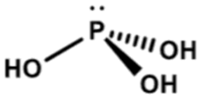
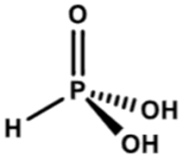
Phosphorous Acid Lab Report

Introduction

This experiment investigates the structure of phosphorous acid (H_3PO_3). The acid is synthesized by the hydrolysis of phosphorus trichloride (PCl_3) using either H_2O or D_2O. Spectroscopy of both the acid and its deuterated analogue provides key information about its structure using a technique called isotopic substitution. The two plausible structures are given below:





This experiment uses multinuclear NMR and IR. NMR spectroscopy is an analytical method that uses the magnetic properties of nuclei with nonzero nuclear spin numbers to elucidate valuable information about chemical structures and bonding. The number of possible orientations or spin states a nucleus can occupy is defined by the formula $(2I + 1)$, where I is the nuclear spin number. For example, hydrogen (^{1}H) is a fermion, meaning it has a nuclear spin of $I = ½$ and 2 possible spin states (-1/2, +1/2). Deuterium (^{2}H) is a boson, meaning it has a nuclear spin of $I = 1$ and 3 possible spin states (-1, 0, +1). Deuterium's spin-1 state also means it has a nuclear quadrupole moment, which is essentially a quantification of the degree to which charge distribution in a nucleus deviates from being spherically symmetrical. This introduces an electric field gradient that can interact with and efficiently relax the nucleus (1). Rapid relaxation also induces peak broadening and can cause multiplets to converge into single observable peaks as this relaxation happens too quickly for NMR to properly resolve it. The difference in spin states manifests in the H_3PO_3 and D_3PO_3 NMR spectra through observable multiplets (as demonstrated in Figures 2 and 3). Even though the structures have uneven numbers of hydroxyl groups, they cannot be detected due to the nature of solvent exchange – the rapid exchange of acidic protons, except those attached directly to the carbon or phosphorus center, with solvent protons -- and are therefore not diagnostic.

IR complements NMR by exploring the nature of vibrational frequency transitions from atomic oscillations. These vibrational frequencies depend on both the strength of the bond (or force constant, κ) and reduced mass, μ. Isotopic substitution, like replacing hydrogen with deuterium, changes the reduced mass and thereby changes the observed vibrational frequencies. In this experiment, these changes are exhibited in the O-H/D and P-H/D stretches (as seen in Figure 1).

Results

Phosphorous acid and its deuterated analogue were synthesized by hydrolysis of phosphorous trichloride (PCl_3) under nitrogen, followed by isolation and drying under vacuum to produce colorless solids in high yield (H_3PO_3: 1.390 g, 16.95 mmol, 94.17%; DPO3: 1.503 g,17.68 mmol, 98.22%)

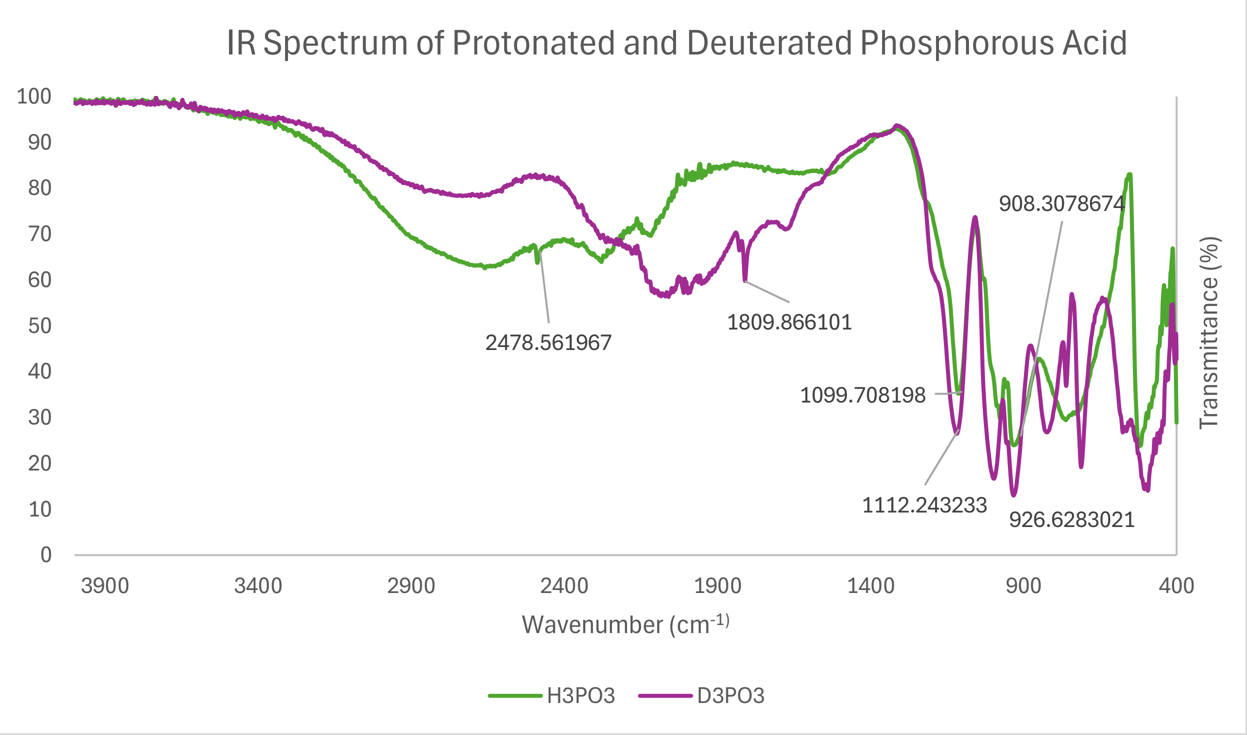


Figure 1: ATR-IR of phosphorous acid (H_3PO_3) and deuterated analogue (D_3PO_3)

Table 1: Tabulated ATR-IR values

Region (cm^{-1})	Functional Groups	Comments	Series
2478.6	P-H	P-H stretch	H3PO3
1809.9	P-D	P-D stretch	D3PO3
1112.2	P=O	P=O stretch	D3PO3
1099.7	P=O	P=O stretch	H3PO3
926.6	P-O	P-O asymmetric stretch	D3PO3
908.3	P-O	P-O asymmetric stretch	H3PO3
~3000-1900	O-H	O-H stretching vibrations	H3PO3
~2400-1400	O-D	O-D stretching vibrations	D3PO3

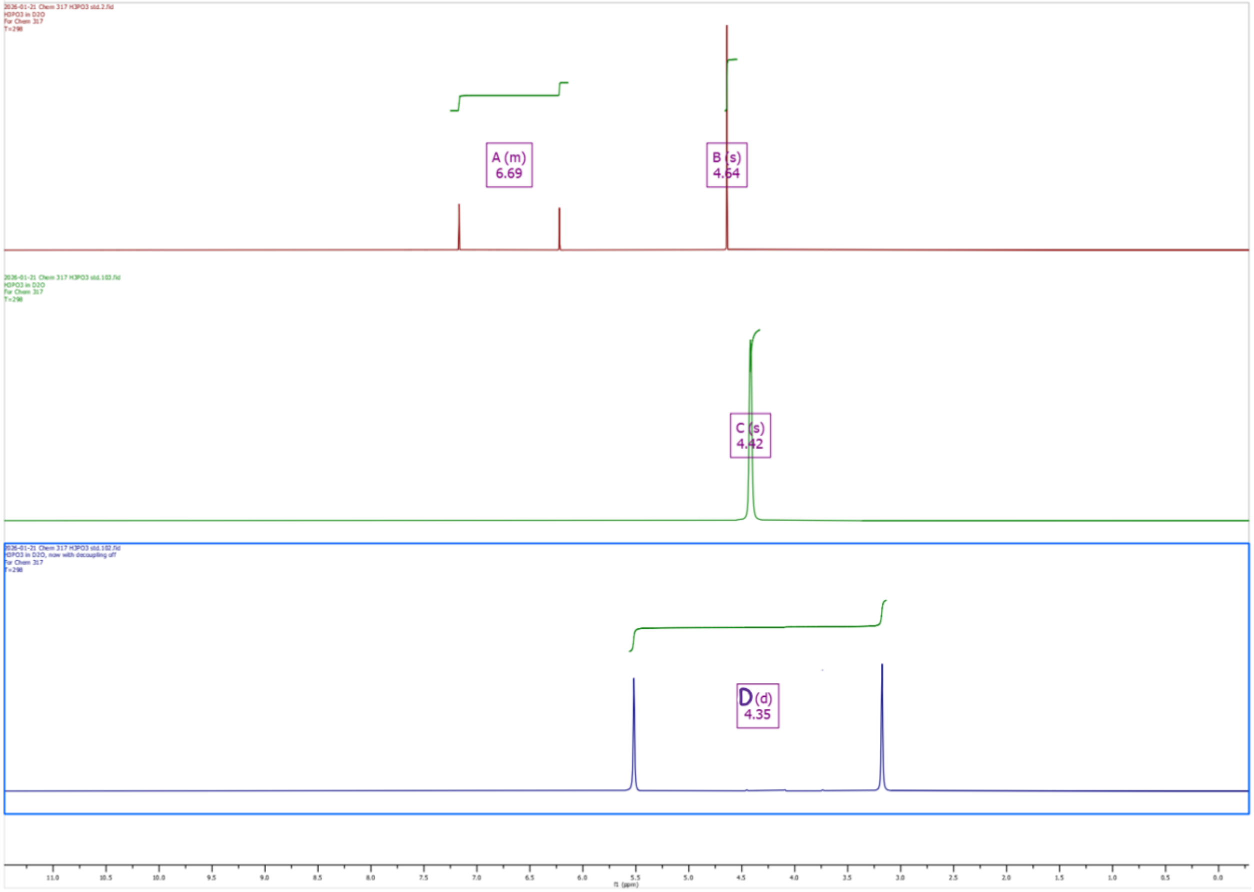


Figure 2: 700 MHz ^{1}H-NMR (top), ^{31}P{^{1}H}-NMR (middle), and ^{31}P-NMR (bottom) of phosphorous acid

Table 2: Tabulated ^{1}H-NMR, ^{31}P{^{1}H}-NMR, and ^{31}P-NMR values

Signal	Peak (ppm)	Multiplicity	Integration	Coupling (Hz)	Identity
A	6.69 (7.17, 6.17)	doublet	1	$J_{P\text{-}H}$ = 704.37	P-H
B	4.64	singlet	1	n/a	D_2O
C	4.42	singlet	1	n/a	P (P center, ^{1}H-decoupled)
D	4.35 (5.52, 3.17)	doublet	1	$J_{H\text{-}P}$ = 666.19	H-P

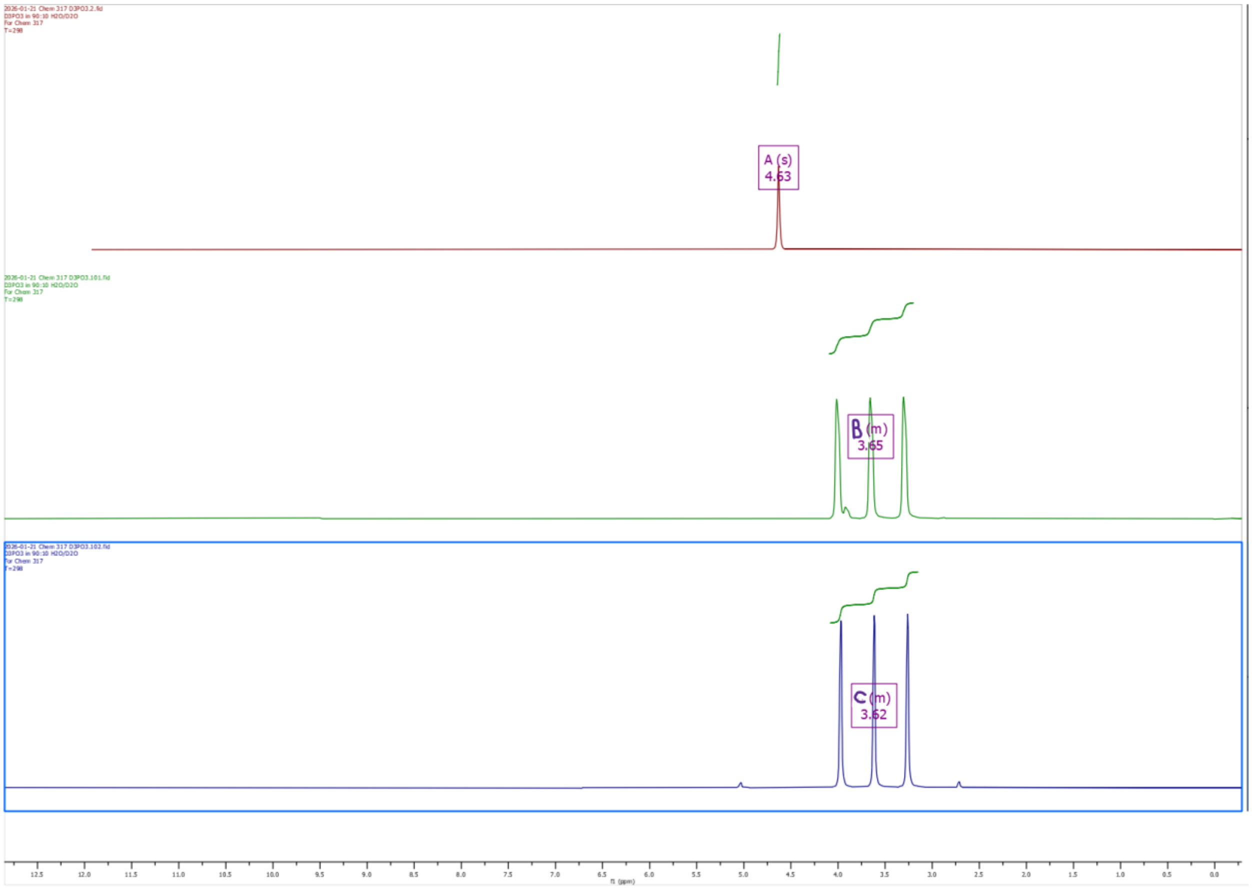


Figure 3: 700 MHz ^{2}H-NMR (top), ^{31}P{^{1}H}-NMR (middle), and ^{31}P-NMR (bottom) of deuterated phosphorous acid

Table 3: Tabulated ^{2}H-NMR, ^{31}P{^{2}H}-NMR, and ^{31}P-NMR values

Signal	Peak (ppm)	Multiplicity	Integration	Coupling (Hz)	Identity
A	4.63	Singlet	1	n/a	P-D
B	3.65 (4.05, 3.65, 3.30)	Triplet	1	J_{D-P} = 109.78	P (P center, ^{2}H-decoupled)
C	3.62 (3.97, 3.62, 3.26)	Triplet	1	J_{D-P}= 101.54	D-P

Discussion

IR and multinuclear NMR were used to elucidate the bonding and structure of phosphorous acid (H_3PO_3) and its deuterated analogue (D_3PO_3). The combined spectroscopic data provide unambiguous evidence of direct P-H and P-D bonds, consistent with OP(=O)(O)H or [^{2}H]P(=O)(O[^{2}H])O[^{2}H] configurations rather than a fully hydroxylated center.

The IR spectra show distinct differences between the P-H and P-D stretching frequencies. In the harmonic oscillator model, vibrational frequency is inversely proportional to the square root of reduced mass, as described by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\kappa}{\mu}}$$

where κ is the force constant and μ is the reduced mass. Replacing hydrogen with deuterium increases the reduced mass, so stretching frequencies are reduced by roughly $\sqrt{\frac{\mu_H}{\mu_D}}$. Consistent with this prediction, H_3PO_3 shows P-H stretching at 2478.6 cm^{-1}, while D_3PO_3 shows a shifted P-D stretch at 1809.9 cm^{-1}. Similar isotopic shifts are observed in the broad O-H and O-D stretching regions (~3000-1900 cm^{-1} and ~2400-1400 cm^{-1}, respectively). The P=O and P-O stretching frequencies remain essentially unchanged across both series because the reduced masses stay the same. This indicates that deuteration does not significantly alter the phosphorous-oxygen bonding framework.

The ^{1}H and ^{31}P NMR spectra of H_3PO_3 provide robust evidence for direct P–H bonding. The presence of large coupling constants ($J_{P\text{-}H}$ = 704.37 and $J_{H\text{-}P}$ = 666.19) in both the ^{1}H and proton-coupled ^{31}P spectra is characteristic of a direct P–H interaction. Phosphorous is a third-row element, and its valence electrons occupy larger, more polarizable orbitals than second-row elements like carbon. Because J coupling is dependent on the transfer of electron spin density between nuclei through bonding electrons, the increased polarizability and s-character of the P-H bond allow more efficient transmission of spin polarization – resulting in a large coupling constant (2). Such coupling would not be observed if the phosphorous had a fully hydroxylated center. In the ^{31}P{^{1}H}-NMR spectrum, ^{31}P resonance collapses into a single peak, confirming the multiplet structure observed comes from coupling to hydrogen rather than any chemical inequivalence. No O-H peaks are observed in any of the spectra due to rapid solvent exchange between the protons and D_2O.

The ^{2}H-NMR spectra are substantially different from the ^{1}H-NMR spectra due to differences in nuclear spin. Hydrogen has a nuclear spin of I = +/- ½, while deuterium has a nuclear spin of I = +/- 1. Based on the formula (2I + 1), hydrogen has 2 allowed spin states (m = -1/2, +1/2) and deuterium has 3 (m = -1, 0, +1). This explains why both the coupled and decoupled ^{31}P-NMR spectrums show three equally intense peaks. It is important to note that these are *not* “traditional” triplets: unlike proton-derived triplets with 1:2:1 intensity patterns, coupling to spin-1 nuclei produces 1:1:1 intensity patterns. By contrast, only one peak is observed in the ^{2}H-NMR spectrum because P-D coupling is unresolved. Deuterium has a nuclear quadrupole moment that allows it to interact with both magnetic and electric field gradients within the molecule. This results in rapid relaxation through interactions with electrical field gradients, causing line broadening and the collapse of any expected splitting into one observable peak. Similar to the H_3PO_3 spectra, both ^{31}P-NMR spectra show large coupling constants: further evidence of direct P-D interaction.

Experimental

General Considerations

All manipulations were carried out using standard Schlenk techniques under a positive pressure of dry nitrogen. Chloroform (CHCl3) and phosphorous trichloride (PCl3) were used as received. Water and D_2O were degassed by repeated nitrogen purges immediately prior to use to minimize isotopic dilution from atmospheric moisture. IR spectra were recorded using an ATR attachment on a Thermo Scientific FTIR spectrometer. NMR spectra were recorded in D2O (H3PO3) or 90:10 H2O:D2O (D3PO3) on Bruker Avance 200 MHz and 700 MHz instruments.

Synthesis of phosphorous acid (H_3PO_3) and deuterated analogue (D3PO3)

A 50-mL Schlenk flask equipped with a magnetic stir bar was charged with chloroform (CHCl3, 20 mL) and sealed with a rubber septum. A nitrogen flushed- syringe was used to transfer PCl_3 (1.60 mL, ~2.5 g, ~0.018 moles) into the chloroform solution. The flask was chilled in an ice bath and open to a flow of dry nitrogen gas to two consecutive bubblers (mineral oil and neutralizing KOH). With a second syringe, degassed water (H2O or D2O) (1.0 mL, ~0.055 moles) was added dropwise. Vigorous evolution of HCl or DCl was observed. When the vigorous reaction concluded, the ice bath was removed and the mixture was stirred at ambient temperature (30 minutes). The solid product was isolated and washed with two aliquots of chloroform (10 mL) to remove excess water. The solid was dried under dynamic vacuum to remove all volatile components and yield a colorless solid (H3PO3: 1.390 g, 16.95 mmol, 94.17%; D3PO3: 1.503 g,17.68 mmol, 98.22%)

Conclusion

IR and multinuclear NMR spectroscopy provided complementary insight into the structure of phosphorous acid and its deuterated analogue. The IR spectra show clearly the isotopic shifts between the P-H/D and O-H/D stretching frequencies: consistent with the harmonic oscillator model, the vibrational frequencies of the deuterated species were lower than its analogue. P-O and P=O stretching frequencies remain essentially unchanged, indicating that deuteration does not upset the phosphorus-oxygen bonding framework. ^1H and ^{31}P-NMR spectra of H_3PO_3 exhibit large coupling constants, which confirms direct P-H bonding. The $^{31}P\{^1H\}$-NMR spectrum collapses into a singlet, demonstrating that the multiplets in the other spectra are due to P-H interactions rather than chemical inequivalence. By contrast, the ^2H-NMR spectrum of D_3PO_3 shows a single peak due to the rapid quadrupolar relaxation of the deuterium nucleus. The ^{31}P-NMR spectra provide further evidence of direct P-D bonding through large coupling constants. Overall, the IR and NMR data are internally consistent. Spectroscopic evidence collectively and unambiguously confirms that phosphorous acid contains direct P-H bonds rather than a fully hydroxylated center, and highlights the value of IR, NMR, and isotopic substitution in elucidating molecular structures.

References

(1) *Quadrupolar Coupling*. Chemistry LibreTexts. https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Magnetic_Resonance_Spectroscopies/Nuclear_Magnetic_Resonance/NMR_-_Theory/NMR_Interactions/Quadrupolar_Coupling.

(2) Autschbach, J.; Le Guennic, B. Analyzing and Interpreting NMR Spin–Spin Coupling Constants Using Molecular Orbital Calculations. *Journal of Chemical Education* **2007**, *84* (1), 156. https://doi.org/10.1021/ed084p156.

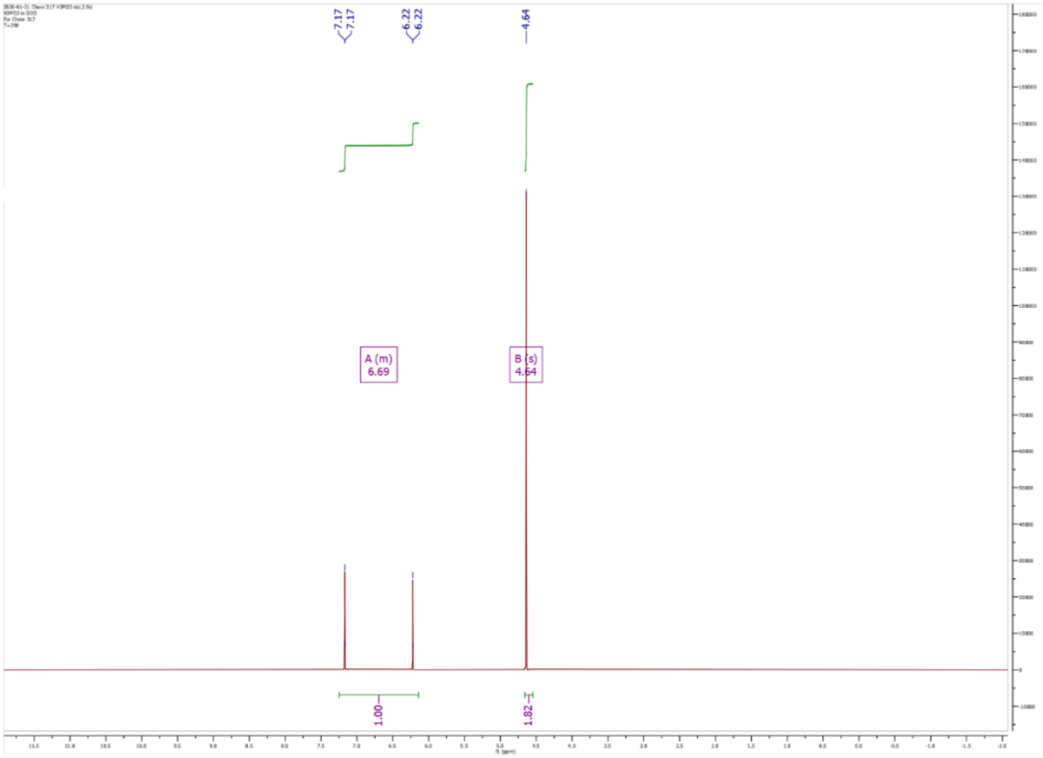


Figure 4: 700 MHz ^{1}H-NMR of phosphorous acid

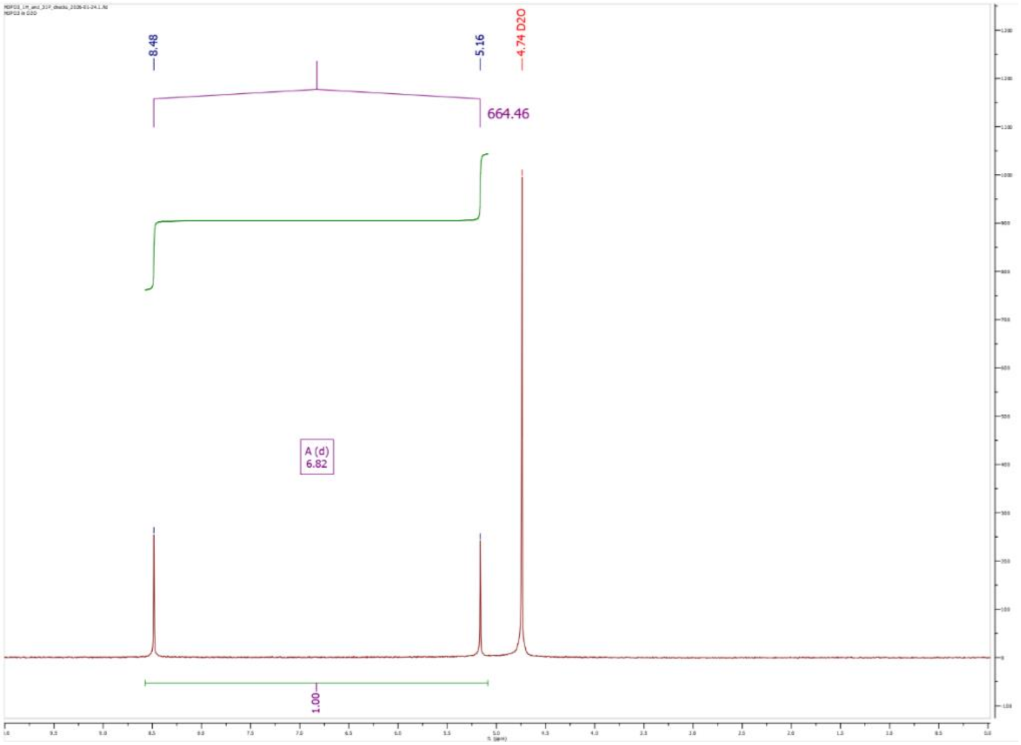


Figure 5: 200 MHz ^{1}H-NMR of phosphorous acid

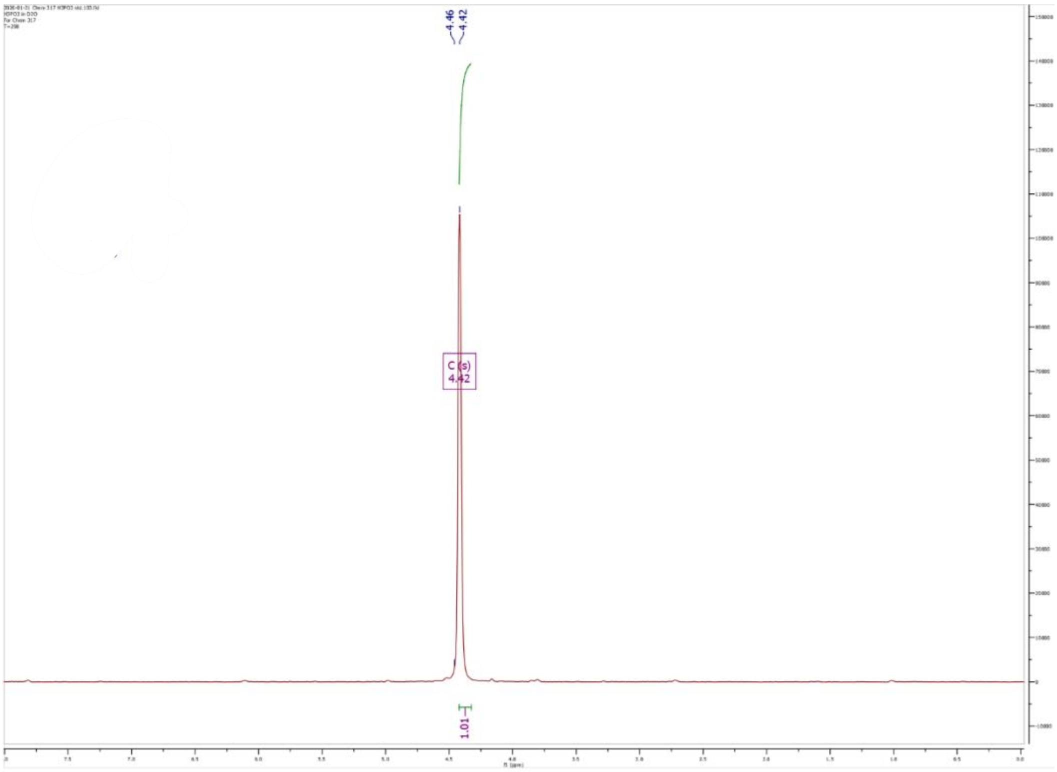


Figure 6: 700 MHz $^{31}P\{^{1}H\}$-NMR of phosphorous acid

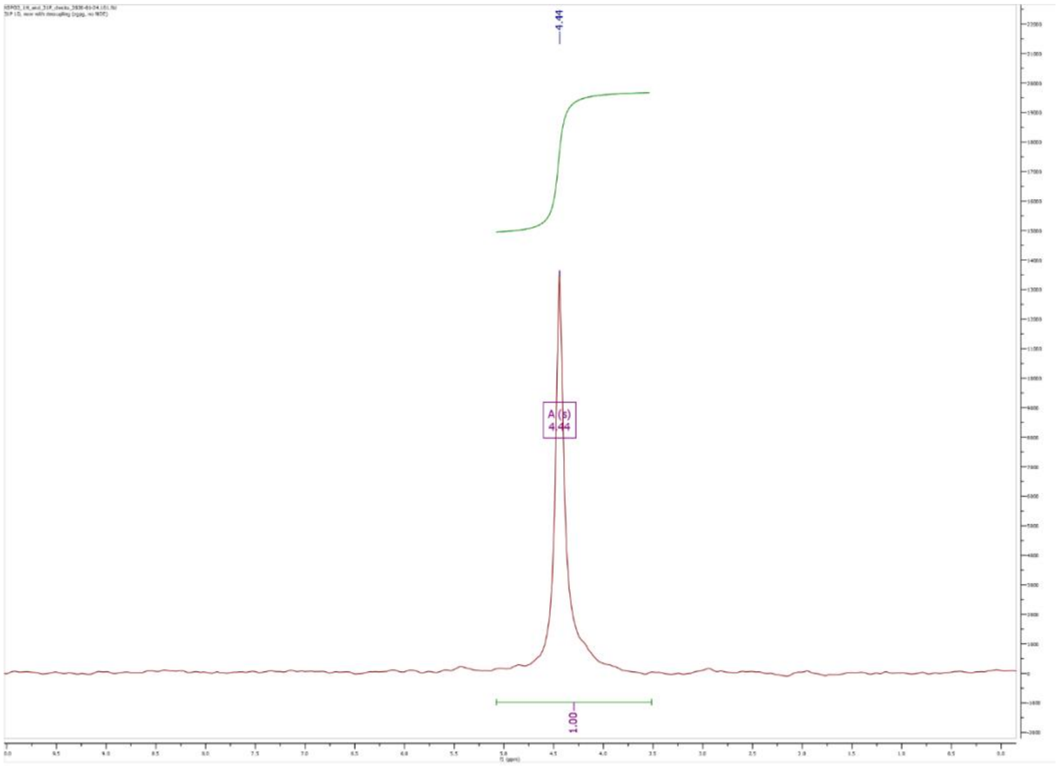


Figure 7: 200 MHz $^{31}P\{^{1}H\}$-NMR of phosphorous acid

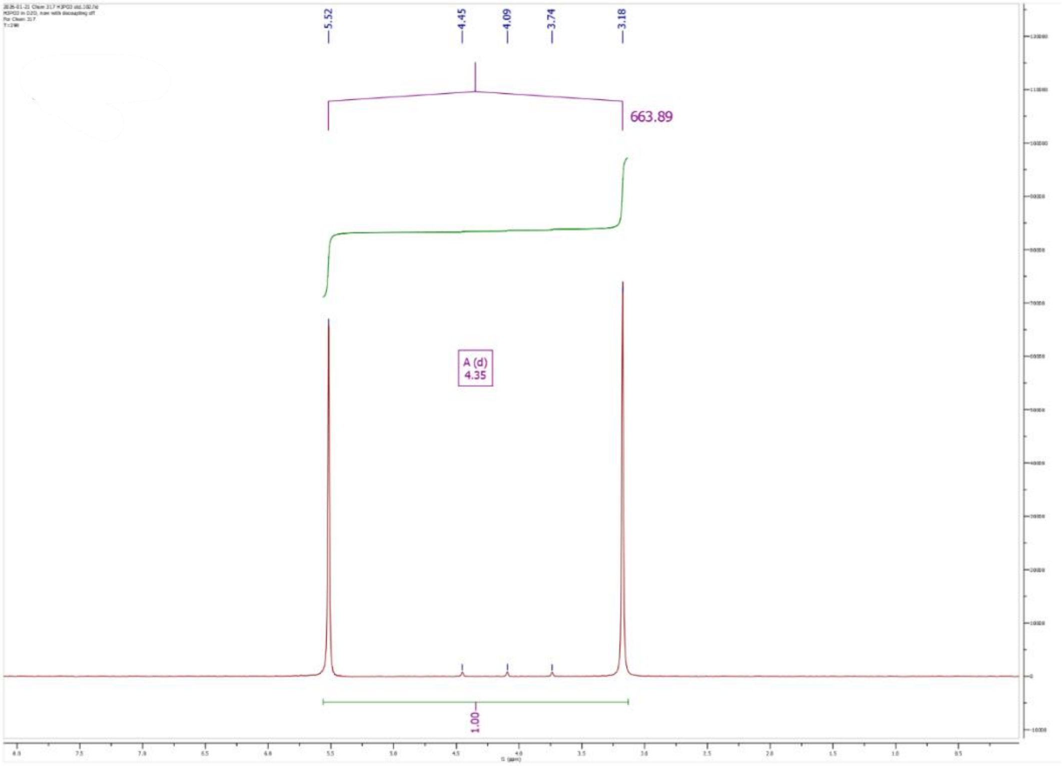


Figure 8: 700 MHz ^{31}P-NMR of phosphorous acid

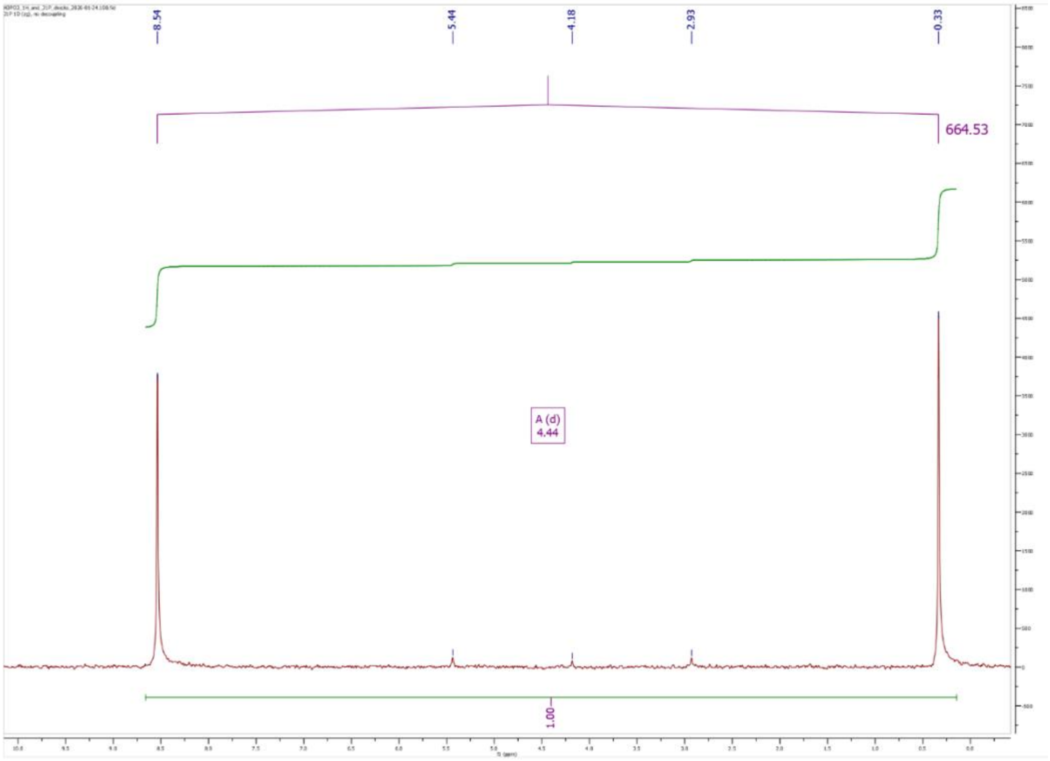


Figure 9: 200 MHz ^{31}P-NMR of phosphorous acid

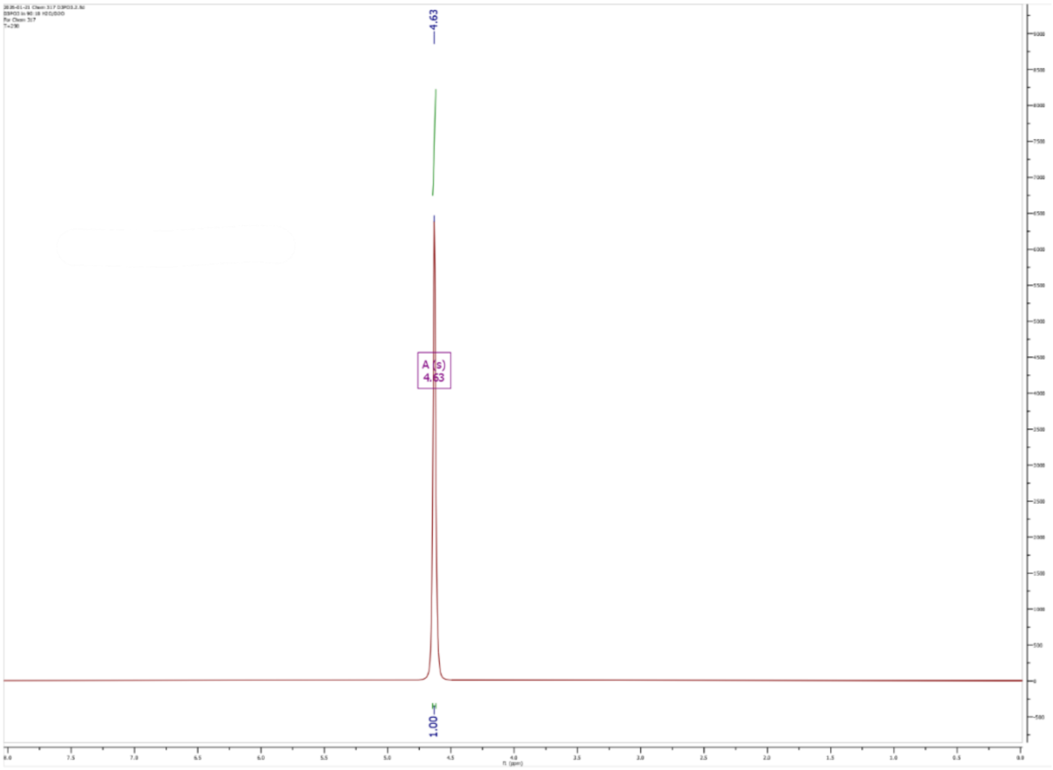


Figure 10: 700 MHz ^{2}H-NMR of deuterated phosphorous acid

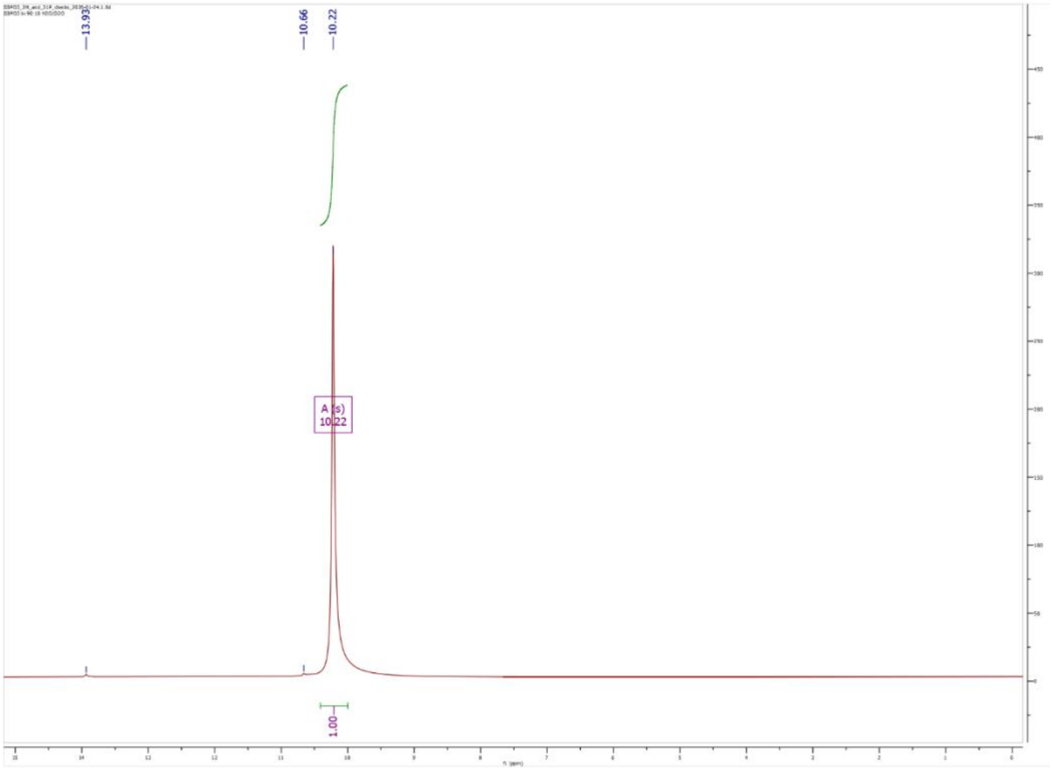


Figure 11: 200 MHz ^{2}H-NMR of deuterated phosphorous acid

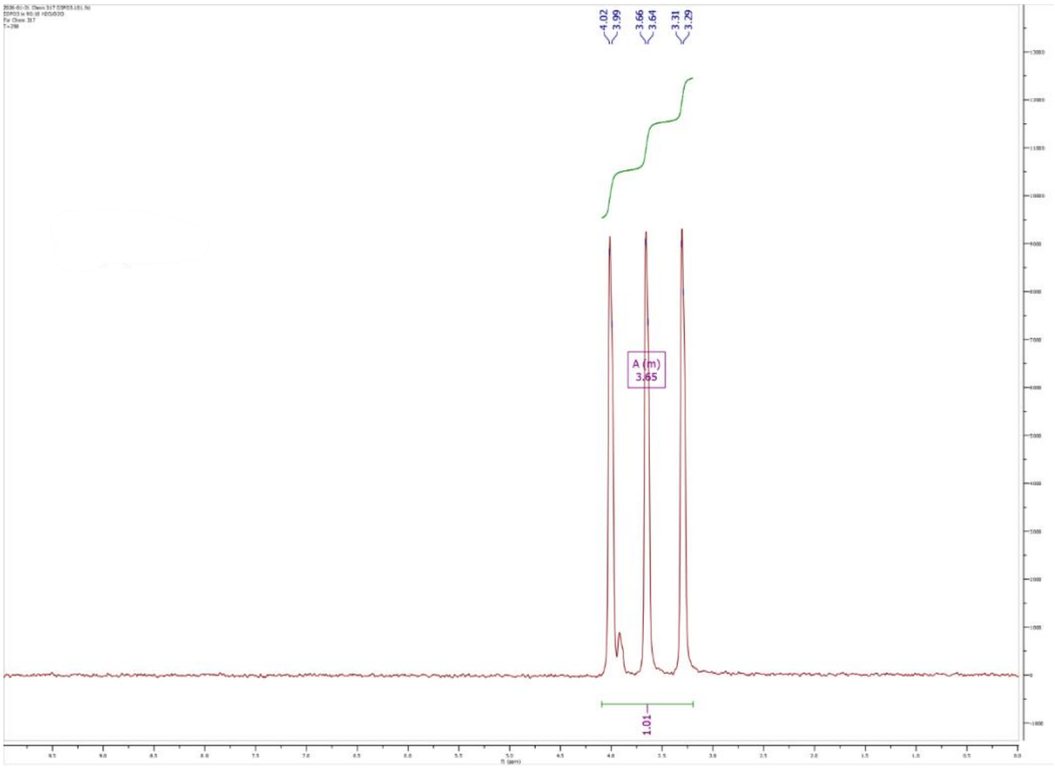


Figure 12: 700 MHz $^{31}P\{^1H\}$-NMR of deuterated phosphorous acid

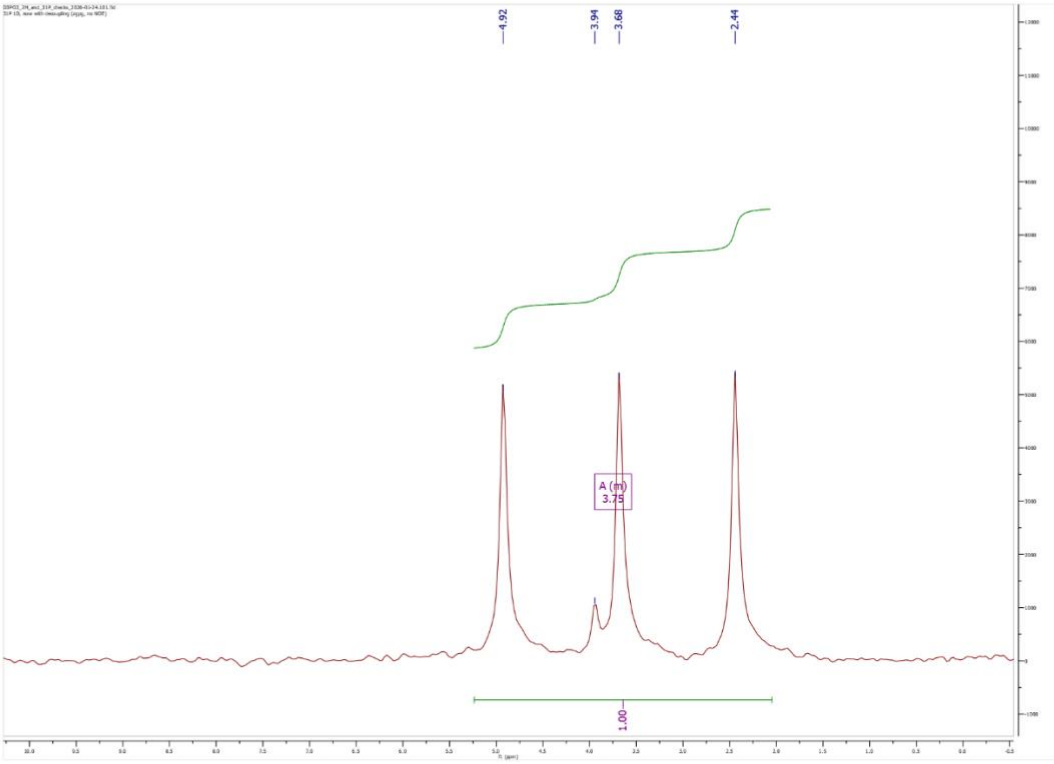


Figure 13: 200 MHz $^{31}P\{^1H\}$-NMR of deuterated phosphorous acid

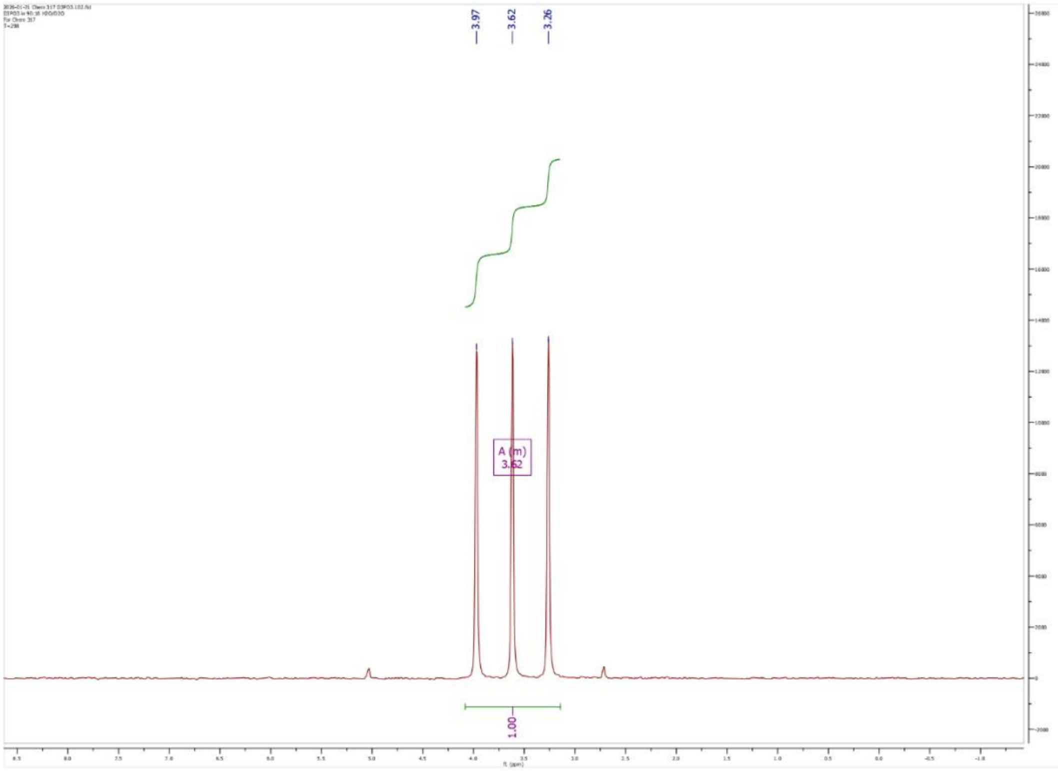


Figure 14: 700 MHz ^{31}P-NMR of deuterated phosphorous acid

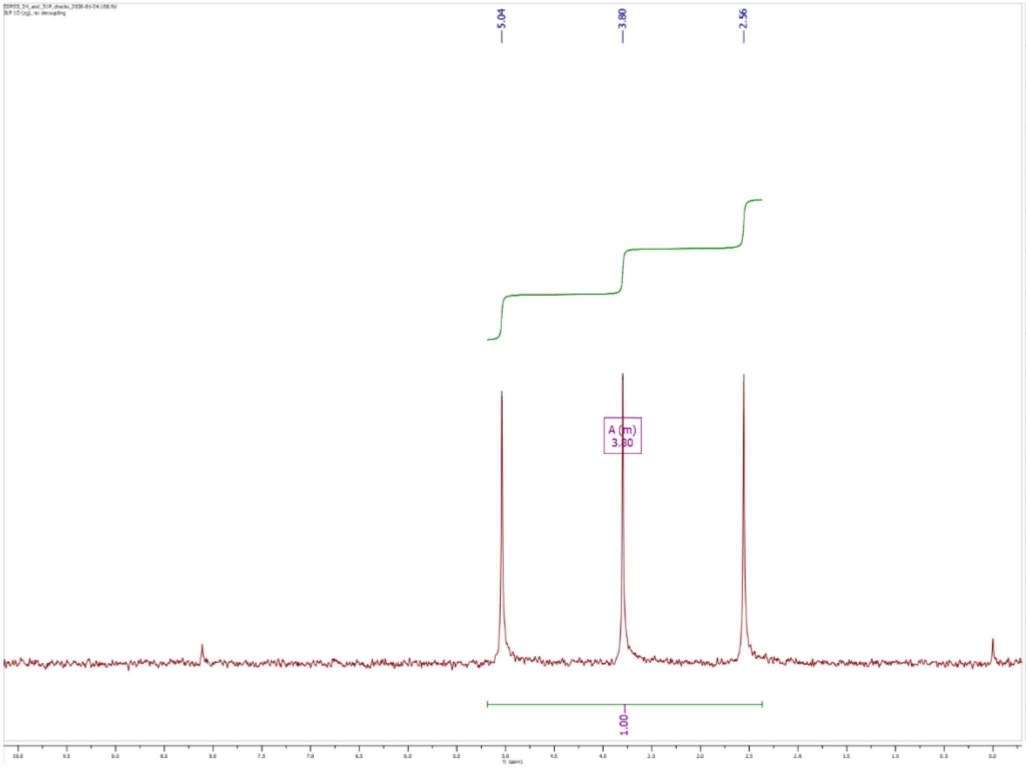


Figure 15: 200 MHz ^{31}P-NMR of deuterated phosphorous acid