

Microwave spectroscopic detection of a transient phosphorus-bearing molecule, H₃PO

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(Received 2 September 1998; accepted 1 October 1998)

The microwave spectrum of the transient phosphine oxide, H₃PO, was detected in the gas phase for the first time using a source-modulated spectrometer. The H₃PO molecule was generated in a free space cell by a dc glow discharge of a mixture of PH₃, CO₂, and H₂ gases and the corresponding spectral lines for each rotational transition of H₃PO formed a pattern clearly indicative of a symmetric top molecule. Isotopomers of H₃PO, i.e., H₃P¹⁸O and D₃PO were also produced; H₃P¹⁸O in the same fashion as for H₃PO, and D₃PO, in a mixture of D₂ and CO₂ gases passing over red phosphorus grains. In total, 54 spectral lines of H₃PO, 55 lines of H₃P¹⁸O, and 61 lines of D₃PO were measured for the fine structure of rotational transitions, $J=2-1$ to $12-11$. The rotational constant, B_0 , and centrifugal constants, D_J , D_{JK} , and H_{KJ} were ascertained by a least squares analysis of the measured frequencies for each of the species. Using the rotational constants of the three isotopic species, the following r_0 structure was determined: $r_0(\text{PO})=1.4763 \text{ \AA}$, $r_0(\text{PH})=1.4406 \text{ \AA}$, and $\angle \text{HPO}=114.26^\circ$. The value of each structural parameter deviates significantly from the most recent results predicted by *ab initio* calculations. © 1999 American Institute of Physics. [S0021-9606(99)04101-X]

INTRODUCTION

Experimental studies of simple intermediates in the oxidation of phosphine are few in number. Among these are PH,¹ PH₂,² PO,³ PO₂,⁴ HPO,⁵ and H₂PO,⁶ all of which have been studied and characterized using microwave spectroscopy. There still remain several interesting transient molecules en route to the final product, H₃PO₄. For example, the third hydrogenated member in the series starting from PO, H₃PO, has to date eluded gas phase spectroscopic detection. Only the mass spectroscopic detection of H₃PO and its related chemistry were reported and discussed by Hamilton and Murrells.⁷ They suggested that H₃PO was formed by the disproportionation reaction of two H₂PO radicals and the third body reaction of PH₃ with the oxygen atom, though they did not refer to the existence of its isomeric forms. The trifluoride and trichloride of H₃PO are known to be symmetric top molecules from their spectroscopic studies.^{8,9} Trialkylphosphines are easily changed into the corresponding phosphine oxides by autoxidation¹⁰ and the simplest trimethyl phosphine oxide also has the structure of a symmetric top.¹¹ Visible photolysis of the phosphine-ozone complex provided infrared spectroscopic evidence that the predominant products were phosphine oxide and the isomeric species, phosphinous acid (H₂POH) for which all the vibrational modes of the three species were identified using ¹⁸O₃ and PD₃ (Ref. 12) as reagents. These results sparked interest in the molecular structure of the three species and their prototropic reaction and incited a wide variety of quantum chemical calculations.¹³⁻²⁵

The isomerisation pathway from H₃PO to H₂POH has been studied in some detail.^{15,19,21,22,24} An important conclusion of these calculations is that H₂POH is found to be the more stable of the two isomers (with an energy difference of

6.5 kcal/mol) and its two forms, *cis* and *trans*, to be nearly equal in energy (0.3 kcal/mol difference).²¹ The barrier between H₃PO and H₂POH was calculated to be 69.2 kcal/mol and that between *trans* and *cis* H₂POH, 4.1 kcal/mol. In a separate study conducted by Kwiatkowski and Leszczynski,^{23,24} the authors were convinced that the photolysis of the phosphine-ozone mixture in a solid argon matrix caused the *cis* form of H₂POH to be generated in greater abundance than H₃PO, in comparison to the relative IR absorbances of both species. Furthermore, the *cis* form of H₂POH was thought to be formed in a slightly higher concentration than the *trans* species. They concluded that phosphinous acid is energetically lower than phosphine oxide and that the *cis* form of H₂POH is more so than the *trans* form to a small extent.

The vibrational IR spectra of H₃PO was also calculated using MP2 theory with the 6-31G** and 6-311G** basis sets,²⁵ and the calculated vibrational spectra compared well with the known experimental data, even upon isotopic substitution. The MP2/6-311G** level calculations agreed better than the MP2/6-31G** approximation, though discrepancies occurred for the symmetric and asymmetric P-H stretching modes. In essence, these results agreed totally with the matrix IR experimental evidence.

Molecular parameters of the H₃PO species, including the dipole moment, have been computed to various levels, the highest level of which was MP2 theory with the 6-311G** basis set.²⁵ In that particular study, the molecular structure and dipole moment of H₃PO were predicted to be $r_e(\text{PO})=1.4855 \text{ \AA}$, $r_e(\text{PH})=1.4061 \text{ \AA}$ and $\angle \text{HPO}=117.68^\circ$ and $\mu=3.4743 \text{ D}$.

This paper presents the first gas-phase identification and characterization of phosphine oxide, H₃PO, by microwave

TABLE I. Observed transition frequencies of the H_3PO , D_3PO , and $\text{H}_3\text{P}^{18}\text{O}$ species (MHz).

$N'_{K'}-N''_{K''}$	$\nu_{\text{obs}}(\Delta\nu)^a$		
	H_3PO^b	D_3PO^c	$\text{H}_3\text{P}^{18}\text{O}^d$
2 ₀ -1 ₀	69706.001 (0.001)		
2 ₁ -2 ₁	69704.953 (-0.054)		
3 ₀ -2 ₀	104558.110 (0.022)		
3 ₁ -2 ₁	104556.601 (0.003)		
3 ₂ -2 ₂	104552.119 (-0.008)		
4 ₀ -3 ₀	139409.106 (0.025)		
4 ₁ -3 ₁	139407.061 (-0.033)		
4 ₂ -3 ₂	139401.219 (0.086) ^e		
4 ₃ -3 ₃	139391.170 (-0.031)		
5 ₀ -4 ₀	174258.604 (-0.011)		162579.987 (0.007)
5 ₁ -4 ₁	174256.135 (0.004)		162577.805 (0.012)
5 ₂ -4 ₂	174248.687 (0.007)		162571.243 (0.010)
5 ₃ -4 ₃	174236.266 (0.002)		162560.273 (-0.030)
5 ₄ -4 ₄	174218.772 (-0.114) ^f		162545.024 (0.021)
6 ₀ -5 ₀	209106.324 (0.001)	175189.230 (0.037)	195092.443 (-0.013)
6 ₁ -5 ₁	209103.352 (0.009)	175187.506 (-0.019)	195089.836 (0.004)
6 ₂ -5 ₂	209094.419 (0.017)	175182.519 (-0.004)	195081.945 (-0.016)
6 ₃ -5 ₃	209079.531 (0.029)		195068.850 (0.007)
6 ₄ -5 ₄	209058.653 (0.004)	175162.522 (0.005)	195050.497 (0.013)
6 ₅ -5 ₅	209031.854 (0.007)		195026.891 (0.002)
7 ₀ -6 ₀	243951.839 (-0.004)	204383.618 (0.030)	227603.027 (0.014)
7 ₁ -6 ₁	243948.372 (0.007)	204381.635 (-0.007)	227599.948 (-0.003)
7 ₂ -6 ₂	243937.938 (0.004)	204375.792 (-0.014)	227590.782 (0.014)
7 ₃ -6 ₃	243920.557 (0.006)	204366.077 (-0.003)	227575.461 (-0.004)
7 ₄ -6 ₄	243896.196 (-0.027)	204352.439 (-0.027)	227554.043 (-0.003)
7 ₅ -6 ₅	243864.930 (-0.023)	204334.905 (-0.060)	227526.531 (0.014)
7 ₆ -6 ₆	243826.747 (-0.005)	204313.563 (-0.019)	227492.907 (0.021)
8 ₀ -7 ₀	278794.808 (0.001)	233576.256 (0.029)	260111.300 (-0.030)
8 ₁ -7 ₁	278790.834 (0.001)	233573.989 (-0.014)	260107.821 (-0.010)
8 ₂ -7 ₂	278778.906 (-0.006)	233567.343 (0.010)	260097.333 (-0.002)
8 ₃ -7 ₃	278759.062 (0.016)	233556.229 (0.011)	260079.852 (0.006)
8 ₄ -7 ₄	278731.228 (-0.014)	233540.658 (-0.001)	260055.328 (-0.039)
8 ₅ -7 ₅	278695.508 (0.003)		260023.957 (0.051)
8 ₆ -7 ₆	278651.815 (-0.032)		259985.450 (-0.021)
8 ₇ -7 ₇	278600.216 (-0.061)	233467.442 (0.096) ^e	259940.093 (0.021)
9 ₀ -8 ₀	313634.870 (0.017)	262766.881 (0.022)	292617.079 (-0.008)
9 ₁ -8 ₁	313630.406 (0.024)	262764.345 (-0.013)	292613.180 (0.030)
9 ₂ -8 ₂	313616.964 (-0.006)	262756.847 (-0.007)	292601.405 (0.062)
9 ₃ -8 ₃	313594.599 (-0.022)	262744.364 (0.015)	292581.619 (-0.048)
9 ₄ -8 ₄	313563.356 (0.015)	262726.840 (-0.005)	292554.177 (0.048)
9 ₅ -8 ₅	313523.163 (0.025)	262704.384 (0.039)	292518.695 (-0.040)
9 ₆ -8 ₆	313474.057 (0.035)	262676.839 (-0.012)	292475.462 (-0.034)
9 ₇ -8 ₇	313416.046 (0.040)	262644.321 (-0.048)	292424.538 (0.117) ^f
9 ₈ -8 ₈	313349.090 (-0.016)		
10 ₀ -9 ₀	348471.591 (-0.023)	291955.269 (0.035)	325119.947 (-0.017)
10 ₁ -9 ₁	348466.636 (-0.010)	291952.469 (0.014)	325115.571 (-0.019)
10 ₂ -9 ₂	348451.716 (-0.028)	291944.116 (-0.001)	325102.436 (-0.035)
10 ₃ -9 ₃	348426.919 (0.007)	291930.217 (-0.006)	325080.623 (0.021)
10 ₄ -9 ₄	348392.156 (0.000)	291910.774 (0.000)	325049.979 (-0.032)
10 ₅ -9 ₅	348347.472 (-0.014)	291885.744 (-0.030)	325010.686 (0.002)
10 ₆ -9 ₆	348292.922 (0.009)	291855.249 (0.024)	324962.681 (0.041)
10 ₇ -9 ₇	348228.469 (0.018)	291819.083 (-0.051)	324905.887 (-0.005)
10 ₈ -9 ₈	348153.942 (-0.175) ^f		324840.397 (-0.057)
10 ₉ -9 ₉	348069.936 (0.005)	291730.408 (0.062)	324766.313 (-0.031)
11 ₀ -10 ₀		321141.076 (-0.025)	357619.640 (-0.002)
11 ₁ -10 ₁		321138.053 (0.009)	357614.846 (0.015)
11 ₂ -10 ₂		321128.868 (-0.004)	357600.411 (0.012)
11 ₃ -10 ₃		321113.593 (0.004)	357576.375 (0.024)
11 ₄ -10 ₄		321092.180 (-0.015)	357542.658 (-0.035)
11 ₅ -10 ₅		321064.720 (0.026)	357499.435 (0.001)
11 ₆ -10 ₆		321031.054 (-0.037)	357446.591 (0.005)
11 ₇ -10 ₇		320991.401 (0.010)	357384.178 (0.016)
11 ₈ -10 ₈		320945.601 (0.002)	357312.240 (0.060)
11 ₉ -10 ₉		320893.681 (-0.043)	357230.618 (-0.041)
11 ₁₀ -10 ₁₀		320835.780 (0.008)	357139.655 (0.034)

TABLE I. (Continued.)

$N'_{K'}-N''_{K''}$	$\nu_{\text{obs}}(\Delta\nu)^a$		
	H_3PO^b	D_3PO^c	$\text{H}_3\text{P}^{18}\text{O}^d$
12 ₀ -11 ₀		350324.184 (-0.024)	
12 ₁ -11 ₁		350320.897 (0.024)	
12 ₂ -11 ₂		350310.869 (0.001)	
12 ₃ -11 ₃		350294.200 (0.005)	
12 ₄ -11 ₄		350270.819 (-0.038)	
12 ₅ -11 ₅		350240.858 (0.002)	
12 ₆ -11 ₆		350204.196 (-0.002)	
12 ₇ -11 ₇			
12 ₈ -11 ₈		350110.966 (0.032)	
12 ₉ -11 ₉		350054.379 (0.037)	
12 ₁₀ -11 ₁₀		349991.147 (0.024)	
12 ₁₁ -11 ₁₁		349921.242 (-0.043)	

^a $\Delta\nu = \nu_{\text{obs}} - \nu_{\text{calc}}$. ν_{calc} is obtained from the molecular constants in Table II.

^bThe standard deviation of the fit is 22.8 kHz.

^cThe standard deviation of the fit is 27.6 kHz.

^dThe standard deviation of the fit is 27.8 kHz.

^eLine weighted to 0.5.

^fLine weighted to 0.0.

spectroscopy. Molecular structural parameters were ascertained for the species and compared to their theoretical counterparts.

EXPERIMENTAL DETAILS

A source-modulated microwave spectrometer, employed in combination with a 2 m free space cell at the Institute for Molecular Science, has been described in detail in an earlier publication.²⁶

Several experimental procedures were adopted in the search for new H, P, and O containing species. Recently, in the same laboratory, the dihydrophosphoryl radical, H_2PO , was detected in a dc glow discharge of a mixture of PH_3 (8 mTorr) and CO_2 (5 mTorr) with a current of 20 mA at a temperature of -100°C .⁶ Initially the same conditions were applied and a frequency search conducted in the region of 348 GHz was unsuccessful in locating the lines of interest. The following gaseous mixtures also failed to detect new lines: PH_3 and H_2O ; and PH_3 , H_2O , and H_2 . When excess H_2 was added to a discharge of PH_3 and CO_2 , new intense diamagnetic lines appeared as a pattern resembling that of a symmetric rotor in the 348–348.5 GHz region. Immediately, these lines were tentatively attributed to the H_3PO radical. In order to assign the molecular species identified, preliminary constants for each species were derived by using the molecular parameters from the work of Kwiatkowski and Leszczynski²⁵ and used to predict the line frequencies for H_3PO , and then $\text{H}_3\text{P}^{18}\text{O}$ and D_3PO , as described below. The optimum conditions were found to be partial pressures of 9, 6, and 15 mTorr of PH_3 , CO_2 , and H_2 , respectively, the current was set to 60 mA, and the temperature of the cell was maintained at -100°C by adjusting the flow of liquid nitrogen around the cell. Relative intensities of the spectral lines, especially those numbered $K=3n$, facilitated the assignment of the K lines.

Spectra of isotopomers of H_3PO , $\text{H}_3\text{P}^{18}\text{O}$, and D_3PO were also recorded. For $\text{H}_3\text{P}^{18}\text{O}$, experimental conditions

matched those of H_3PO using C^{18}O_2 , whereas for D_3PO , a mixture of D_2 , PH_3 , and CO_2 did not generate the required lines even on increase of current to 200 mA. Eventually, D_2 (15 mTorr) and CO_2 (15 mTorr) were discharged and passed over three glass boats containing red phosphorus grains located in the center of the 2 m cell, and lines due to the D_3PO species were detected. A current of 100 mA was applied and the most favorable temperature was found to be around -150°C . No signal was observed at a temperature of lower than -165°C . The observations of these isotopomers verified the identification of H_3PO in the gas phase.

For H_3PO , 54 spectral lines of nine rotational transitions from $N=10-9$ to $N=2-1$ were recorded over the 69.7–348.5 GHz region. For $\text{H}_3\text{P}^{18}\text{O}$, 55 lines were detected for transitions ranging from $N=11-10$ to $N=5-4$ in the 162.5–357.7 GHz region, and for D_3PO , 61 lines assigned to transitions $N=12-11$ to $N=6-5$ were identified between

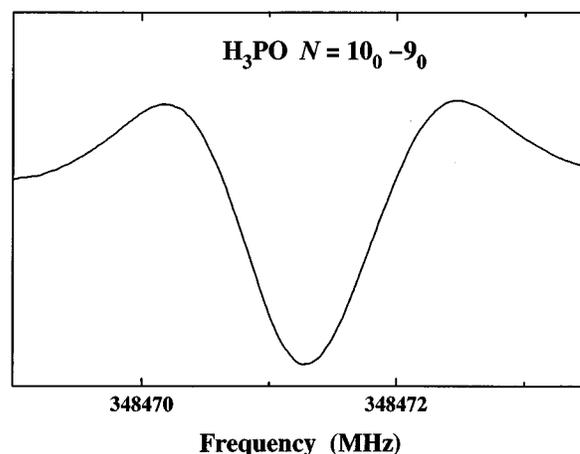


FIG. 1. $K=0$ line of the $N=10-9$ transition of H_3PO observed by dc glow discharge (60 mA) of PH_3 , (9 mTorr) CO_2 (6 mTorr) and H_2 (15 mTorr) in the free space cell maintained at -100°C . The integration time was 8 s.

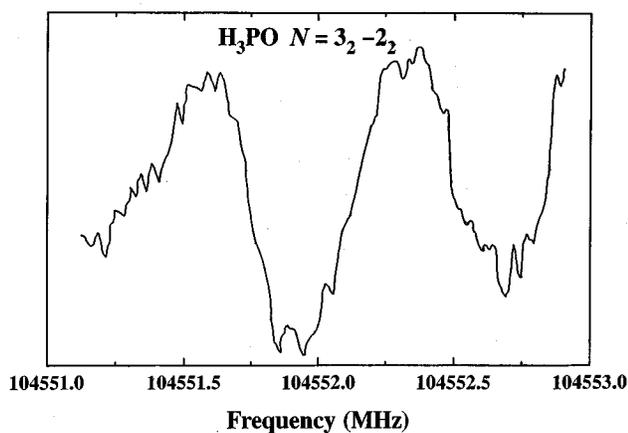


FIG. 2. No effect of nuclear spin rotation of the phosphorus nucleus is shown for the $K=2$ line of the $N=3-2$ transition of H_3PO . The integration time was 160 s. The line that appears on the higher frequency side is due to the impurity.

175.1–350.3 GHz. Each line frequency was determined by averaging three pairs of upward and downward frequency sweep measurements. All the observed line frequencies are listed in Table I for H_3PO , $\text{H}_3\text{P}^{18}\text{O}$, and D_3PO .

Effect of the phosphorus nuclear spin-rotation interaction upon the spectral lines of H_3PO was investigated. This type of interaction, if noticeable, causes splitting of the high K lines which are then observed as doublets for the P atom

TABLE II. Molecular constants for H_3PO , D_3PO , and $\text{H}_3\text{P}^{18}\text{O}$ (MHz).^a

	H_3PO	D_3PO	$\text{H}_3\text{P}^{18}\text{O}$
B_0	17 426.6217 (20)	14 599.851 9 (21)	16 258.664 6 (22)
D_J	0.015 205 (13)	0.010 450 9 (95)	0.013 332 (12)
D_{JK}	0.248 390 (87)	0.138 966 (56)	0.218 681 (75)
H_{KJ}	0.000 005 4 (13)	0.000 001 80 (54)	0.000 004 90 (87)

^aValues in parentheses denote three times the standard deviation and apply to the last digits of the constants.

with unequal intensities. Such an interaction was seen in high K_a lines of HPO where the splitting was on the order of 0.25–0.60 MHz.⁵ No hyperfine structure was able to be observed for any of the lines in this study. Comparison of Figs. 1 and 2 demonstrates unmistakably that no similar trait occurs for H_3PO . Figure 1 is of a low K line ($K=0$) of a relatively high lying transition ($N=10-9$), whereas Fig. 2 is of a high K line ($K=2$) of a low lying transition ($N=3-2$). Though the signal to noise ratio in both spectra are widely dissimilar, it is unequivocally evident that no splitting or broadening of these lines occur. Molecular constants of H_3PO and its isotopomers were determined by a least-squares fit of the frequencies to the usual symmetric top energy formula. These molecular constants are listed in Table II.

TABLE III. Comparison of the structural parameters of H_3PO with those of the related molecules.

Molecules	$r(\text{P}-\text{O})$ (Å)	$r(\text{P}-\text{H})$ (Å)	$\angle \text{HPO}$ (°)	$\angle \text{HPH}$ (°)	Methods
H_3PO					
expt. (r_0)	1.4763	1.4406	114.26	104.29	microwave ^{a,b}
(MP2/6-311G**)	1.4855	1.4061	117.68	100.16	<i>ab initio</i> ^c
<i>cis</i> - H_2POH					
(MP2/6-311G**)	1.6584	1.4171	101.64	92.32	<i>ab initio</i> ^c
<i>trans</i> - H_2POH					
(MP2/6-311G**)	1.6708	1.4099	99.10	92.92	<i>ab initio</i> ^c
H_2PO					
expt. (r_0)	1.4875(4)	1.4287(14)	115.52(10)	102.56(14)	microwave ^d
HPO					
(r_0)	1.480(15)	1.4656(9)	103.5(75)		optical ^e
(CASPT2)	1.490	1.452	104.1		<i>ab initio</i> ^f
PO					
expt. (r_e)	1.476370(15)				IR ^g
PH_3					
expt. (r_e)		1.41154(50)		93.36(8)	microwave ^h
PH_2					
expt. (r_z)		1.43365(23)		91.622(32)	microwave ⁱ
PH					
expt. (r_e)		1.42140(22)			LMR ^j

^aValues in parentheses denote three times the standard deviation and apply to the last digits of the quoted figures.

^bPresent study.

^cReference 25.

^dReference 6.

^eReference 27.

^fReference 28.

^gReference 29.

^hReference 30.

ⁱReference 31.

^jReference 32.

DISCUSSION

In the present study, the existence of a new phosphorus bearing symmetric top molecule, H_3PO , has been identified in the gas phase for the first time by microwave spectroscopy. This observation contradicts results of the various *ab initio* calculations reported so far^{13,15,19–22,24} whereby the isomeric forms of H_3PO , *cis* and *trans* H_2POH , are predicted to be energetically more stable than H_3PO . The transient H_3PO molecule was produced efficiently by a dc glow discharge of a gaseous mixture of PH_3 , CO_2 , and H_2 or by the discharge of the same gas mixture over red phosphorus grains. The same chemical systems were also found to generate transient HPO and H_2PO .

In our initial survey, no *a*-type spectral pattern was recognised in the 347 GHz region, where the *a*-type *R* branch, $J=12-11$, *K* structure of *cis* H_2POH was also expected. The detection limit in the survey conducted was about 10% of the intensity of the $J=10-9$, $K=3$ transition for H_3PO , deduced from the observed signal to noise ratio of the latter transition. The dipole moments of H_3PO and *cis* H_2POH are predicted to be 3.743 D and 2.207 D,²⁵ respectively. The intensity ratio between the $J=10-9$, $K=3$ transition of H_3PO and the *a*-type $12_{0,12}-11_{0,11}$ transition of *cis* H_2POH is calculated to be about 11. If H_3PO and *cis* H_2POH are generated in equal amounts in the present discharge chemical system, detection of the *cis* H_2POH line seems to be marginal. Therefore, it is concluded that the *cis* H_2POH species is not preferentially generated in the present chemical system. This does not reconcile with the results of *ab initio* calculations.^{23,24}

The r_0 structure of H_3PO was determined from the observed rotational constants of the three isotopic species to be $r_0(\text{PO})=1.4763 \text{ \AA}$, $r_0(\text{PH})=1.4406 \text{ \AA}$, $\angle\text{HPO}=114.26(19)^\circ$, and $\angle\text{HPH}=104.29^\circ$. The structure is ascertained solely from the rotational constants and the structural errors involved originate from experimental uncertainties in the rotational constants which are generally small when compared with those due to the vibration-rotation effect. Referring to the r_0 structure of H_2PO where four structural parameters were determined from six observed rotational constants of H_2PO and $\text{H}_2\text{P}^{18}\text{O}$ by the least squares method,⁶ the four or five figures quoted for the present molecular structural parameters are considered to be significant.

The determined structure is compared with its theoretically predicted counterpart and also those of related molecules in Table III. Comparison with the theoretical values shows some deviations in $r_0(\text{PH})$ and $\angle\text{HPO}$,²⁵ whereas the r_0 structure of H_3PO is very similar to that of H_2PO .⁶ Hirao *et al.*⁶ studied the microwave spectrum of the H_2PO radical and determined the magnetic dipolar tensor of the phosphorus nucleus, which enabled the *z* axis direction of the unpaired π electron to be located. Using that result, the angle between the PO bond and the *z* axis of the tensor is calculated to be 113.7° . This bond angle is very close to the HPO angle of H_2PO , 115.52° , and more so to that of H_3PO , 114.26° . This implies that detaching one of the three hydrogens in H_3PO does not significantly disturb the molecular orbitals of the remaining part, i.e., H_2PO . The result is also consistent with the fact that similar dipole moments have

been predicted, 3.743 D and for H_3PO (Ref. 25) and 3.6 D for H_2PO .³³

On the other hand, the bond angle of HPO (Ref. 28) differs somewhat from those of H_3PO and H_2PO , though their PO bond lengths do not vary much. This is because the PO bond in HPO is a typical double bond made up of one p_σ bond and one p_π bond, whereas the PO bond in H_3PO and H_2PO is a resonance hybrid between a single and triple bond structure or a dative single bond augmented by π back donation to the vacant *d* orbital of P from the O lone pairs.^{15,17} Contribution of the *d* orbital to the phosphorus $3p$ orbital introduces a change in the *sp* hybridization, that is a change in the HPO angle, though the apparent PO bond lengths in HPO and H_3PO are not so different. The nature of the PO bond in H_3PO and its related molecules has been an old but intriguing subject for quantum chemical theories.^{13,14,34–38} Because of this, it is very desirable to experimentally determine the precise molecular structure of HPO.

ACKNOWLEDGMENTS

The authors thank K. Takagi of Toyama University for the supply of C^{18}O_2 gas. I.K.A. expresses her gratitude to the Japan Society for the Promotion of Science (J.S.P.S.) and the Royal Society (UK) for the award of a fellowship.

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