# Microwave spectra of HPO and DPO: molecular structure

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# Microwave spectra of HPO and DPO: molecular structure

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## Abstract

Microwave spectra of the unstable phosphorus containing molecule, HPO, and its deuterated species were measured in the frequency range of 70–380 GHz. The molecule was produced by a DC-glow discharge of a gas mixture of $PH_3$, $CO_2$, and $H_2(D_2)$. Rotational constants and centrifugal distortion constants for HPO and DPO were determined accurately. Harmonic force constants were evaluated from the centrifugal distortion constants determined in the present study, and with vibrational frequencies reported previously. The zero-point average structure for HPO was obtained by taking the isotopic difference of the PH bond length into consideration: $r_z(\mathrm{PH}) = 1.473(7)$ Å, $r_z(\mathrm{PO}) = 1.4843(9)$ Å, and $\theta_z = 104.57(16)^\circ$. The errors were estimated from the residual inertial defect. Equilibrium bond lengths for the PH and PO bonds were derived as 1.455(7) and 1.4800(9) Å, respectively, by assuming anharmonic constants of the corresponding diatomic molecules.

*Keywords:* Microwave spectroscopy; Unstable molecule; Phosphine oxide; Molecular structure; Harmonic force field

## 1. Introduction

A wide variety of phosphorus containing molecules show a striking contrast to the corresponding nitrogen analogues because of the hypervalent nature of the phosphorus atom itself. This property attracted much attention in the field of chemistry and triggered numerous experimental and theoretical studies [1]. Since the late 1960s, the wealth of publications concerning this issue have focused on the PO bond nature [2] and the phosphine oxide, $H_3PO$, is now accepted as a prototype for the study. One of the highlighted topics revolving around the PO bond nature was the role of *d* functions as polarization functions rather than primary valence orbitals as concluded by Magnusson [3,4]. Gilheany [5] presented an exhaustive review of the PO bond nature in phosphine oxide to support Magnusson's idea and this concept has been widely accepted up to the present day. However, the exact description of the PO bond was not agreed upon in detail probably due to the difference in the interpretation of the bond based on the various approaches adopted in theoretical calculations [6,7]. In order to evaluate and validate these theoretical studies, molecular structural parameters derived by experimental means are essential because the quality of the calculation can be compared with the experimental results.

The $H_3PO$ molecule is a member of the phosphine oxide derivatives $H_nPO$ ($n = 1, 3$), all of which can be observed in a discharge mixture of $PH_3$ in an oxidative atmosphere and are considered intermediates of the $PH_3$ oxidation reaction generating phosphoric acid, $H_3PO_4$. Recently, we have measured microwave spectra of the $H_3PO$ [8] and $H_2PO$ [9] molecules and determined their effective molecular structures from the obtained rotational constants of the normal and isotopic species. Microwave spectroscopy of the HPO molecule has been carried out by Saito et al. [10] They observed a nuclear spin–rotation splitting due to the phosphorus nucleus which is usually too small to be resolved with the typical resolution attained by microwave spectroscopy. However the number of observed transitions was limited and no spectra of isotope species were recorded. Thus, the molecular structure was not inferred on the basis of their experimental results.

As for the molecular structure of HPO, Thanh My and Peyron [11–13] observed the rovibronic transition of $\tilde{A}^1A'' - \tilde{X}^1A'$ and it was later analyzed to derive the molecular structure [14–16]. Larzillière and Jacox [16] measured IR spectra of HPO trapped in a low temperature Ar matrix and they conducted normal coordinate analysis by assuming the molecular structure derived from optical measurements reported previously. The errors for the structure were relatively large especially for the HPO bond angle. If the molecular structure for the HPO molecule is accurately determined, it might be possible to define the PO bond nature by making a comparison with other PO bond containing molecules. In the present study, an extension of the previous microwave spectroscopic measurement on HPO as well as a new observation of the isotopic species, DPO, are presented. In order to provide a definitive structure for the molecule, the vibrationally averaged structure was estimated in accordance with the harmonic force field. The equilibrium distances of the PH and PO bonds were also estimated.

## 2. Experiment

A 100 kHz source modulated microwave spectrometer combined with a 2-m long free space discharge cell was used to detect the HPO molecule. The details of the apparatus are essentially the same as previously reported [17]. The HPO molecule was generated by a DC-glow discharge of $PH_3$, $CO_2$, and $H_2$. In the previous study, the HPO molecule was detected in a discharge mixture of $PH_3$, $H_2$, and $O_2$ [10]. We found in the present study, however, that the production efficiency of HPO was much higher on using $CO_2$ instead of $O_2$ for oxidizing $PH_3$. It is worthwhile noting that the high production efficiency upon using $CO_2$ as an oxidant for $PH_3$ is commonly observed in the series of the phosphine oxides, $H_nPO$ ($n = 1, 2$, and 3) [8,9]. The optimum production conditions were partial pressures of $PH_3$, $CO_2$, and $H_2$ to be 15, 10, and 5 mTorr, respectively, the discharge current was set at 100 mA and the temperature of the cell was kept at around $-150\,^\circ$C. $D_2$ gas was employed instead of $H_2$ in order to measure the deuterated species, DPO; this gas has already proved to be successful in the production of the fully deuterated species of $H_3PO$ [8].

Spectral measurements of HPO were made over the frequency region of 160–370 GHz resulting in the detection of 51 spectral lines which correspond to $N = 5$–4 to 9–8 transitions. For the DPO molecule, 78 lines assigned to transitions $N = 2$–1 to 10–9 were identified in the frequency range of 73–385 GHz. Each line frequency was determined by averaging five pairs of upward and downward frequency sweep measurements. All the observed frequencies for both HPO and DPO as well as those detected in the previous study are listed in Table 1. Effect of nuclear spin–rotation interaction causes sizable spectral splitting, for high $K_a$ transitions of the HPO molecule as was the case in the previous microwave spectroscopic study [10]. For the DPO molecule, an attempt to resolve the hyperfine splitting failed as shown in Fig. 1, presumably due to a small splitting caused by a smaller A rotational constant than that of HPO. All the lines observed in the present study are $a$-type transitions. The observed transition frequencies were analyzed by using an $A$-reduced Hamiltonian including the nuclear spin– rotation interaction term. Combined with the results of the previous measurement, 69 line frequencies of HPO were subjected to a least squares fit to determine the rotational, centrifugal, and nuclear spin–rotation coupling constants. The $\Delta_K$ constant was not able to be floated in the fit and was fixed to 29.1 MHz from the optical spectra [15]. In the analysis of the transition frequencies of the DPO molecule, all the quartic centrifugal distortion constants were obtained. Significantly, the $\Delta_K$ constant was determined to be 4.4 MHz with an error of 3.8 MHz ($3\sigma$). The standard deviation of the fit was 25 kHz for both HPO and DPO and is comparable to the experimental errors. The derived molecular constants are summarized in Table 2.

## 3. Results and discussion

In the present study, rotational constants for both HPO and DPO were accurately determined. We can calculate an effective structure for the molecule from the six molecular constants obtained, i.e., $r_0(\text{PH}) = 1.477$ Å, $r_0(\text{PO}) = 1.478$ Å, and $\theta_0(\text{HPO}) = 106.3°$. Since the HPO molecule forms a bent shape with an angle of $\theta_0$, rotational transitions of both $a$-type and $b$-type are feasible. We have tried to measure $b$-type transitions of HPO but without success. Tapia et al. [18] calculated the dipole moment components for HPO to be $\mu_a = 2.335$ and $\mu_b = 0.507$ D. These values correspond to the square ratio of the $a$- and $b$-components of the dipole moment $(\mu_a/\mu_b)^2$ and is 21. This ratio is much smaller than we observed in the present study, approximately 200. If the overall dipole moment of the HPO molecule is assumed to be a simple sum of the bond moment of the PO and PH bonds, the dipole moment along each axis can be estimated by projecting each component onto the corresponding rotational principal axis. The bond moment of the PO bond is much larger than that of the PH bond and the amount of the $b$-axis component of the dipole moment is very sensitive to the crossing angle between the PO-bond and the $a$-principal axis. The effective structure of the HPO molecule tells us that this angle is about 3.8°, suggesting that the square ratio is approximately 140. This ratio is in reasonable agreement with our experimental results. However, in the case

Table 1
Observed transition frequencies of the HPO and DPO molecules in MHz

| $N'_{K_a'K_c'}-N_{K_aK_c}$ | $F'-F$ | $\nu$ (obs. − calc.) | |
|---|---|---|---|
| | | HPO | DPO |
| $1_{01}-0_{00}$ | | 40539.048(−0.029)$^{a}$ | |
| $2_{02}-1_{01}$ | | 81069.613(−0.007)$^{a}$ | 75951.416(0.020) |
| $2_{12}-1_{11}$ | 2.5–1.5 | 79463.801(0.019)$^{a}$ | 73373.104(0.025)$^{b}$ |
| | 1.5–0.5 | 79464.084(−0.012)$^{a}$ | |
| $2_{11}-1_{10}$ | 2.5–1.5 | 82684.112(0.034)$^{a}$ | 78608.632(0.003)$^{b}$ |
| | 1.5–0.5 | 82684.364(0.001)$^{a}$ | |
| $3_{03}-2_{02}$ | | 121583.085(0.002)$^{a}$ | 113820.747(0.011) |
| $3_{13}-2_{12}$ | | 119189.471(−0.016)$^{a}$ | 110032.575(0.103)$^{d}$ |
| $3_{12}-2_{11}$ | | 124019.635(−0.011)$^{a}$ | 117885.002(0.006) |
| $3_{22}-2_{21}$ | 3.5–2.5 | 121593.354(−0.020)$^{a}$ | 113973.337(−0.019)$^{b}$ |
| | 2.5–1.5 | 121593.852(0.014)$^{a}$ | |
| $3_{21}-2_{20}$ | 3.5–2.5 | 121625.042(−0.040)$^{a}$ | 114141.356(−0.028)$^{b}$ |
| | 2.5–1.5 | 121625.559(0.014)$^{a}$ | |
| $4_{04}-3_{03}$ | | 162070.974(0.027)$^{a}$ | 151562.910(0.027) |
| $4_{14}-3_{13}$ | | 158907.562(0.001)$^{a}$ | 146659.902(0.023) |
| $4_{13}-3_{12}$ | | 165347.219(0.008)$^{a}$ | 157127.255(0.017) |
| $4_{23}-3_{22}$ | | 162115.841(0.010)$^{a}$ | 151929.588(0.052) |
| $4_{22}-3_{21}$ | | 162195.104(0.019)$^{a}$ | 152349.057(−0.053) |
| $4_{32}-3_{31}$ | 4.5–3.5 | 162101.960(−0.013)$^{a,c}$ | 152018.960(0.204)$^{b,d}$ |
| | 3.5–2.5 | 162102.563(0.028)$^{a,c}$ | |
| $4_{31}-3_{30}$ | | | 152021.063(−0.218)$^{d}$ |
| $5_{05}-4_{04}$ | | 202524.722(0.013) | 189136.792(−0.031) |
| $5_{15}-4_{14}$ | | 198615.656(0.006) | 183254.619(0.008) |
| $5_{14}-4_{13}$ | | 206664.165(0.003) | 196323.033(0.041) |
| $5_{24}-4_{23}$ | | 202788.924(−0.033) | 189855.856(0.074)$^{e}$ |
| $5_{23}-4_{22}$ | | | 190692.848(−0.047) |
| $5_{33}-4_{32}$ | | 202630.588(−0.093)$^{c,e}$ | 190056.466(0.140)$^{d}$ |
| $5_{32}-4_{31}$ | | | 190065.016(0.143)$^{d}$ |
| $5_{4}-4_{4}$ | 5.5–4.5 | 202558.621(−0.015) | 189963.901(0.050)$^{b}$ |
| | 4.5–3.5 | 202559.276(0.012) | |
| $6_{06}-5_{05}$ | | 242935.921(0.003) | 226503.984(−0.003) |
| $6_{16}-5_{15}$ | | 238311.337(−0.007) | 219780.812(0.018) |
| $6_{15}-5_{14}$ | | 247967.726(−0.025) | 235459.053(0.013) |
| $6_{25}-5_{24}$ | | 243135.677(0.021) | 227744.665(0.027) |
| $6_{24}-5_{23}$ | | 243412.774(−0.042) | 229203.238(−0.015) |
| $6_{34}-5_{33}$ | | 243160.867(0.193)$^{d}$ | 228113.530(−0.016) |
| $6_{33}-5_{32}$ | | 243161.753(−0.281)$^{d}$ | 228137.048(−0.036) |
| $6_{4}-5_{4}$ | | 243070.020(−0.006) | 227981.995(0.007) |
| $6_{5}-5_{5}$ | 6.5–5.5 | 242966.806(0.010) | 227873.612(−0.015)$^{b}$ |
| | 5.5–4.5 | 242967.383(−0.088) | |
| $7_{07}-6_{06}$ | | 283296.228(0.013) | 263630.290(0.003) |
| $7_{17}-6_{16}$ | | 277992.290(−0.009) | 256257.524(−0.022) |
| $7_{16}-6_{15}$ | | 289255.171(−0.005) | 274521.098(0.014) |
| $7_{26}-6_{25}$ | | 283629.424(0.024) | 265588.679(−0.003) |
| $7_{25}-6_{24}$ | | 284072.533(0.027) | 267906.192(0.013) |
| $7_{35}-6_{34}$ | | 283692.867(0.037) | 266192.150(0.023) |
| $7_{34}-6_{33}$ | | 283695.785(−0.104)$^{e}$ | 266245.000(−0.029) |
| $7_{4}-6_{4}$ | | 283580.765(−0.018) | 266013.948(−0.018) |
| $7_{5}-6_{5}$ | | 283457.695(−0.007) | 265871.584(−0.003) |
| $7_{6}-6_{6}$ | 7.5–6.5 | 283315.255(0.041) | 265739.651(−0.055)$^{b}$ |
| | 6.5–5.5 | 283315.968(0.044) | |
| $8_{08}-7_{07}$ | | 323597.393(0.000) | |
| $8_{18}-7_{17}$ | | 317656.260(0.015) | 292669.128(0.002) |
| $8_{17}-7_{16}$ | | 330523.571(0.010) | 313493.495(−0.033) |
| $8_{27}-7_{26}$ | | 324109.826(−0.007) | 303380.562(0.015) |
| $8_{26}-7_{25}$ | | 324773.725(0.006) | 306820.438(−0.026) |
| $8_{36}-7_{35}$ | | 324227.146(0.015) | 304292.636(−0.002) |
| $8_{35}-7_{34}$ | | 324233.203(−0.045) | 304398.243(−0.023) |
| $8_{4}-7_{4}$ | | 324091.133(0.010) | 304062.121(0.020) |
| $8_{5}-7_{5}$ | | 323946.498(−0.023) | 303878.338(0.012) |
| $8_{6}-7_{6}$ | | 323781.960(−0.009) | 303716.581(−0.012) |
| $8_{7}-7_{7}$ | | | 303553.434(−0.005) |

Table 1 (*continued*)

| $N'_{Ka'Kc'}-N_{KaKc}$ | $F'-F$ | $\nu$ (obs. − calc.) | |
|---|---|---|---|
| | | HPO | DPO |
| $9_{09}-8_{08}$ | | 363831.478(−0.002) | 337062.583(0.008) |
| $9_{19}-8_{18}$ | | 357300.982(−0.015) | 329010.046(−0.016) |
| $9_{18}-8_{17}$ | | 371769.936(−0.010) | 352359.252(−0.022) |
| $9_{28}-8_{27}$ | | 364575.054(−0.007) | 341112.938(−0.018) |
| $9_{27}-8_{26}$ | | 365521.925(0.010) | 345954.742(0.024) |
| $9_{37}-8_{36}$ | | 364763.661(0.018) | 342414.358(−0.029) |
| $9_{36}-8_{35}$ | | 364774.833(−0.021) | 342607.567(−0.001) |
| $9_{46}-8_{45}$ | | 364600.995(0.011)[c] | 342127.405(0.060) |
| $9_{45}-8_{44}$ | | | 342129.968(−0.132)[d] |
| $9_5-8_5$ | | 364433.252(0.014) | 341895.085(−0.012) |
| $9_6-8_6$ | | 364245.518(0.006) | 341699.113(0.008) |
| $9_7-8_7$ | | 364031.717(−0.022) | 341507.307(0.037) |
| $9_8-8_8$ | | | 341306.562(0.053) |
| $10_{010}-9_{09}$ | | | 373347.493(−0.004) |
| $10_{110}-9_{19}$ | | | 365276.236(0.007) |
| $10_{19}-9_{19}$ | | | 391099.554(0.005) |
| $10_{29}-9_{29}$ | | | 378778.751(−0.007) |
| $10_{28}-9_{29}$ | | | 385304.712(0.001) |
| $10_{38}-9_{39}$ | | | 380555.331(−0.002) |
| $10_{37}-9_{39}$ | | | 380885.375(−0.006) |
| $10_{47}-9_{49}$ | | | 380213.226(0.030) |
| $10_{46}-9_{49}$ | | | 380219.206(0.047) |
| $10_5-9_5$ | | | 379923.133(−0.024) |
| $10_6-9_6$ | | | 379687.949(0.005) |
| $10_7-9_7$ | | | 379464.469(−0.033) |
| $10_8-9_8$ | | | 379234.809(−0.037) |

[a] Observed in the previous study [10].
[b] Hyperfine structure was not resolved.
[c] K-doublet was not resolved.
[d] Weight was set to 0.0.
[e] Weight was set to 0.1.

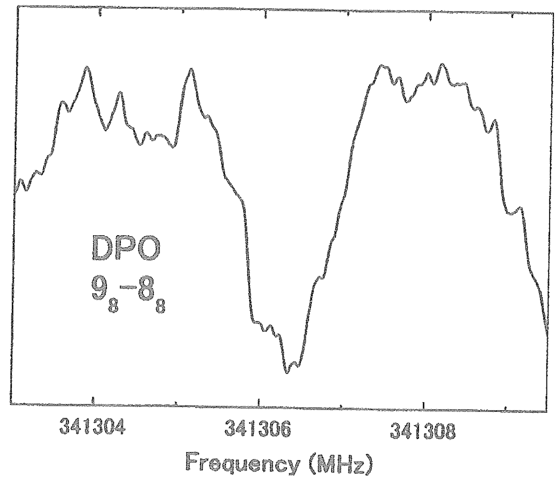

Fig. 1. Microwave spectra of the $9_9-8_8$ transition of the DPO molecule. Neither K-type doubling nor hyperfine splitting due to the nuclear spin-rotation interaction was observed. The spectrum was taken with an accumulation time of 80 s.

of DPO, as the angle between the PO bond and *a*-principal axis increases to 7.7°, the ratio becomes approximately 40. Since the production efficiency of the DPO molecule was found to be lower than that of HPO by a factor of 3, the gain in the dipole moment almost compensated for its low production.

Table 2
Molecular constants for HPO and DPO in MHz

| | HPO | DPO |
|---|---|---|
| $A$ | 264967.8(139)[a] | 141153.7(75) |
| $B$ | 21075.835(41) | 20308.286(42) |
| $C$ | 19463.344(41) | 17688.790(42) |
| $\Delta_J$ | 0.025456(38) | 0.022839(26) |
| $\Delta_{JK}$ | 0.88650(28) | 0.64216(20) |
| $\Delta_K$ | 29.1[b] | 4.4(38) |
| $\delta_J$ | 0.002004(33) | 0.003168(26) |
| $\delta_K$ | 0.571(20) | 0.405(21) |
| $\Phi_{KJ}$ | 0.0001235(57) | 0.0000453(32) |
| $\phi_K$ | −0.00093(40) | −0.000210(68) |
| $Caa$ | −1.02(25) | |
| $Cbb$ | −0.058(186) | |

[a] Values in the parenthesis denote three times the standard deviation and apply to the last digit of the constants.
[b] Fixed.

The harmonic force field of the HPO molecule can be expressed in terms of six independent force constants. If we employ the internal coordinates, $S_1$, $S_2$, and $S_3$ to be $\Delta r$(PH), $\Delta r$(PO), and $\Delta\theta$(HPO), respectively, diagonal components of the force constants are then $f_{11}$ (PH stretch), $f_{22}$ (PO stretch), and $f_{33}$ (HPO bend). Nine quartic centrifugal distortion constants determined in this study in conjunction with vibrational frequencies reported previously [14–16] were subjected to the determination of the force constants. Since the observed vibrational frequencies include anharmonic contribution, its effective errors were assumed to be the order of 10 cm$^{-1}$. The effect of matrix shift has been also taken into account. Computation was performed by using an ASYM40 package coded by Hedberg and Mills [19,20]. The effective structure was used in the calculations. Calculated centrifugal distortion constants and harmonic vibrational frequencies are summarized in Table 3 and the calculated harmonic force constants are listed in Table 4. The stretching and bending force constants derived compare well with those reported previously by Larzillière and Jacox [16].

The vibrationally averaged structure ($r_z$) [21–24] can be calculated from the vibrationally averaged rotational constants, $B_z$, by correcting the observed rotational constants $B_0$ for harmonic vibrational effects using the following equation:

$$B_z = B_0 + \sum_v \frac{1}{2}\alpha_v(\text{har.}), \tag{1}$$

where $\alpha_v$(har.) denotes the harmonic part of the vibration–rotation constant for the vibrational mode $v$. The calculated values of $B_z$ and $\alpha_v$(har.) are summarized in Table 5. The corrected constants give a small residual inertial defect that gives rise to a small systematic error when deriving a molecular structure. In addition, the vibrationally averaged structure has a rigorous physical meaning which enables us to make a critical comparison of the structures obtained by other types of methods or calculations. Since the corrected moments of inertia for both the HPO and DPO molecules are to be used for estimating the vibrationally averaged structure, a sizable difference in the bond lengths between PH and PD would occur as a result of anharmonicity. This isotopic difference of the bond length, $\Delta r_z$, can be expressed approximately as the following [25]:

Table 4
Harmonic force field for HPO

| Force constant | Present study[a] | IR and UV in matrix[b] |
|---|---|---|
| $f_{11}$, aJ Å$^{-2}$ | 2.54(13) | 2.52(2) |
| $f_{12}$, aJ Å$^{-2}$ | 0.335(34) | |
| $f_{22}$, aJ Å$^{-2}$ | 8.867(22) | 8.67(16) |
| $f_{13}$, aJ Å$^{-1}$ rad$^{-1}$ | −0.081(49) | |
| $f_{23}$, aJ Å$^{-1}$ rad$^{-1}$ | 0.333(12) | 0.06(12) |
| $f_{33}$, aJ rad$^{-2}$ | 1.070(20) | 1.08(2) |

[a] The internal coordinates used are $S_1 = \Delta r$(PH), $S_2 = \Delta r$(PO), and $S_3 = \Delta\theta$(HPO). The effective structure ($r_0$) was used for the geometry, i.e., $r$(PH) = 1.477 Å, $r$(PO) = 1.478 Å, and $\theta$(HPO) = 106.3°.

[b] Larzillière and Jacox [16]. The following molecular structure was assumed; $r$(PH) = 1.433 Å, $r$(PO) = 1.512 Å, and $\theta$(HPO) = 104.73°.

Table 5
Vibrationally averaged rotational constants and harmonic vibration–rotation constants

| Constant | HPO | DPO |
|---|---|---|
| $A_z$, MHz | 260948.3(47)[b] | 139455.6(26)[b] |
| $B_z$, MHz | 20998.1(32)[b] | 20226.8(24)[b] |
| $C_z$, MHz | 19435.3(16)[b] | 17665.9(30)[b] |
| $\Delta_z$[a], uÅ$^2$ | −0.0015 | −0.0019 |
| $\alpha_1^A$, MHz | −6014.2 | −2241.9 |
| $\alpha_1^B$, MHz | −2.9 | −5.3 |
| $\alpha_1^C$, MHz | −47.3 | −55.2 |
| $\alpha_2^A$, MHz | −27.5 | −38.3 |
| $\alpha_2^B$, MHz | −74.2 | −68.2 |
| $\alpha_2^C$, MHz | −81.6 | −57.7 |
| $\alpha_3^A$, MHz | −1997.3 | −1116.1 |
| $\alpha_3^B$, MHz | −78.4 | −89.6 |
| $\alpha_3^C$, MHz | 72.9 | 67.0 |

[a] Residual inertial defect.

[b] Errors are estimated by the contributions from uncertainty of the effective rotational constants ($B_0$) and residual inertial defect.

Table 3
Observed and calculated centrifugal distortion constants, vibrational frequencies and inertial defect of HPO and its deuterated species.

| Parameter | HPO | | DPO | |
|---|---|---|---|---|
| | Obs. | Calc. | Obs. | Calc. |
| $\Delta_J$, kHz | 25.456(13)[a] | 25.461 | 22.839(9)[a] | 22.835 |
| $\Delta_{JK}$, kHz | 886.50(9)[a] | 886.50 | 642.16(7)[a] | 642.17 |
| $\Delta_K$, kHz | 29.1[b] | 21.9 | 4.4(13)[a] | 6.2 |
| $\delta_J$, kHz | 2.004(11)[a] | 1.963 | 3.168(9)[a] | 3.195 |
| $\delta_K$, kHz | 571.(7)[a] | 516. | 405.(7)[a] | 394. |
| $\omega_1$, cm$^{-1}$ | 2095.(20)[c] | 2105. | 1530.(20)[c] | 1505. |
| $\omega_2$, cm$^{-1}$ | 1188.043(10000)[d] | 1186. | 1186.(20)[c] | 1184. |
| $\omega_3$, cm$^{-1}$ | 985.542(10000)[d] | 966. | 750.(10)[c] | 717. |

[a] 1$\sigma$ error.

[b] Not included in the fit as the constant was not derived directly from the present microwave experiment.

[c] Larzillière and Jacox [16]. Estimated errors due to matrix shift and anharmonicity.

[d] Larzillière et al. [15]. Estimated errors due to anharmonicity.

$$\Delta r_z = \frac{3}{2} a_3 \Delta\langle \Delta z^2 \rangle - \frac{\Delta(\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)}{2 r_e}, \tag{2}$$

where $\Delta x$, $\Delta y$, and $\Delta z$ are displacements of local Cartesian coordinates, $a_3$ and $r_e$ denote the third-order anharmonic constant for the PH bond and equilibrium bond length, respectively. $\Delta\langle\,\rangle$ refers to the difference of the average value in question between the PH and PD bonds. In this case the $z$-axis is taken to be that which lies along the PH(PD) bond. The $a_3$ value for the PH molecule is listed in the table (1.659 $\text{Å}^{-1}$ for PH, 1.654 $\text{Å}^{-1}$ for PD) compiled by Kuchitsu et al. [25]. Though this reference is useful for our purpose, it is advisable to adopt a more recent value, if one is available. Since an RKR potential for the PH molecule was proposed by Ram and Bernath [26] which was obtained from their FT-IR study, we evaluated $a_3$ to be 1.487 $\text{Å}^{-1}$ in order to reproduce the lower shape of the potential. By taking this value, the difference between the PH and PD bonds, $\Delta r_z$, is estimated to be 0.0054 Å. Here we have employed the $r_e$ value of the PH bond to be 1.452 Å, which was obtained by an ab initio (CASPT2) calculation by Luna et al. [27] Since the value $\Delta r_z$ is dominated by the first term of the right-hand side in Eq. (2), it is not sensitive to the choice of the calculated equilibrium bond length. The isotopic difference in bond length is quite similar to the value of 0.0051 Å obtained for the $PH_2$–$PD_2$ system [28], suggesting validity of the present estimation. Given the difference of the bond length, $r_z$(PH)–$r_z$(PD), is 0.0054 Å, we derived the molecular structure for HPO from the six corrected rotational constants, i.e., $r_z(\text{PH}) = 1.473(7)$ Å, $r_z(\text{PO}) = 1.4843(9)$ Å, and $\theta_z(\text{HPO}) = 104.57(16)°$. The errors in parenthesis were estimated from the errors of the corrected constants. We assumed common values of $r_z$(PO) and $\theta_z$(HPO) for the normal and deuterated species in the structure derivation. Though the error in the PH bond length is relatively large, our result shows the longest bond length obtained thus far by either experimental or theoretical means. The derived PO bond length is much shorter than the value obtained by Thanh My and Peyron (1.512 Å) [13] but is comparable to the more recent results of Larzillière et al.(1.480 Å) [15]. They reported the bond angle to be 103.75° with a large error of 2.5° ($1\sigma$). This experimental ambiguity has been made significantly smaller in the present study as the bond nature of the PO bond has been discussed quantitatively.

The equilibrium bond distance can be evaluated by estimating the anharmonic correction from the following approximation relation [25]:

$$r_z - r_e = \left(\frac{3}{2}\right) a_3 \langle \Delta z^2 \rangle - \frac{(\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle)}{2 r_e}. \tag{3}$$

Table 6
Vibrationally averaged and equilibrium structure for HPO

| | $r_z$ | $r_e$ |
|---|---|---|
| $r$(PH), Å | 1.473(7) | 1.455(7) |
| $r$(PO), Å | 1.4843(9) | 1.4800(9) |
| $\theta$(HPO), degree | 104.57(16) | 104.57[a] |

[a] Assumed to be equal to $\theta_z$(HPO)

Table 7
Comparison of the structural parameters of HPO with those of related molecules

| Molecules | $r$(PH), Å | $r$(PO), Å | $\theta$(HPO), degree | $\theta$(HPH), degree | Method |
|---|---|---|---|---|---|
| HPO | 1.473(7) | 1.4843(9) | 104.57(16) | | MW, $r_z$[a] |
| | 1.455(7) | 1.4800(9) | 104.57 | | MW, $r_e$[a] |
| | 1.433 | 1.512 | 104.73 | | Optical, $r_0$[b] |
| | 1.456(3) | 1.480(5) | 103.5(25) | | Optical, $r_0$[c] |
| | 1.452 | 1.490 | 104.1 | | Ab initio, $r_e$[d] |
| $H_2PO$ | 1.4287(5) | 1.4875(2) | 115.52(3) | 102.56(5) | MW, $r_0$[e] |
| $H_3PO$ | 1.4406 | 1.4763 | 114.26 | 104.29 | MW, $r_0$[f] |
| | 1.4061 | 1.4855 | 117.68 | 100.16 | Ab initio, $r_e$[g] |
| *cis*-$H_2POH$ | 1.4171 | 1.6584 | 101.64 | 92.32 | Ab initio, $r_e$[h] |
| PO | | 1.476370(5) | | | IR, $r_e$[i] |
| $PH_3$ | 1.41154(17) | | | 93.36(3) | MW, $r_e$[j] |
| $PH_2$ | 1.43365(8) | | | 91.622(11) | MW, $r_z$[k] |
| PH | 1.42140(8) | | | | MW, $r_e$[l] |

[a] Present study.
[b] Thanh My and Peyron [13].
[c] Larzallière et al. [16].
[d] Luna et al. [27].
[e] Hirao et al. [9].
[f] Ahmad et al. [8].
[g] Kwiatkowski and Leszczyñski [34].
[h] Kwiatkowski and Leszczyñski [29].
[i] Butler et al. [30].
[j] Chu and Oka [35].
[k] Hirao et al. [28].
[l] Ohashi et al. [36].

As for the PH bond length, the corresponding value amounts to 0.0184 Å and consequently the equilibrium distance for the PH bond, $r_e$(PH), is estimated to be 1.455(7) Å. Similarly, $r_e$(PO) was derived as 1.4800(9) Å with the aid of the anharmonic constant, $a_3$, of the PO radical (2.101 Å$^{-1}$) [25]. The estimated structures of the HPO molecule in the present study are summarized in Table 6. These bond lengths can compare well with the recent ab initio calculation. The results of the CASPT2 level calculation of Luna et al. [27] suggest that $r_e$(PH) and $r_e$(PO) are 1.452 and 1.490 Å, respectively.

Table 7 summarizes the structural parameters of HPO and its related compounds, measured or calculated by various methods. The HPO molecule can be formally described as H–P=O, where the PH and PO bonds denote typical single and double bonds, respectively. The PO bond length ($r_z = 1.4843$ Å) is almost similar to that for $H_2PO$ (1.4875 Å) and $H_3PO$ (1.4763 Å) [8,9], and is much shorter than that of *cis*-$H_2POH$ (1.6584 Å) [29], suggesting that the PO bond order is approximately 2. The equilibrium bond distance of the PO radical (1.476370 Å) [30] is almost the same as that of HPO ($r_e = 1.4800$ Å). The harmonic frequency of the PO stretching mode (1193 cm$^{-1}$) is comparable to the PO radical ($\nu_0 = 1220.24901$ cm$^{-1}$) [30]. In support of this, Essefar et al. [31] suggested from the topological features of HPO that the density of charge in the bond critical point remains almost unchanged by the addition of a hydrogen atom. Contrary to the above, however, we see some evidence suggesting deviations from the conventional formulation. First, the PH bond length ($r_z = 1.473$ Å, $r_e = 1.455$ Å) is the longest amongst the molecules listed in Table 7 even though the estimated error in the present study is relatively large. This fact is supported by the vibrational frequency of the corresponding mode. The harmonic frequency for the PH bond stretch (2058 cm$^{-1}$) is much lower than that for the PH radical ($\omega_e = 2363.774$ cm$^{-1}$) [32]. Second, the HPO bond angle value of 104.57° is extraordinary. This value is far from a typical angle for $sp^2$ hybridization and is much smaller than those for $H_2PO$ (115.52°) and $H_3PO$ (114.26°) [8,9], but is comparable to that of *cis*-$H_2POH$ (101.64°) [29]. Third, even for the PO bond, atoms in molecule (AIM) study by Chesnut [7] revealed the two bonding orbitals involving phosphorus and oxygen atoms to be highly localized and also strongly ionic. Combining the evidence available thus far, it might be easier to understand the HPO molecular structure by considering the contribution of the resonance forms, $H^-$ $P^+$=O, and H–$P^+$–$O^-$, to the normal form, H–P=O. This idea is feasible by taking the electronegativity of each atom ($\chi(H) = 2.2$, $\chi(P) = 2.1$, $\chi(O) = 3.5$) into account [33].

In summary the present microwave experiment of HPO and its deuterated species provides a definitive molecular structure of the molecule, completing the previous experimental results with respect to the structural parameters for the phosphine oxide compounds ($H_nPO$, $n = 1$, 2, and 3). As for the molecular structure of HPO, a resonance structure, $H^-$ $P^+$=O ↔ H–P=O ↔ H–$P^+$–$O^-$, can adequately explain the experimental results. This information will promote further theoretical studies to conclude the PO bond nature of the phosphine oxide as yet in controversy.

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