we aimed to predict the molecular structure and acidity strength of P_4O_n (n=6-10) type oxides. For this purpose, neutral phosphorus oxides

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and their protonated species were optimized at the PBE1PBE/6-311+G(2d) level. Bond lengths, bond angles, IR spectra of neutral oxides were obtained from the optimized structures. Proton affinity of the oxides was calculated from the total energies of neutral and protonated species and acidity strength sequences were estimated.

2. Methods and techniques

Molecular structures of P_4O_n (n = 6-10) phosphorus oxides with cage type were drawn in GaussView 6.0.16 program [13]. Phosphorus oxides were optimized at PBE1PBE/6-311G(2d) level with the Gaussian 09: AS64L-G09RevD.01 program [14]. PBE1PBE is a pure functional of density functional theory (DFT) developed in 1996 by Perdew, Burke and Ernzerhof [15]. This functional was transformed into a hybrid functional by Adamo [16] and shown with the PBE1PBE keyword. This hybrid functional uses 25% exact exchange and 75% DFT exchange. It is known in the literature as PBE0 [16] and PBE hybrid [17]. 6-311+G(2d) is a basis set with high angular momentum. Such basis sets add multiple polarized functions per atom and diffuse functions to heavy atoms [18]. The reason for choosing such a level in this study is that the vibration spectra of P_4O_6 and P_4O_{10} oxides were studied by P. Carbonniere and C. Pouchan. In their study, benchmark analysis was done and PBE1PBE/6-311+G(2d) level was found as the best level [1].

Bond lengths, bond angles and vibrational spectrum analysis were performed from the optimized structures of neutral phosphorus oxides. To calculate the proton affinity of phosphorus oxides, a proton was added to the atom with the most negative charge and the total energy was calculated. As shown in Equation (1), the proton affinity in the energies of neutral and protonated species was determined [18].

$$P_4O_{n(g)} + H^+_{(g)} \rightarrow P_4O_nH^+_{(g)}$$

$$PA=E(P_4O_n)-E(P_4O_nH^+) \qquad (1)$$

3. Findings and Discussion

3.1. Optimized structures of phosphorus oxides

The structures of P_4O_n (n = 6-10) type phosphor oxides drawn in GaussView 6.0.16 program were optimized in the gas phase at the level of PBE1PBE/6-311+G(2d) in Gaussian 09 calculation program. Optimized structures are given in Fig. 1 with atomic labeling. Bond lengths and bond angles obtained from the optimized structures in Fig. 1 are given in Table 1. Experimental values in Table 1 are taken from reference [1]. Only one of the equivalent bond lengths and bond angles was shown.

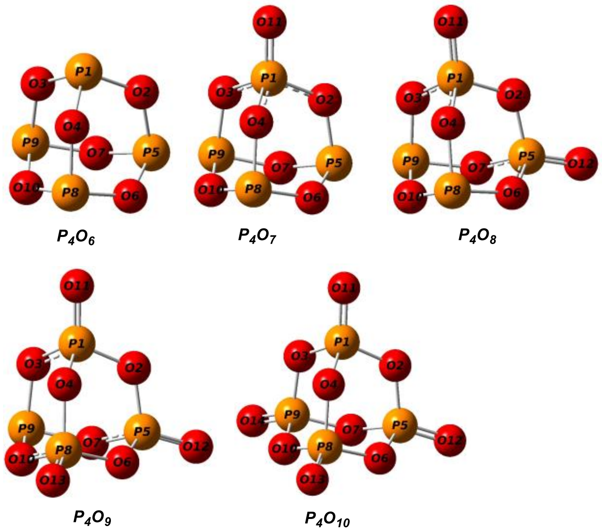

Fig. 1 Optimized structures of P_4O_n (n = 6-10) phosphor oxides with cage type.

As seen in Fig. 1, P1-O11, P5-O12, P8-O13 and P9-O14 bonds show the bonding of terminal oxygen with phosphorus. These bonds are equivalent length and are shown in Table 1 as P1-O11 and their length is given as approximately 1.44 Å. Other P-O bonds belong to bridge oxygen. P-Ob bond lengths vary between 1.60-1.66 Å. This difference between P-Ot and P-Ob lengths is explained by the formation of π-bonds. π-bond is formed between terminal oxygen pπ-orbital and phosphor atom dπ-orbital. π-bond formation causes the P-Ot bond to be shorter.

The change of P-Ob bond lengths between 1.60-1.66 Å in P4O7 and P4O8 is due to their distance from terminal oxygen. It can be seen from Table 1 and Figure 1 that the P-Ob bond, which is farther away from the terminal oxygen atom, is longer than the closer one.

As can be seen from Table 1, there are three types of bond angles for phosphorus oxides ranging from about 100, 115 and 122-127 degrees. Ob-P-Ob bond angles are approximately 100 degrees, Ob-P-Ot bond angles are about 115 degrees and P-Ob-P bond angles range from 122-127 degrees. These angles neither belong to the ideal tetrahedral geometry nor the ideal triangular plane. Therefore, the geometries of oxides are given by symmetry point groups. Considering the symmetry operation of the molecules, it was found that P_4O_6 and P_4O_{10} are in the T_d symmetry point group, P_4O_7 and P_4O_9 are in the C_{3v} symmetry point group and P_4O_8 in the C_{2v} symmetry point group.

Table 1 Molecular structure parameters of phosphorus oxides calculated at PBE1PBE/6-311+G(2d) level in gas phase

Molecule	Bond	Length (Å)	Exp. [1]	Bond	Angle (°)	Exp. [1]
P_4O_6	P1-O2	1.654	1.638	O2-P1-O3	100.0	99.8
	-	-	-	P1-O2-P5	126.1	126.7
P_4O_7	P1-O2	1.602	1.644	O2-P1-O3	103.0	-
	P5-O2	1.668	1.684	O2-P5-O6	99.3	-
	P5-O6	1.651	1.595	O2-P1-O11	115.3	-
	P1-O11	1.443	1.450	P1-O4-P8	124.1	-
	-	-	-	P5-O7-P9	126.6	-
P_4O_8	P1-O2	1.612	1.633	O2-P1-O3	102.3	-
	P1-O3	1.601	1.668	O3-P1-O4	103.1	-
	P8-O4	1.665	1.576	O2-P1-O11	115.2	-
	P8-O10	1.649	1.596	O3-P1-O11	115.9	-
	P1-O11	1.440	1.414	P1-O2-P5	122.7	-
	-	-	-	P1-O4-P8	124.4	-
	-	-	-	P8-O10-P9	127.1	-
P_4O_9	P1-O2	1.611	1.661	O2-P1-O3	102.3	-
	P1-O3	1.602	1.605	O2-P1-O4	102.1	-
	P1-O11	1.438	1.418	O2-P1-O11	115.6	-
	-	-	-	O3-P1-O11	116.7	-
	-	-	-	O3-P9-O7	99.2	-
	-	-	-	P1-O2-P5	122.9	-
	-	-	-	P1-O3-P9	124.5	-
P_4O_{10}	P1-O2	1.610	1.604	O2-P1-O11	116.1	116.5
	P1-O11	1.436	1.429	O2-P1-O3	102.0	101.6
	-	-	-	P1-O2-P5	122.8	123.5

Table 2 Basic vibration modes of phosphorus oxides and IR active modes.

Molecule	Point group	Fundamental vibration modes	IR active modes	Peak number
P_4O_6	T_d	$1A_1+2E+2T_1+4T_2$	$4T_2$	4
P_4O_7	C_{3v}	$7A_1+2A_2+9E$	$7A_1+9E$	16
P_4O_8	C_{2v}	$10A_1+5A_2+7B_1+8B_2$	$10A_1+7B_1+8B_2$	25
P_4O_9	C_{3v}	$7A_1+4A_2+11E$	$7A_1+11E$	18
P_4O_{10}	T_d	$3A_1+3E+3T_1+6T_2$	$6T_2$	6

3.2. IR spectra of phosphorus oxides and symmetry labeling of peaks

IR spectra were calculated at the optimization level and symmetry labeling of the peaks was performed to test the correctness of the molecular structure of phosphor oxides. Symmetry species of the basic vibrational modes of molecules, IR active modes and expected peak numbers in the IR spectrum were obtained by symmetry application [19] and are given in Table 2.

As seen in Table 2, the vibration modes A_2, E and T_1 of the molecules in the T_d point group and A_2 vibration modes of the molecules in the C_{3v} and C_{2v} point group are IR inactive. Peak intensities of vibration modes with IR inactive are zero. Therefore, IR inactive modes do not generate peaks. When the peak intensities of the vibration modes with IR active below a certain value, they do not generate peaks. Therefore, fewer peaks are observed in the IR spectrum than expected.

P_4O_6 and P_4O_{10} molecules are in the T_d point group. In the T_d point group, only T_2 symmetry modes is IR active. Since the T_2 symmetry species is triple degenerate, four peaks are expected in the IR spectrum of the P_4O_6 molecule and six peaks in the IR spectrum of the P_4O_{10} molecule

P_4O_7 and P_4O_9 molecules are in the C_{3v} point group. A_2 modes of molecules in C_{3v} point group are IR inactive, A1 and E modes are IR active. E is a double degenerate symmetry type. Sixteen peaks are expected in the IR spectrum of P_4O_7 molecule and eighteen peaks in P_4O_9 P_4O_8 molecule is in the C_{2v} point group. A_2 modes of molecules in the C_{2v} point group are IR inactive and other vibration modes are IR active. Therefore, 25 peaks are expected in the IR spectrum.

In this study, IR spectra of the phosphorus oxides were calculated in gas phase at PBE1PBE/6-311+G(2d) level. Peaks with intensity greater than 10 km/mol [20] are given with their labels in Figure 2.

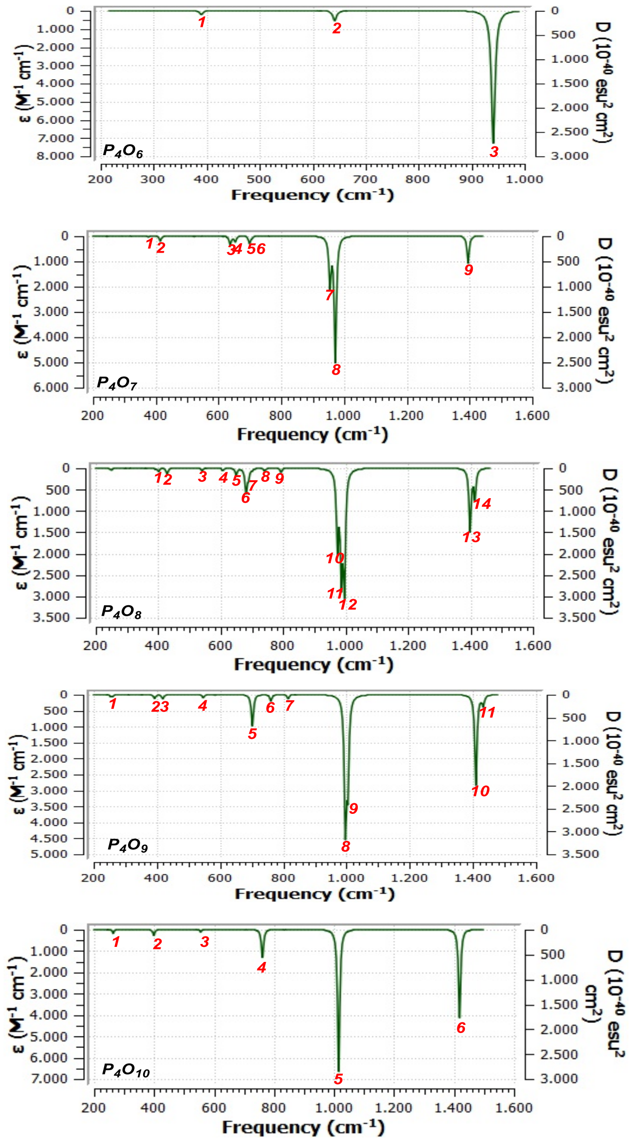

Fig. 2 IR spectra of phosphorus oxides calculated at PBE1PBE/6-311+G(2d) level.

As seen in Figure 2, while four peaks are expected in the IR spectrum of P_4O_6 molecule, three peaks are calculated. This is because the peak intensity of one of the vibration modes in the T_2 symmetry is greater than zero but less than 10 km/mol. The same is true for other molecules except P_4O_{10}. In P_4O_{10}, the expected peak number was equal to the calculated peak number. The vibration modes, frequencies and symmetry labeling of the peaks in Figure 2 are given in Table 3.

As seen in Table 3, around 1400 cm^{-1} peaks were obtained for P_4O_7, P_4O_8, P_4O_9 and P_4O_{10} molecules. This peak belongs to the P-Ot stretching vibration. For P_4O_{10}, this peak was calculated comparatively at 1418 cm^{-1} and experimentally observed at 1406 cm^{-1} [21]. These results are quite compatible with each other. Since this bond is not in the P_4O_6 molecule, no IR peak around 1400 cm^{-1} was observed. Since the P-Ot bond has a double bond character, it occurs at high frequency, that is, in the double bond stretching region. Other P-Ob bonds have a single bond character. Therefore, it appeared at low frequency, that is, in the single bond stretching region.

Both the compatibility of molecular structure parameters with experimental values and IR spectrum analyzes show that the point groups and structures of molecules are determined correctly.

3.3 Proton affinities and acidity strengths of phosphorus oxides

Proton affinity was calculated for prediction the acidity strength of oxides. To calculate proton affinity, a proton was connected to the atom with the most negative charge, it was optimized and the total energy was calculated. The most negative formal charged atom was determined by considering Mulliken charges. Mulliken charges of atoms are given in Fig. 3.

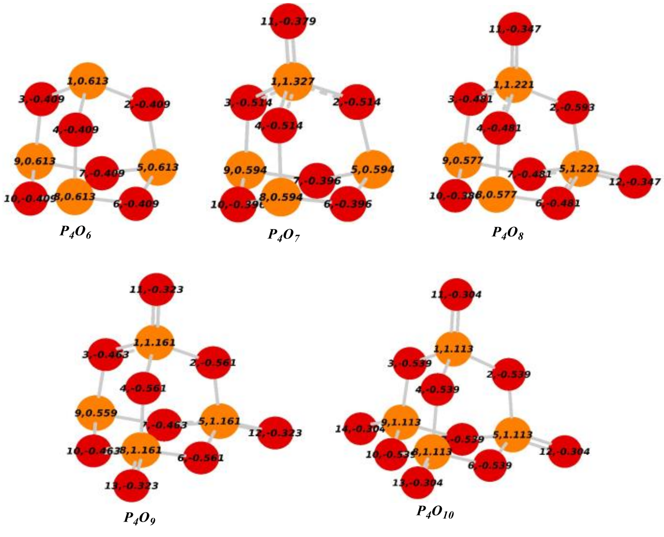

Fig. 3 Mulliken charges of atoms calculated at PBE1PBE/6-311+G(2d) level in gas phase.

As seen in Figure 3, P_4O_6 can be protonated from any oxygen atom and P_4O_{10} any of the bridge oxygen atoms. P_4O_7 can be protonated from one of the oxygen atoms numbered with 2, 3 or 4, P_4O_8 oxygen atom numbered with 2, and P_4O_9 any of the oxygen atoms numbered with 2, 4 and 6. According to the Equation (1), the proton affinity were calculated from the total energies of the neutral and protonated species and given in Table 4.

Table 3 Vibration modes, frequencies and symmetry labeling of phosphorus oxides computed at PBE1PBE/6-311+G(2d) level

Peak	Modes	Freq. (cm^{-1})	Symmetry	Peak	Modes	Freq. (cm^{-1})	Symmetry
P_4O_6				**P_4O_9**			
1	6,7,8	391.6	T_2	1	6	259.9	A_1
2	16,17,18	646.3	T_2	2	11,12	392.2	E
3	22,23,24	942.6	T_2	3	14	418.9	A_1
P_4O_7				4	15	545.8	A_1
1	8	375.5	A_1	5	20,21	701.8	E
2	9,10	413.4	E	6	22	759.7	A_1
3	16	635.8	A_1	7	25,26	813.7	E
4	17,18	651.6	E	8	28,29	996.4	E
5	19,20	698.3	E	9	30	1003.8	A_1
6	21	705.7	A_1	10	31,32	1409.5	E
7	24	955.0	A_1	11	33	1432.7	A_1
8	25,26	972.3	E	**P_4O_{10}**			
9	27	1395.3	A_1	1	6,7,8	264.4	T_2
P_4O_8				2	11,12,13	400.8	T_2
1	11	401.1	A_1	3	18,19,20	555.8	T_2
2	12	428.7	B_1	4	22,23,24	769.6	T_2
3	14	541.2	A_1	5	30,31,32	1018.1	T_2
4	16	606.3	A_1	6	33,34,35	1418.4	T_2
5	17	649.8	A_1				
6	18	681.3	B_2				
7	19	689.2	B_1				
8	22	740.3	B_1				
9	25	793.9	A_1				
10	26	973.9	B_2				
11	27	986.5	A_1				
12	28	996.3	B_1				
13	29	1398.6	B_2				
14	30	1414.1	A_1				

Table 4 Total energies and proton affinity (PA) of phosphorus oxides calculated at PBE1PBE/6-311+G(2d) level in gas phase

Molecule	E(neutral) (Hartree)	E(protonated) (Hartree)	PA (eV)
P_4O_6	-1816.211019	-1816.495185	7.73
P_4O_7	-1891.431078	-1891.701142	7.35
P_4O_8	-1966.646769	-1966.894749	6.75
P_4O_9	-2041.857303	-2042.089442	6.32
P_4O_{10}	-2117.061515	-2117.277013	5.86

As can be seen from Table 4, as the number of terminal oxygen atoms increases, the proton affinity decreases. Acidity increases as proton affinity decreases. Because, according to the Lowry-Bronsted acid base definition, the acidity of a species depends on the tendency to give protons. According to this definition, the species that can give proton acts as acid and the species that can take proton acts as base. The tendency to give protons is inversely proportional to the proton interest. According to the proton affinity values, the acidity strength of phosphor oxides with cage structure is as follows:

$P_4O_6 < P_4O_7 < P_4O_8 < P_4O_9 < P_4O_{10}$

It can be said that the P_4O_{10} molecule is a strong dehydration agent and the formation of H_3PO_4 as a result of its hydrolysis is related to its acidity strength.

4. Conclusions

As a result of this study, molecular structures, molecular structure parameters and IR spectra of phosphorus oxides were calculated. Calculations were made at the PBE1PBE/6-311+G(2d) level. It was found that P_4O_6 and P_4O_{10} molecules are in the Td point group, P_4O_7 and P_4O_9 molecules in the C_{2v} point group and P_4O_8 molecule in the C_{2v} point group. Symmetry labeling of the peaks in the IR spectra of the studied molecules was performed. Protonated species were also optimized at the computation level. Proton affinity values were calculated using the total energies of neutral and protonated species. Acidity strength ranking according to proton affinity values was obtained as $P_4O_6 < P_4O_7 < P_4O_8 < P_4O_9 < P_4O_{10}$.

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