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Supporting Information for

Molecules of life: studying the interactions between water and phosphine in rare gas matrices

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1. Methods

1.1 Experimental

The matrix isolation Fourier transform infrared (MI-FTIR) spectroscopy apparatus used throughout this work has been described previously,[1, 2] and only the pertinent details will be described here. Infrared spectra were recorded using a Digilab Excalibur 2000 FTS, at a resolution of 0.25 cm^{-1}, averaged over 1000 scans. Matrices were deposited onto a KBr cold window with the temperature being held at 10 K. Matrices were annealed to 30 K before being cooled back down to 10 K. Spectra were recorded at each of these stages (i.e., three spectra per experiment). Spectra presented in this paper have been smoothed using a second order Savitzky-Golay algorithm[3] over 15 points in Igor Pro.

Gas mixtures of argon (99.999% purity, Scientific and Technical Gases), H_2O (Milli-Q), and PH_3 at various concentrations were prepared using standard manometric techniques. The dilute PH_3 and H_2O gas mixtures were held in separate reservoirs prior to deposition. The mixtures in both reservoirs were sprayed onto the cold window simultaneously, such that the gas mixtures combined en route to the window. Isotopic substitution experiments were also conducted using D_2O (100 atom % D, Aldrich), $H_2{}^{18}O$ (97 atom % ^{18}O, Sigma), and D_3P. The ^1H_3P sample was prepared by the reduction of phosphorus acid (H_3PO_3).[4] The D_3P sample was synthesised by condensing deuterium chloride solution (in D_2O, 99 atom % D, Aldrich) onto Zn_3P_2 (99.999%, Alfa Aesar).

1.2 Computational

Ab initio and DFT calculations were performed to aid in the characterisation of the species investigated. In order to calculate accurate vibrational transition energies, harmonic frequency calculations were conducted using MP2,[5] CCSD(T),[6, 7] B3LYP[8] with and without the D3 correction,[9] and DSD-PBEP86-D3(BJ)[10, 11] levels of theory. Harmonic and anharmonic frequencies were obtained for the DFT methods. All calculations were conducted using the augmented correlation consistent basis sets of Dunning (aug-cc-pV*X*Z, *X*=D, T, Q, 5);[12] additional diffuse functions were added to the phosphorus atom where relevant (aug-cc-pV(*X*+d)Z, henceforth abbreviated to AV*X*Z).

Binding energies were calculated on CCSD(T)/AVTZ geometries and extrapolated to the complete basis set (CBS) limit using the equation of Peterson et al.:[13, 14]

$$D_e(n) = D_e(\infty) + Ae^{-(n-1)} + Be^{-(n-1)^2}$$

where n corresponds to the cardinal number of the basis set ($n = 3, 4, 5$ for AVTZ, AVQZ, and AV5Z, respectively), $D_e(n)$ is the energy calculated with the basis set n, and $D_e(\infty)$ is the CBS energy. A counterpoise correction was performed in order to remove any further trace of basis set superposition error.[15] All coupled cluster calculations were performed using ORCA 5.0.[16-18] Geometry optimisations were converged using the criteria: TolE = 1e-9 a.u.; TolMaxD = 1e-6 a.u.; TolMaxG = 1e-6 a.u. Energies were calculated using the 'verytightscf' keyword. All other calculations were conducted in Gaussian 16,[19] optimising geometries using the 'vtight' keyword, a superfine grid (for DFT calculations), and symmetry features, when relevant. Anharmonic frequencies were calculated using generalised second order vibrational perturbation theory (GVPT2)[20, 21] as implemented in Gaussian 16. Basis sets not native to Gaussian were obtained from the Basis Set Exchange.[22]

2. Tables

Table S1: PH_3 spectral analysis. Spectrum of PH_3/Ar mixture at 1:500 ratio, recorded at 10 K following deposition.

	^1H_3P		**D_3P**	
Assignment	**Wavenumber**	**Intensity**	**Wavenumber**	**Intensity**
ν_2	994.1	0.0350	729.5	0.0263
ν_4	1114.1	0.0101	803.4	0.0101
ν_1	2340.5	0.0265	1697.5	0.0057
ν_3	2346.5	0.0862	1704.8	0.0784

Table S2: ^1H_2O spectral analysis. Spectrum of ^1H_2O/Ar mixture at 1:500 ratio, recorded at 10 K following deposition.

Assignment		**Wavenumber**	**Intensity**	**Notes**
ν_2	**Band Centre**	1589.1		Calculated by Perchard.[23]
	$1_{11} \rightarrow 0_{00}$	1556.6	0.0015	
	$1_{10} \rightarrow 0_{01}$	1573.1	0.0114	
	nrm	1589.5	0.0015	
	$1_{01} \rightarrow 1_{10}$	1607.9	0.0998	
	$0_{00} \rightarrow 1_{11}$	1623.9	0.1630	
	$1_{01} \rightarrow 2_{12}$	1636.5	0.0157	
	RTC-para	1657.8	0.0015	Assigned by Michaut et al.[24]
	RTC-ortho	1661.1	0.0114	Assigned by Michaut et al.[24]
ν_1	**Band Centre**	3639.2		Calculated by Perchard.[23]
	$1_{10} \rightarrow 0_{01}$	3622.8	0.0005	
	$1_{10} \rightarrow 1_{01}$	3622.8	0.0005	
	nrm	3638.9		Shoulder
	$1_{01} \rightarrow 1_{10}$	3653.5	0.0050	
	$0_{00} \rightarrow 1_{11}$	3670.2	0.0081	
ν_3	**Band Centre**	3732.2		Calculated by Perchard.[23]
	$1_{01} \rightarrow 0_{00}$	3711.4	0.0511	
	$1_{10} \rightarrow 1_{11}$	3724.8	0.0027	
	nrm	3736.4	0.0009	
	$0_{00} \rightarrow 1_{01}$	3756.6	0.1331	
	$1_{01} \rightarrow 2_{02}$	3776.4	0.0500	
	$1_{10} \rightarrow 2_{11}$	3784.0		Appears as shoulder

Table S3: $H_2{}^{18}O$ spectral analysis. Spectrum of $H_2{}^{18}O$/Ar mixture at 1:500 ratio, recorded at 10 K following deposition.

Assignment		**Wavenumber**	**Intensity**	**Notes**
ν_2	**Band Centre**	1582.5		Calculated by Perchard.[23]
	$1_{11} \rightarrow 0_{00}$	1551.4	0.0017	
	$1_{10} \rightarrow 0_{01}$	1567.4	0.0101	
	nrm	1583.1	0.0039	
	$1_{01} \rightarrow 1_{10}$	1600.7	0.0726	
	$0_{00} \rightarrow 1_{11}$	1616.1	0.1209	
ν_1	**Band Centre**	3631.5		Calculated by Perchard.[23]
	nrm	3633.3	0.0014	
	$1_{01} \rightarrow 1_{10}$	3645.7	0.0038	
	$0_{00} \rightarrow 1_{11}$	3661.6	0.0059	
ν_3	**Band Centre**	3718.8		Calculated by Perchard.[23]
	$1_{01} \rightarrow 0_{00}$	3697.7		
	$1_{10} \rightarrow 1_{11}$	3711.3	0.0076	
	nrm	3722.2	0.0015	
	$1_{11} \rightarrow 1_{10}$	3724.7		Approximate position
	$0_{00} \rightarrow 1_{01}$	3742.4	0.1229	
	$1_{01} \rightarrow 2_{02}$	3760.9	0.0277	
	$1_{10} \rightarrow 2_{11}$	3711.3	0.0076	

Table S4: D_2O spectral analysis. Spectrum of D_2O/Ar mixture at 1:500 ratio, recorded at 10 K following deposition.

Assignment		**Wavenumber**	**Intensity**	**Notes**
ν_2	**Band Centre**	1175		Calculated by Redington and Milligan.[25]
	0_0–1_0	1154.5	0.0071	
	1_{-1}–1_{+1}	1164.0	0.0035	
	(0_0–0_0)	1177.3	0.0113	
	1_{+1}–1_{-1}	1185.4	0.0105	
	2_{-2}–1_0	1188.3	0.0011	
	1_0–0_0	1195.0	0.1168	
	2_{-1}–1_{-1}	1203.5	0.0052	
	2_{+1}–1_{+1}	1228.2	0.0019	
ν_1	**Band Centre**	2657		Calculated by Redington and Milligan.[25]
	$1_0 \rightarrow 0_0$	2677.4	0.0096	
ν_3	**Band Centre**	2770		Calculated by Redington and Milligan.[25]
	0_0–1_{-1}	2758.7	0.0084	
	1_{+1}–1_0	2770.9	0.0044	
	1_{-1}–0_0	2782.3	0.0958	
	2_{-2}–1_{-1}	2793.5	0.0137	
	2_0–1_{+1}	2803.4	0.0006	

Table S5: Theoretical frequencies of $^{1}H_2O$ calculated at various levels of theory.

	MP2/AVQZ		**CCSD(T)/AVTZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	3965.5	78.4	3919.9	53.4
ν_1	3839.7	6.1	3810.8	2.8
ν_2	1632.4	73.2	1645.9	68.1
	B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	3905.9	63.5	3723.1	58.7
ν_1	3803.9	4.7	3634.4	3.5
ν_2	1629.0	76.2	1576.3	77.2
	DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	3939.2	59.7	3746.1	55.5
ν_1	3816.9	3.6	3635.5	2.5
ν_2	1634.5	69.5	1583.6	70.4

Table S6: Theoretical frequencies of $H_2{}^{18}O$ calculated at various levels of theory.

	MP2/AVQZ		**CCSD(T)/AVTZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	3949.4	76.8	3904.0	52.2
ν_1	3831.6	5.8	3802.8	2.6
ν_2	1625.7	72.6	1639.1	67.5
	B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	3889.8	62.1	3708.8	57.5
ν_1	3796.0	4.4	3627.1	3.3
ν_2	1622.2	75.6	1569.9	76.6
	DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	3923.2	58.4	3731.8	54.3
ν_1	3808.8	3.4	3628.1	2.3
ν_2	1627.7	69.0	1577.2	69.9

Table S7: Theoretical frequencies of D_2O calculated at various levels of theory.

	MP2/AVQZ		**CCSD(T)/AVTZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	2905.3	46.5	2880.5	32.4
ν_1	2767.9	4.7	2756.2	2.5
ν_2	1194.8	38.9	1208.3	36.5

	B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	2862.7	38.0	2763.6	35.8
ν_1	2741.5	3.8	2653.9	3.2
ν_2	1192.5	40.6	1164.5	41.0

	DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_3	2885.9	35.9	2781.6	33.9
ν_1	2752.0	3.0	2657.8	2.5
ν_2	1196.0	37.0	1169.5	37.4

Table S8: Theoretical frequencies of $^{1}H_{3}P$ calculated at various levels of theory.

	MP2/AVQZ		**CCSD(T)/AVTZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_{3s}	2492.0	47.9	2416.3	46.6
ν_{3a}	2492.0	47.9	2416.3	46.6
ν_{1}	2480.7	25.9	2409.2	24.9
ν_{4s}	1162.2	14.5	1143.0	11.0
ν_{4a}	1162.2	14.5	1143.0	11.0
ν_{2}	1015.0	21.3	1012.8	17.2

	B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_{3s}	2394.3	57.6	2330.9	310.1
ν_{3a}	2394.3	57.6	2330.9	310.1
ν_{1}	2386.9	34.1	2338.8	463.8
ν_{4s}	1137.9	12.2	1106.5	12.1
ν_{4a}	1137.9	12.2	1106.5	12.1
ν_{2}	1018.0	21.2	977.6	18.4

	DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_{3s}	2439.6	59.3	2392.6	128.4
ν_{3a}	2439.6	59.3	2392.6	128.4
ν_{1}	2425.5	33.2	2392.3	157.0
ν_{4s}	1144.3	11.9	1100.8	11.7
ν_{4a}	1144.3	11.9	1100.8	11.7
ν_{2}	1013.9	18.6	974.9	16.5

Table S9: Theoretical frequencies of D_3P calculated at various levels of theory.

	MP2/AVQZ		**CCSD(T)/AVTZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_{3s}	1791.6	25.1	1742.8	24.4
ν_{3a}	1791.6	25.1	1742.8	24.4
ν_{1}	1775.8	14.4	1730.4	13.8
ν_{4s}	829.2	7.0	818.2	5.3
ν_{4a}	829.2	7.0	818.2	5.3
ν_{2}	740.3	11.1	741.0	9.0
	B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_{3s}	1721.5	30.1	1687.9	42.8
ν_{3a}	1721.5	30.1	1687.9	42.8
ν_{1}	1708.8	18.8	1685.1	39.6
ν_{4s}	811.8	5.9	793.6	5.9
ν_{4a}	811.8	5.9	793.6	5.9
ν_{2}	742.5	11.0	713.7	9.7
	DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
	Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
ν_{3s}	1753.9	30.9	1727.4	36.9
ν_{3a}	1753.9	30.9	1727.4	36.9
ν_{1}	1736.6	18.2	1718.0	28.0
ν_{4s}	816.4	5.7	787.8	5.5
ν_{4a}	816.4	5.7	787.8	5.5
ν_{2}	739.4	9.6	712.6	8.8

Table S10: Theoretical frequencies of $^1H_2O{\cdot}^1H_3P$ calculated at various levels of theory.

		MP2/AVQZ		**CCSD(T)/AVTZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
^1H_3P	ν_{3s}	2508.8	32.6	2434.0	31.8
	ν_{3a}	2506.8	34.9	2432.0	34.4
	ν_1	2494.2	25.0	2423.8	24.6
	ν_{4s}	1160.2	11.9	1141.5	10.1
	ν_{4a}	1160.4	13.4	1141.2	9.0
	ν_2	1011.4	34.0	1008.2	28.2
^1H_2O	ν_3	3932.7	157.0	3893.8	129.4
	ν_1	3774.4	191.1	3768.1	133.4
	ν_2	1639.0	35.2	1653.1	33.6
		B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
^1H_3P	ν_{3s}	2414.5	40.1	2288.5	47.2
	ν_{3a}	2412.1	43.1	2320.8	37.6
	ν_1	2403.5	34.6	2326.5	29.6
	ν_{4s}	1136.1	10.0	1114.7	6.6
	ν_{4a}	1136.4	11.4	1105.4	6.8
	ν_2	1012.8	36.7	1006.8	25.4
^1H_2O	ν_3	3876.6	121.1	3692.9	95.1
	ν_1	3726.9	241.5	3570.3	141.6
	ν_2	1635.4	37.7	1575.1	30.9
		DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
^1H_3P	ν_{3s}	2458.2	41.5	2388.6	29.5
	ν_{3a}	2455.6	44.0	2364.8	36.4
	ν_1	2440.3	32.9	2325.5	44.2
	ν_{4s}	1142.9	9.9	1120.5	7.8
	ν_{4a}	1142.8	11.2	1123.3	7.5
	ν_2	1010.4	32.2	996.3	21.3
^1H_2O	ν_3	3908.5	138.2	3711.2	108.6
	ν_1	3757.4	179.3	3583.6	104.4
	ν_2	1640.8	32.7	1578.3	27.2

Table S11: Theoretical frequencies of $H_2{}^{18}O\cdot{}^{1}H_3P$ calculated at various levels of theory.

		MP2/AVQZ		**CCSD(T)/AVTZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
$^{1}H_3P$	**ν_{3s}**	2508.8	32.6	2434.0	31.8
	ν_{3a}	2506.8	34.9	2432.0	34.4
	ν_1	2494.2	25.0	2423.8	24.6
	ν_{4s}	1160.2	11.9	1141.2	9.0
	ν_{4a}	1160.4	13.4	1141.5	10.1
	ν_2	1011.4	34.0	1008.2	28.2
$H_2{}^{18}O$	**ν_3**	3917.7	149.6	3878.7	123.1
	ν_1	3765.4	194.2	3759.4	136.2
	ν_2	1632.4	34.9	1646.4	33.4

		B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
$^{1}H_3P$	**ν_{3s}**	2414.5	40.1	2297.0	47.6
	ν_{3a}	2412.1	43.0	2316.2	37.7
	ν_1	2403.5	34.6	2333.7	30.0
	ν_{4s}	1136.1	10.0	1132.7	7.4
	ν_{4a}	1136.4	11.4	1137.0	6.8
	ν_2	1012.8	36.7	1001.2	25.8
$H_2{}^{18}O$	**ν_3**	3862.1	112.7	3680.5	79.8
	ν_1	3717.5	245.4	3564.8	172.7
	ν_2	1628.8	37.4	1590.2	30.2

		DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
$^{1}H_3P$	**ν_{3s}**	2458.2	41.5	2390.4	29.5
	ν_{3a}	2455.6	44.0	2363.4	36.1
	ν_1	2440.3	32.9	2322.3	44.1
	ν_{4s}	1142.9	9.9	1119.1	7.9
	ν_{4a}	1142.8	11.2	1123.3	7.2
	ν_2	1010.4	32.2	996.1	21.5
$H_2{}^{18}O$	**ν_3**	3893.5	131.3	3697.8	104.7
	ν_1	3748.4	182.2	3575.5	109.3
	ν_2	1634.3	32.5	1572.4	27.1

Table S12: Theoretical frequencies of $D_2O\cdot{}^1H_3P$ calculated at various levels of theory.

		MP2/AVQZ		**CCSD(T)/AVTZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
^1H_3P	**ν_{3s}**	2508.8	32.4	2434.0	31.7
	ν_{3a}	2506.8	34.8	2431.9	34.2
	ν_1	2494.2	26.2	2423.7	25.3
	ν_{4s}	1159.2	7.9	1140.8	7.4
	ν_{4a}	1160.3	12.9	1141.4	9.7
	ν_2	1011.4	34.4	1008.2	28.5
D_2O	**ν_3**	2877.5	105.8	2858.8	86.7
	ν_1	2725.4	86.0	2728.3	59.8
	ν_2	1199.4	23.2	1212.9	19.9

		B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
^1H_3P	**ν_{3s}**	2414.5	39.9	2293.9	43.0
	ν_{3a}	2412.1	42.9	2319.2	36.2
	ν_1	2403.4	36.0	2325.3	27.6
	ν_{4s}	1135.5	7.8	1103.5	8.8
	ν_{4a}	1136.3	10.9	1104.2	6.7
	ν_2	1012.7	37.0	988.9	30.6
D_2O	**ν_3**	2835.2	91.9	2737.1	75.3
	ν_1	2692.9	107.0	2609.4	68.9
	ν_2	1196.6	22.7	1162.0	14.0

		DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
^1H_3P	**ν_{3s}**	2458.2	41.3	2385.1	28.5
	ν_{3a}	2455.6	43.8	2360.4	34.0
	ν_1	2440.2	34.2	2325.2	43.7
	ν_{4s}	1142.1	7.5	1108.0	10.6
	ν_{4a}	1142.8	10.7	1121.6	6.8
	ν_2	1010.4	32.5	994.2	27.0
D_2O	**ν_3**	2859.9	94.0	2755.5	71.9
	ν_1	2713.3	80.6	2621.7	56.7
	ν_2	1200.3	20.4	1176.1	10.5

Table S13: Theoretical frequencies of $^{1}H_2O \cdot D_3P$ calculated at various levels of theory.

		MP2/AVQZ		**CCSD(T)/AVTZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
D_3P	**ν_{3s}**	1804.1	18.1	1755.9	18.3
	ν_{3a}	1802.6	18.8	1754.4	18.5
	ν_1	1784.8	13.7	1740.3	13.5
	ν_{4s}	827.8	6.1	817.1	4.6
	ν_{4a}	828.0	7.3	817.2	5.5
	ν_2	739.0	16.8	738.9	14.0
$^{1}H_2O$	**ν_3**	3932.7	157.3	3893.8	129.6
	ν_1	3774.3	191.8	3768.0	133.9
	ν_2	1638.8	34.0	1652.9	32.1

		B3LYP-D3/AVQZ		**GVPT2/B3LYP-D3/AVQZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
D_3P	**ν_{3s}**	1736.4	22.7	1706.8	19.2
	ν_{3a}	1734.6	23.1	1681.0	21.4
	ν_1	1720.1	18.8	1647.4	21.2
	ν_{4s}	810.6	5.1	797.0	6.1
	ν_{4a}	810.8	6.2	779.0	4.9
	ν_2	740.0	18.1	725.0	13.2
$^{1}H_2O$	**ν_3**	3876.5	121.3	3692.1	93.0
	ν_1	3726.8	242.5	3567.9	145.6
	ν_2	1635.2	36.0	1573.9	27.0

		DSD-PBEP86-D3(BJ)/AVDZ		**GVPT2/DSD-PBEP86-D3(BJ)/AVDZ**	
		Wavenumber	**Intensity**	**Wavenumber**	**Intensity**
D_3P	**ν_{3s}**	1767.7	23.1	1725.7	18.4
	ν_{3a}	1765.8	23.5	1718.8	20.5
	ν_1	1746.5	17.9	1690.3	21.4
	ν_{4s}	815.4	5.0	802.9	4.2
	ν_{4a}	815.4	6.1	801.8	5.4
	ν_2	738.2	15.7	727.3	23.8
$^{1}H_2O$	**ν_3**	3908.5	138.5	3710.2	109.2
	ν_1	3757.3	180.1	3583.6	102.8
	ν_2	1640.6	31.3	1577.0	24.0

Table S14: Geometries optimised for H_2O at various levels of theory. Coordinates are given in angstroms (Å).

CCSD(T)/aug-cc-pV(T+d)Z	*x*	*y*	*z*
O	-0.00528	-0.00629	0.00000
H	0.95567	-0.04135	0.00000
H	-0.20667	0.93397	0.00000
Electronic Energy (Hartree)	-76.3423		
MP2/aug-cc-pV(Q+d)Z	*x*	*y*	*z*
O	0.00137	0.00000	0.00107
H	0.00003	0.00000	0.95993
H	0.93098	0.00000	-0.23398
Electronic Energy (Hartree)	-76.3519		
B3LYP-D3/aug-cc-pV(Q+d)Z	*x*	*y*	*z*
O	0.00050	0.00000	0.00038
H	0.00027	0.00000	0.96099
H	0.92791	0.00000	-0.24998
Electronic Energy (Hartree)	-76.4722		
DSD-PBEP86-D3BJ/aug-cc-pV(D+d)Z	*x*	*y*	*z*
O	-0.03991	0.00000	-0.03349
H	-0.07528	0.00000	0.93024
H	0.90303	0.00000	-0.23567
Electronic Energy (Hartree)	-76.1952		
DSD-PBEP86-D3BJ/aug-cc-pV(Q+d)Z	*x*	*y*	*z*
O	0.00243	0.00000	0.00189
H	-0.00159	0.00000	0.96091
H	0.93154	0.00000	-0.23578
Electronic Energy (Hartree)	-76.2202		

Table S15: Geometries optimised for PH_3 at various levels of theory. Coordinates are given in angstroms (Å).

CCSD(T)/aug-cc-pV(T+d)Z	*x*	*y*	*z*
P	0.00293	0.00311	0.00331
H	1.41958	0.00257	0.00274
H	-0.08193	1.41721	0.00274
H	-0.08194	-0.08697	1.41454
Electronic Energy (Hartree)	-342.6990		

MP2/aug-cc-pV(Q+d)Z	*x*	*y*	*z*
P	0.00087	0.00093	0.00081
H	-0.00022	-0.00024	1.40933
H	1.40651	-0.00024	-0.08911
H	-0.09492	1.40330	-0.08911
Electronic Energy (Hartree)	-342.6777		

B3LYP-D3/aug-cc-pV(Q+d)Z	*x*	*y*	*z*
P	0.00045	-0.00049	0.00043
H	0.00004	-0.00005	1.41757
H	1.41481	-0.00005	-0.08843
H	-0.09413	-1.41168	-0.08843
Electronic Energy (Hartree)	-343.1868		

DSD-PBEP86-D3BJ/aug-cc-pV(D+d)Z	*x*	*y*	*z*
P	-0.00359	-0.00384	-0.00336
H	-0.00259	-0.00277	1.42229
H	1.41925	-0.00277	-0.09295
H	-0.09906	1.41579	-0.09295
Electronic Energy (Hartree)	-342.7498		

DSD-PBEP86-D3BJ/aug-cc-pV(Q+d)Z	*x*	*y*	*z*
P	-0.00046	-0.00049	-0.00043
H	-0.00146	-0.00157	1.41358
H	1.41067	-0.00157	-0.09061
H	-0.09652	1.40737	-0.09061
Electronic Energy (Hartree)	-342.7661		

Table S16: Geometries optimised for $H_2O\cdot PH_3$ at various levels of theory. Coordinates are given in angstroms (Å).

CCSD(T)/aug-cc-pV(T+d)Z	***x***	***y***	***z***
P	0.00000	0.00000	0.00000
H	1.41433	0.00000	0.00000
H	-0.10934	1.41009	0.00000
H	-0.11028	-0.11915	1.40461
H	-1.54764	-1.67487	-1.33879
O	-2.15926	-2.33771	-1.68217
H	-2.08698	-2.25465	-2.63727
Electronic Energy (Hartree)	-419.0456		

MP2/aug-cc-pV(Q+d)Z	***x***	***y***	***z***
P	-0.00002	-0.00001	-0.00002
H	-0.00002	-0.00002	1.40634
H	1.40155	-0.00002	-0.11607
H	-0.12748	1.39525	-0.11737
H	-1.63980	-1.35966	-1.50964
O	-2.30177	-1.70441	-2.11906
H	-2.22110	-2.65675	-2.04479
Electronic Energy (Hartree)	-419.0339		

B3LYP-D3/aug-cc-pV(Q+d)Z	***x***	***y***	***z***
P	-0.00098	-0.00107	0.00153
H	0.00156	0.00170	1.41557
H	1.40850	-0.00176	-0.11728
H	-0.12603	1.40285	-0.11728
H	-1.61144	-1.76050	-1.06497
O	-2.24116	-2.44847	-1.31474
H	-2.24336	-2.45087	-2.27486
Electronic Energy (Hartree)	-419.6632		

DSD-PBEP86-D3BJ/aug-cc-pV(D+d)Z	***x***	***y***	***z***
P	0.00164	0.00179	-0.00867
H	-0.00850	-0.00931	1.41391
H	1.42083	0.00428	-0.11454
H	-0.12377	1.41543	-0.11454
H	-1.60597	-1.75784	-1.07809
O	-2.24122	-2.45316	-1.30463

H	-2.24968	-2.46242	-2.26854
Electronic Energy (Hartree)	-418.9485		

DSD-PBEP86-D3BJ/aug-cc-pV(Q+d)Z	***x***	***y***	***z***
P	-0.00165	-0.00180	0.00377
H	0.00394	0.00431	1.41499
H	1.40460	-0.00321	-0.11945
H	-0.12804	1.39876	-0.11945
H	-1.60512	-1.75473	-1.05684
O	-2.23371	-2.44191	-1.30482
H	-2.23096	-2.43891	-2.26355
Electronic Energy (Hartree)	-418.9897		

References

1. V. S. Langford, A. J. McKinley and T. I. Quickenden, *J. Am. Chem. Soc.*, 2000, **122**, 12859-12863.

2. M. H. V. Graneri, D. A. Wild and A. J. McKinley, *J. Mol. Spectrosc.*, 2021, **378**, 111440.

3. A. Savitzky and M. J. E. Golay, *Anal. Chem.*, 1964, **36**, 1627-1639.

4. S. D. Gokhale, W. L. Jolly, S. Thomas and D. Britton, in *Inorg. Synth.*, ed. S. Y. Tyree, Jr., McGraw-Hill, Inc., 1967, vol. 9, pp. 56-58.

5. C. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618-622.

6. K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479-483.

7. F. Wennmohs and F. Neese, *Chem. Phys.*, 2008, **343**, 217-230.

8. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.

9. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

10. S. Kozuch and J. M. L. Martin, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20104-20107.

11. S. Kozuch and J. M. L. Martin, *J. Comput. Chem.*, 2013, **34**, 2327-2344.

12. R. A. Kendall, T. H. Dunning, Jr. and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796-6806.

13. K. A. Peterson, D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.*, 1994, **100**, 7410-7415.

14. V. Vasilyev, *Comput. Theor. Chem.*, 2017, **1115**, 1-3.

15. S. F. Boys and F. Bernardi, *Mol. Phys.*, 2002, **100**, 65-73.

16. F. Neese, *WIREs Comput. Mol. Sci.*, 2018, **8**, e1327.

17. F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys.*, 2020, **152**, 224108.

18. F. Neese, *WIREs Comput. Mol. Sci.*, 2022, DOI: 10.1002/wcms.1606, e1606.

19. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16*, Rev. A.03; Gaussian, Inc.: Wallingford, CT, 2016.

20. V. Barone, *J. Chem. Phys.*, 2005, **122**, 014108.

21. J. Bloino and V. Barone, *J. Chem. Phys.*, 2012, **136**, 124108.

22. B. P. Pritchard, D. Altarawy, B. Didier, T. D. Gibson and T. L. Windus, *J. Chem. Inf. Model.*, 2019, **59**, 4814-4820.

23. J. P. Perchard, *Chem. Phys.*, 2001, **273**, 217-233.

24. X. Michaut, A.-M. Vasserot and L. Abouaf-Marguin, *Vib. Spectrosc.*, 2004, **34**, 83-93.

25. R. L. Redington and D. E. Milligan, *J. Chem. Phys.*, 1962, **37**, 2162-2166.