Hydration of Arsenic Oxyacid Species

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Supplementary Material

Appendix 1 - References from Crystal structure database search

Table S1 - Reported crystal structures of H_3AsO_4: The molecule has three longer distances corresponding to protonated oxygen atoms and one shorter distance corresponding to a non-protonated oxygen atom.

H_3AsO_4

	(1/4)	(3/4)								
Structure	**Short**	**Long**	**Mean**	**-O1**	**-O2**	**-O3**	**-O4**			**Ref**
34686	1.608	1.682	1.663	1.608	1.652	1.688	1.705	Å	$(H_3AsO_4)_2(H_2O)$	1
163455	1.622	1.673	1.660	1.622	1.625	1.681	1.712	Å	$Cs_4(SeO_4)(HSeO_4)_2(H_3AsO_4)$	2
CUHDAK	1.659	1.676	1.672	1.659	1.660	1.677	1.690	Å	$((CH_3)_3NCH_2COO)\cdot H_3AsO_4$	3
CUHDAK01	1.650	1.673	1.667	1.650	1.653	1.674	1.691	Å	$((CH_3)_3NCH_2COO)\cdot D_3AsO_4$	4
CUHDAK02	1.663	1.689	1.683	1.663	1.675	1.683	1.710	Å	$((CH_3)_3NCH_2COO)\cdot D_3AsO_4$	5
PASWIP	1.640	1.698	1.684	1.640	1.691	1.700	1.703	Å	$C_{24}H_{20}P^+$, H_3AsO_4, Cl^-	6
RIGFOD	1.645	1.689	1.678	1.645	1.679	1.690	1.699	Å	$(C_2H_5)_4N(H_2AsO_4)(H_3AsO_4)$	7
RIGFUJ	1.637	1.686	1.674	1.637	1.679	1.687	1.693	Å	$(C_6H_{14}N_2)(H_2AsO_4)_2(H_3AsO_4)$	7
XICNUS	1.644	1.698	1.684	1.644	1.690	1.699	1.704	Å	$(C_6H_{10}N_3O_2)(H_2AsO_4)(H_3AsO_4)$	8
YASKEJ	1.639	1.693	1.680	1.639	1.677	1.699	1.704	Å	$C_4H_9NO_3$, H_3AsO_4	9
No of struct.			**10**							
Mean	**1.641**	**1.686**	**1.674**	1.641	1.668	1.688	1.701			
Stdev	0.016	0.010	0.009	0.016	0.020	0.009	0.008			
Ditto*2	0.033	0.019	0.018	0.033	0.041	0.019	0.015			
Not included										
-										

Table S2 - $H_2AsO_4^-$ structure solutions without differentiation between long and short As-O distances: These data have not been used.

$H_2AsO_4^-$

				(2/4)	(2/4)			
Structure	**Shor**	**Long**	**Mea**					**Ref**
27101			1.760			Å	$NH_4H_2AsO_4\cdot H_2O$	10
28155			1.685			Å	$NH_4H_2AsO_4\cdot H_2O$	11
29092			1.741			Å	$KH_2AsO_4\cdot H_2O$	12
39928			1.687			Å	KH_2AsO_4	13
44799			1.742			Å	CsH_2AsO_4	14
66203			1.675			Å	$NH_4H_2AsO_4$	15
66204			1.677			Å	$NH_4H_2AsO_4$	15
66205			1.680			Å	$NH_4H_2AsO_4$	15
66206			1.680			Å	$NH_4H_2AsO_4$	15
93926			1.686			Å	KH_2AsO_4	16
93927			1.687			Å	KH_2AsO_4	16
93928			1.686			Å	KH_2AsO_4	16
93929			1.688			Å	KH_2AsO_4	16
9767			1.685			Å	CsD_2AsO_4	17
174061			1.680			Å	$NH_4H_2AsO_4$	18
200219			1.684			Å	$NH_4H_2AsO_4$	19
No of struct			16					
Mean			1.695			Å		

Stdev	0.027	Å

Table S3 - $H_2AsO_4^-$ crystal structures: The ions have two longer distances corresponding to protonated oxygen atoms and two shorter distances corresponding to non-protonated oxygen atoms

Structure	(2/4) Short	(2/4) Long	Mean	-O1	-O2	-O3	-O4			Ref
62024	1.653	1.720	1.687	1.647	1.659	1.713	1.727	Å	LiH_2AsO_4	20
66208	1.659	1.708	1.683	1.658	1.659	1.708	1.708	Å	$NH_4H_2AsO_4$	15
66209	1.658	1.710	1.684	1.656	1.659	1.710	1.710	Å	$NH_4H_2AsO_4$	15
66210	1.658	1.713	1.686	1.658	1.658	1.712	1.714	Å	$NH_4H_2AsO_4$	15
109787 (JAXQIJ)	1.654	1.714	1.684	1.653	1.654	1.714	1.714	Å	$(C(NH_2)_3)$ (H_2AsO_4)	21
173457 (LOCLAR)	1.658	1.705	1.681	1.649	1.666	1.704	1.705	Å	$(C_2H_7N_4S)$ (H_2AsO_4)	22
174062 (66207)	1.659	1.706	1.682	1.659	1.659	1.703	1.708	Å	$NH_4H_2AsO_4$	18
ADASUU	1.654	1.703	1.678	1.653	1.654	1.700	1.705	Å	$(C_5H_{14}N_2)(H_2AsO_4)_2$	23
AMINIT	1.653	1.713	1.683	1.643	1.662	1.710	1.716	Å	$(C_5H_{12}N)(H_2AsO_4)$	24
CENROD	1.661	1.707	1.684	1.653	1.669	1.696	1.718	Å	$(p\text{-}ClC_6H_4NH_3)\text{-}H_2AsO_4$	25
DAYQAV	1.658	1.704	1.681	1.653	1.662	1.701	1.706	Å	$(H_3NCH_2COOH)H_2AsO_4$	26
FONFIY	1.654	1.707	1.680	1.651	1.656	1.701	1.713	Å	$(C_4H_8N_3O)(H_2AsO_4)_2$	27
GELHIO10	1.660	1.714	1.687	1.657	1.662	1.709	1.718	Å	$(C_6H_{16}N_4O_2)(H_2AsO_4)_2$	28
JAKRAO	1.662	1.714	1.688	1.658	1.665	1.708	1.719	Å	$(p\text{-}ClC_6H_4NH_3)\text{-}H_2AsO_4\cdot H_2O$	29
KORSAL	1.657	1.707	1.682	1.638	1.676	1.699	1.715	Å	$(H_3NC(OH)_3)H_2AsO_4$	30
KORSAL01	1.657	1.709	1.683	1.641	1.673	1.706	1.711	Å	$(H_3NC(OH)_3)H_2AsO_4$	31
KORSAL02	1.660	1.708	1.684	1.643	1.677	1.702	1.713	Å	$(H_3NC(OH)_3)H_2AsO_4$	32
OBUYOA	1.655	1.705	1.680	1.641	1.669	1.704	1.705	Å	$(C(CH_3)_3NH_3)H_2AsO_4$	33
OBUYOA01	1.655	1.709	1.682	1.642	1.668	1.707	1.710	Å	$(C(CH_3)_3NH_3)H_2AsO_4$	34
PIFBUC	1.645	1.709	1.677	1.637	1.653	1.703	1.714	Å	$(H_3N(CH_2)_2NH_3)(H_2AsO_4)_2$	35
QIBLAO	1.658	1.709	1.684	1.657	1.659	1.707	1.711	Å	$(CH_3(CH_2)_4NH_3)H_2AsO_4$	36
QIJXAI	1.654	1.708	1.681	1.653	1.655	1.706	1.709	Å	$(CH_3(CH_2)_6NH_3)H_2AsO_4$	37
RIGFOD	1.651	1.698	1.675	1.651	1.651	1.698	1.698	Å	$(C_2H_5)_4N(H_2AsO_4)(H_3AsO_4)$	7
RIGFUJ	1.654	1.705	1.679	1.648	1.659	1.704	1.705	Å	$(C_6H_{14}N_2)(H_2AsO_4)_2(H_3AsO_4)$	7
SEZVOJ	1.651	1.703	1.677	1.648	1.653	1.697	1.708	Å	$(C_5H_{14}N_2)(H_2AsO_4)_2$	38
SEZXOL	1.658	1.709	1.683	1.650	1.666	1.700	1.717	Å	$(C_5H_{14}N_2)(H_2AsO_4)_2$	38
TEVPAM	1.661	1.715	1.688	1.658	1.663	1.709	1.721	Å	$C_4H_{12}N_2^{2+}$, $2(H_2AsO_4^-)$	39
TICBIR	1.654	1.716	1.685	1.648	1.660	1.715	1.717	Å	$(C_6H_{13}N_2)(H_2AsO_4)_2\cdot H_2O$	40
VAMZOY	1.661	1.711	1.686	1.660	1.661	1.702	1.719	Å	$(C_7H_8NO)H_2AsO_4$	41
WANVAI	1.655	1.709	1.682	1.649	1.660	1.699	1.719	Å	$(C_5H_6N_3O_2)H_2AsO_4$	42
WEDDEP	1.643	1.698	1.670	1.642	1.644	1.699	1.696	Å	$(C_6H_9N_2)H_2AsO_4$	43
WOVMUP	1.650	1.701	1.676	1.645	1.656	1.698	1.705	Å	$(CH_3(CH_2)_5NH_3)H_2AsO_4$	44
WOVNAW	1.650	1.704	1.677	1.641	1.659	1.701	1.708	Å	$(CH_3(CH_2)_7NH_3)H_2AsO_4$	44
XAPWOB	1.653	1.713	1.683	1.638	1.667	1.707	1.718	Å	$(H_3N(CH_2)_3NH_3)(H_2AsO_4)_2$	45
XECJAR	1.650	1.704	1.677	1.643	1.656	1.700	1.708	Å	(C_7H_9ClN) $H_2AsO_4\cdot H_2O$	46
XEPKOT	1.654	1.703	1.678	1.633	1.674	1.703	1.703	Å	$(C_6H_9N_2)H_2AsO_4$	47
XICNUS	1.657	1.709	1.683	1.657	1.657	1.702	1.715	Å	$(C_6H_{10}N_3O_2)(H_2AsO_4)(H_3AsO_4)$	8
ZUZVUL	1.653	1.702	1.677	1.647	1.658	1.700	1.704	Å	$(C_7H_{10}NO)H_2AsO_4$	48
No of struct			**38**							
Average	**1.655**	**1.708**	**1.681**	1.649	1.661	1.704	1.711			
Stdev	0.004	0.005	0.004	0.007	0.007	0.005	0.007			
Ditto *2	0.009	0.010	0.008	0.015	0.014	0.010	0.013			
Not included:										
4284	1.655	1.729	1.692	1.650	1.660	1.711	1.748	Å	$NaH_2AsO_4\cdot H_2O$	49

201168	1.674	1.721	1.698	1.674	1.674	1.721	1.721	Å	CsD_2AsO_4	50
HQUOAS	1.665	1.704	1.684	1.649	1.681	1.702	1.705	Å	$C_{10}H_{10}NO)H_2AsO_4$	51

Table S4 - $HAsO_4^{2-}$ crystal structures: The ions have one longer As-O distance corresponding to the protonated oxygen atom, and three shorter distances corresponding to non-protonated oxygen atoms.

	(3/4)	(1/4)							
Structure	**Short**	**Long**	**Mean**	**-O1**	**-O2**	**-O3**	**-O4**			**Ref**
9063	1.669	1.742	1.687	1.660	1.668	1.679	1.742	Å	$Na_2HAsO_4·7H_2O$	52
14283	1.678	1.747	1.696	1.672	1.678	1.685	1.747	Å	$(NH_4)_2HAsO_4$	53
14300	1.669	1.742	1.687	1.659	1.670	1.678	1.742	Å	$Na_2HAsO_4·7H_2O$	53
14301	1.662	1.728	1.679	1.654	1.662	1.670	1.728	Å	$[Na_2(H_2O)_7]HAsO_4$	54
CASLAK	1.672	1.730	1.687	1.661	1.675	1.681	1.730	Å	$(H_3N(CH_2)_3NH_3)HAsO_4·H_2O$	55
IKEZUT	1.666	1.730	1.682	1.658	1.667	1.673	1.730	Å	$(H_3NCH(CH_3)CH_2NH_3)HAsO_4·H_2O$	56
INEBUY	1.674	1.732	1.688	1.666	1.674	1.681	1.732	Å	$(C_6H_5CH_2NH_3)_2HAsO_4·H_2O$	57
JAXMUR	1.670	1.734	1.686	1.664	1.666	1.681	1.734	Å	$(H_3NCH_2CH(CH_3)NH_3)HAsO_4$	58
REZKOX	1.669	1.726	1.683	1.663	1.668	1.676	1.726	Å	$(C_4H_{12}N_2)H_2AsO_4·H_2O$	59
YASGUV	1.672	1.747	1.691	1.664	1.673	1.679	1.747	Å	$(C_7H_{16}N)_2HAsO_4·H_2O$	60
No of struct			**10**							
Mean	**1.670**	**1.736**	**1.687**	1.662	1.670	1.678	1.736	Å		
Stdev	0.004	0.008	0.005	0.005	0.005	0.004	0.008	Å		
Ditto*2	0.009	0.016	0.009	0.010	0.010	0.009	0.016	Å		
Not included										
FUCNIA	1.599	1.733	1.633	1.463	1.657	1.678	1.733	Å	$(H_3N(CH_2)_2NH_3)HAsO_4$	61

Table S5 - AsO_4^{3-} crystal structures: All As-O distances are unprotonated and equivalent in this symmetrical ion. (4/4)

Structure	**Short**	**Long**	**Mean**	**-O1**	**-O2**	**-O3**	**-O4**			**Ref**
1319	1.685		1.685	1.671	1.683	1.686	1.700	Å	$(NH_4)_3AsO_4$	62
2832	1.674		1.674	1.666	1.666	1.682	1.682	Å	$CaKAsO_4(H_2O)_8$	63
24548	1.657		1.657	1.657	1.657	1.657	1.657	Å	$CsMg(AsO_4)(H_2O)_6$	64
36533	1.688		1.688	1.674	1.677	1.700	1.700	Å	Cs_2NaAsO_4	65
87465	1.689		1.689	1.683	1.683	1.694	1.694	Å	$SrK(AsO_4)(H_2O)_8$	66
412391	1.677		1.677	1.670	1.670	1.679	1.689	Å	Cs_3AsO_4	67
419835	1.659		1.659	1.655	1.655	1.661	1.663	Å	$Rb(Mg(H_2O)_6)(AsO_4)$	68
419836	1.674		1.674	1.671	1.671	1.673	1.68	Å	$Rb(Mg(H_2O)_6)(AsO_4)$	68
BIRSUO	1.661		1.661	1.658	1.659	1.659	1.668	Å	$[Co(H_2NCH_2CH_2NH_2)_3]_6AsO_4·3H_2O$	69
No of struct			**9**							
Mean	**1.674**		**1.674**		1.667	1.669	1.677			
Stdev	0.012		0.012		0.009	0.011	0.016			
Ditto*2	0.025		0.025		0.018	0.021	0.031			
Not included										
412392	1.702		1.702	1.700	1.700	1.702	1.705	Å	Cs_3AsO_4	67

Table S6: $RAsO(OH)_2$ structures.

	1/3	2/3		1	2	3			
Structure	**Short**	**Long**	**Mean**	**AsO1**	**AsO2**	**AsO3**			
BUTDUP	1.652	1.719	1.697	1.652	1.712	1.726	Å	$C_6H_9AsNO_4^+$, Cl^-, $2(H_2O)$	70
GORKAZ	1.652	1.696	1.681	1.652	1.695	1.697	Å	$C_6H_2AsF_5O_3$	71
JACFUO	1.652	1.708	1.689	1.652	1.707	1.708	Å	$C_{13}H_{11}AsO_4$	72
LACJII	1.651	1.712	1.691	1.651	1.699	1.724	Å	$C_8H_{10}AsNO_5$	73
LACJOO	1.650	1.709	1.689	1.65	1.707	1.711	Å	$C_9H_{12}AsNO_5$, H_2O	73
LUYLIA	1.655	1.694	1.681	1.655	1.693	1.695	Å	$C_3H_{10}As_2O_7$	74
NHXPAS	1.673	1.720	1.704	1.673	1.707	1.732	Å	$C_6H_6AsNO_6$	75
NHXPAS02	1.653	1.697	1.682	1.653	1.689	1.704	Å	$C_6H_6AsNO_6$	76
OAPASA01	1.644	1.694	1.677	1.644	1.689	1.699	Å	$C_6H_8AsNO_3$	77
POVMUI	1.643	1.713	1.689	1.643	1.71	1.715	Å	$C_6H_7AsO_4$	78
POVNAP	1.660	1.699	1.686	1.66	1.696	1.701	Å	$C_7H_8AsNO_6$	78
PRARSA	1.663	1.692	1.682	1.663	1.684	1.699	Å	$C_3H_9AsO_3$	79
SIHTOS	1.667	1.709	1.695	1.667	1.706	1.712	Å	$C_{16}H_{13}AsN_2O_{11}S_2$, $3(H_2O)$	80
VAZFOS	1.642	1.704	1.683	1.642	1.687	1.72	Å	$C_9H_{10}AsNO_4$	81
WUKKOC01	1.644	1.702	1.683	1.644	1.701	1.703	Å	$C_{10}H_{12}AsNO_4$	82
WUKKOK	1.657	1.716	1.696	1.657	1.702	1.73	Å	$C_{10}H_{12}AsNO_4$	82
XUTFAT	1.651	1.705	1.687	1.651	1.703	1.706	Å	$C_{10}H_{12}AsNO_4$, $0.5(H_2O)$	77
No of struct			17						
Mean	1.653	1.705	1.688	1.653	1.699	1.711			
Stdev	0.009	0.009	0.007	0.009	0.009	0.012			
Ditto*2	0.017	0.018	0.014	0.017	0.017	0.024			
Not included									
AMBARS	1.728	1.779	1.762	1.728	1.777	1.781	Å	$C_6H_8AsNO_3$	83
ARSACP	1.624	1.726	1.692	1.624	1.72	1.731	Å	$C_6H_7AsO_3$	84
ARSACP01	1.651	1.748	1.716	1.651	1.743	1.753	Å	$C_6H_7AsO_3$	85
OAPASA	1.637	1.725	1.695	1.637	1.701	1.748	Å	$C_6H_8AsNO_3$	75
WAMFUM	1.604	1.721	1.682	1.604	1.703	1.739	Å	$C_6H_6AsNO_5$	86
ZAYWOL	1.560	1.705	1.656	1.56	1.703	1.706	Å	$C_9H_{11}AsN_6O_3$, $2(H_2O)$	87

Table S7: R_2AsOOH structures

	(1/2)	(1/2)		1	2			
Structure	**Short**	**Long**	**Mean**	**AsO1**	**AsO2**			
LAJJIP	1.617	1.720	1.669	1.617	1.72	Å	$C_4H_7AsO_2$	88
BENJUZ	1.638	1.713	1.676	1.638	1.713	Å	$C_{12}H_{11}AsO_2$	89
XEWVAX	1.654	1.719	1.687	1.654	1.719	Å	$C_7H_9AsO_2$	90
TIVMIU	1.661	1.742	1.702	1.661	1.742	Å	$C_{12}H_{11}AsO_2$, $C_{12}H_{11}AsOS$	91
BUASIN	1.668	1.745	1.707	1.668	1.745	Å	$C_8H_{19}AsO_2$	79
REQQOT	1.691	1.749	1.720	1.691	1.749	Å	$C_6H_{19}As_3O_{13}W_2$, H_2O	92
No of struct			6					

Mean	1.655	1.731	1.693	1.655	1.731		
Stdev	0.025	0.016	0.020	0.025	0.016		
Ditto*2	0.051	0.031	0.039	0.051	0.031		
Not included							
CADYLA	1.608	1.625	1.617	1.608	1.625	$C_2H_7AsO_2$	[93]

Appendix 2 - Supplementary XAFS material

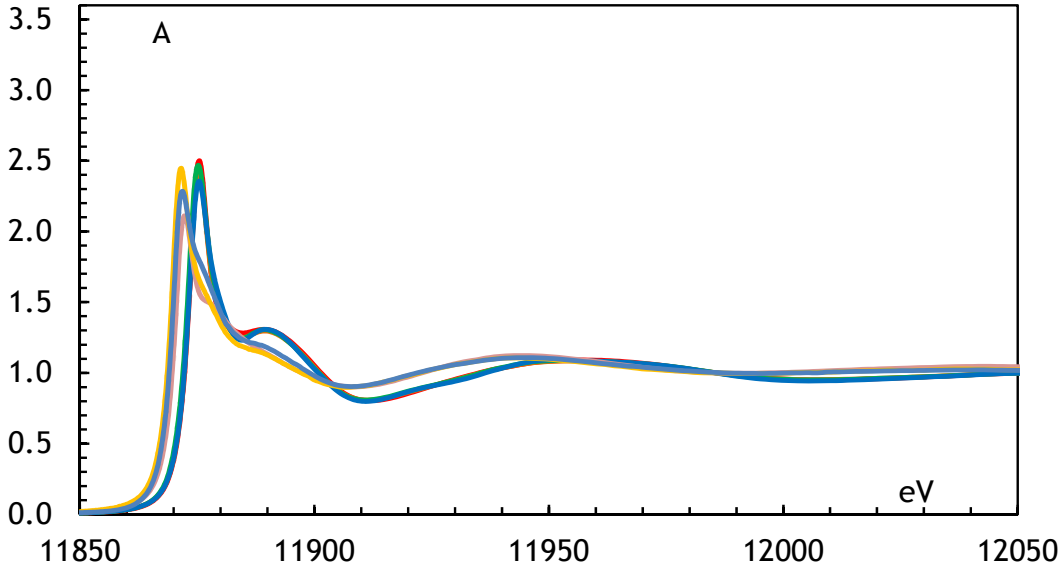

Figure S1: As K_α edges of inorganic arsenic compounds. Light red: $As(OH)_3$; light orange $AsO(OH)_2^-$; light blue AsO_3^{3-}, Red: H_3AsO_4; Orange: $H_2AsO_4^-$; green $HAsO_4^{2-}$; blue AsO_4^{3-}.

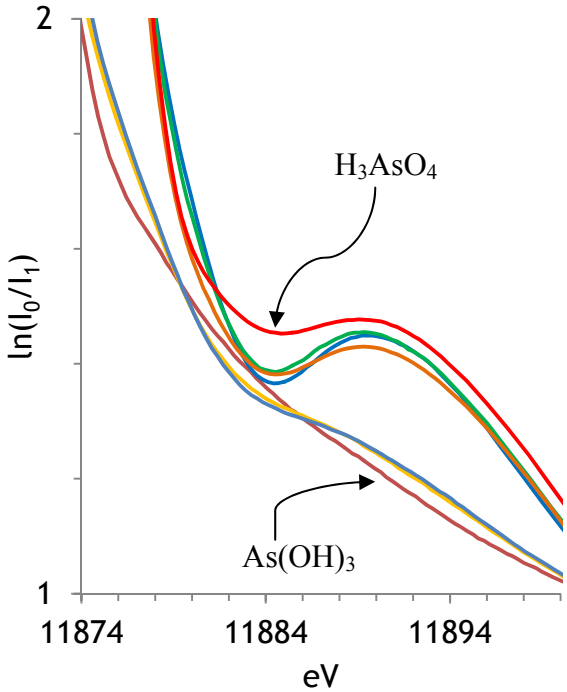

Figure S2: As K_α edges of inorganic arsenic compounds. Light red: $As(OH)_3$; light orange $AsO(OH)_2^-$; light blue AsO_3^{3-}, Red: H_3AsO_4; Orange: $H_2AsO_4^-$; green $HAsO_4^{2-}$; blue AsO_4^{3-}

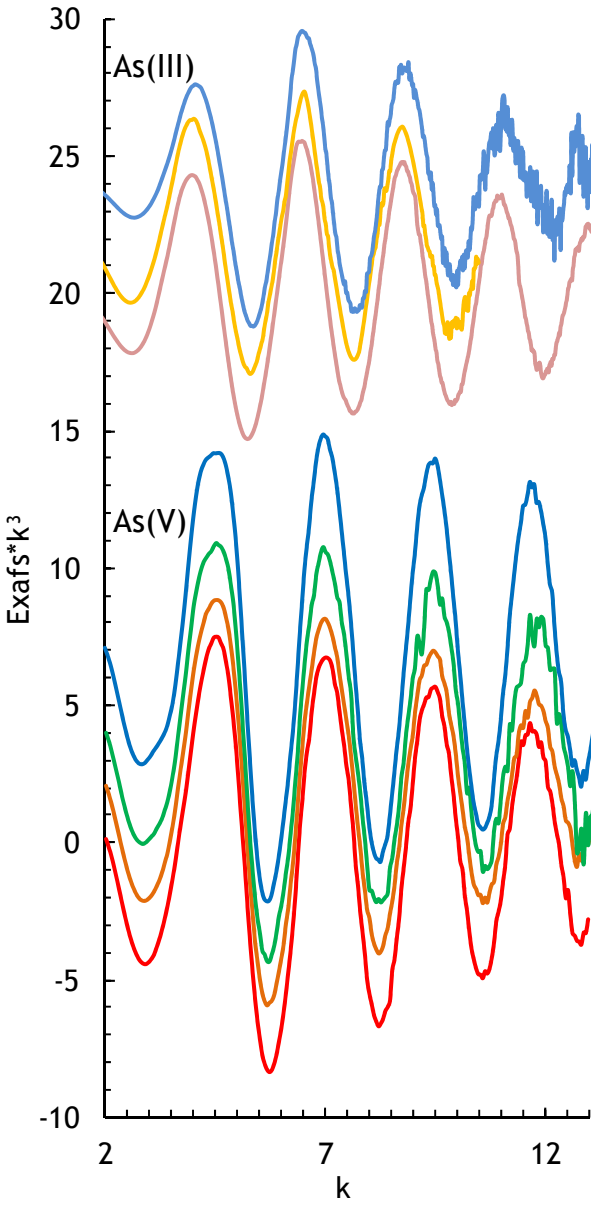

Figure S3: (Lower functions): EXAFS functions of H_3AsO_4 (red); $H_2AsO_4^-$ (orange); $HAsO_4^{2-}$ (green); AsO_4^{3-} (blue). (Upper functions): $As(OH)_3$ (light red); $AsO(OH)_2^-$ (light orange); AsO_3^{3-}(light blue). All functions but the one for H_3AsO_4 is offset for clarity.

Table S8: White line maxima for inorganic arsenic species in varied states of protonation. *)The literature value reported for trivalent arsenic were obtained at pH 9, and thus speciation $As(OH)_3/AsO(OH)_2^-$ is unclear. The results are shown with two decimals in order to underline the constant difference between As(V) and As(III) species of the same degree of protonation (see bottom of table), rather than to claim the absolute values with such high certainity.

Species	Peak eV	Smith eV
H_3AsO_4	11875.54	
$H_2AsO_4^-$	11875.22	11875.3
$HAsO_4^{2-}$	11875.26	
AsO_4^{3-}	11875.43	
As(V)av.	***11875.36***	
$As(OH)_3$	11871.53	11871.7
$AsO(OH)_2^-$	11871.22	
AsO_3^{3-}	11871.43	
As(III) av.	***11871.39***	
Difference		
H_3AsO_4-$As(OH)_3$	4.01	
$H_2AsO_4^-$-$AsO(OH)_2^-$	4.00	
AsO_4^--AsO_3^-	4.00	

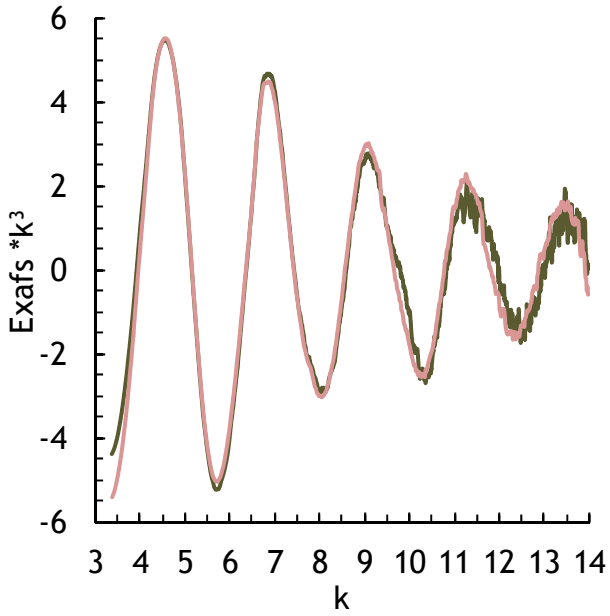

Figure S4: EXAFS waves for 1) 0.1196M As(OH)3 from $NaAsO_2$ at pH 3.15 (light red), and 2) a ca 0.5M oversaturated solution of $As(OH)_3$ from As_2O_3 at pH 3.6 (brown).

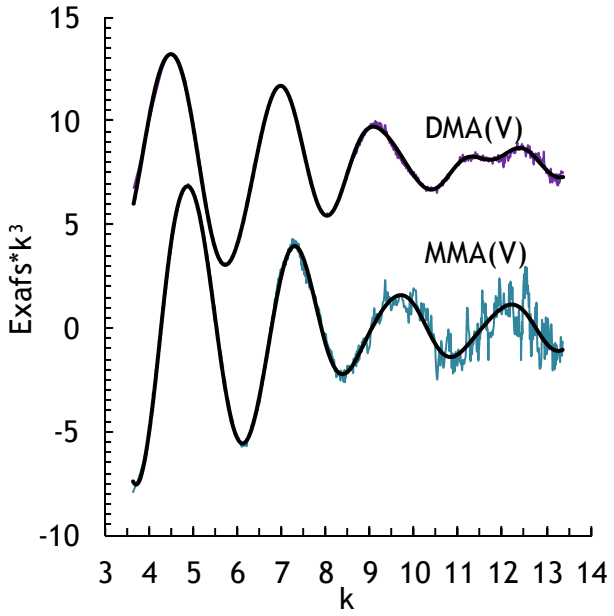

Figure S5: EXAFS waves for dimethylarsenate (purple) and monomethylarsenate (turquoise). Data is fitted to models shown with black lines.

Appendix 3 – Large angle X-ray scattering of $Te(OH)_6$

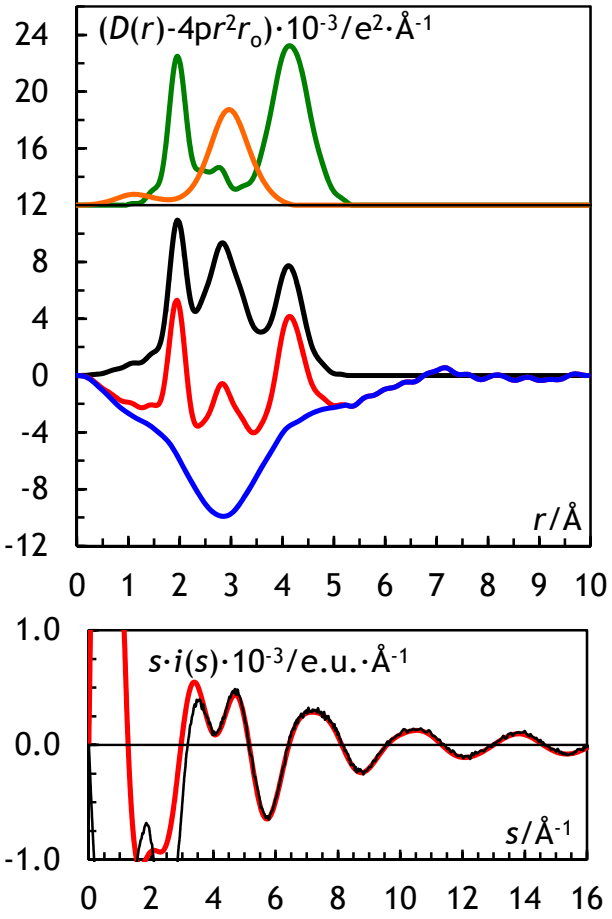

Figure S6: (Top) LAXS radial distribution curves for a 2.000 mol·dm^{-3} aqueous solution of $Te(OH)_6$. Upper part: Separate model contributions (offset: 12) of Te-O distances (green line) and the aqueous bulk (orange line). (Middle) Experimental RDF: $D(r)$-$4\pi r^2\rho_o$ (red line), sum of model contributions (black line) and the difference between experimental and calculated functions (blue line). (Bottom) Reduced LAXS intensity functions s·i(s) (black line); model $s \cdot i_{calc}(s)$ (red line).

Appendix 4 – Alternatively interpreted DDIR peaks at 2564 and 2474 cm^{-1}

In the main article it was suggested that the subpeaks at 2564 and 2474 cm^{-1} were merely a result of an asymmetry in a peak located at 2533 cm^{-1} or with a weighted center at 2513 cm^{-1}. If, however, there is physical significance to these sub-peaks, the following more speculative explanation is offered:

It could be argued that O-D oscillators in molecules interacting with the D-end of HDO molecules should show a different behavior than O-D oscillators in HDO molecules interacting with the H-end. The Lindgren group, developers of double difference IR, proposed that only HDO molecules interacting with the D-end were spectroscopically distinguishable.[94] However, later research has shown that the relationship between the affected number and the hydration number is less straightforward than previously thought,[95] and therefore we lack knowledge about the difference in the spectroscopical behavior of D-donating and H-donating HDO molecules. Assuming that the two subpeaks of the hydroxyl oxygen depend on whether the D-end or H-end of HDO is the one accepting electron density from the hydroxyl oxygen atom, we can discuss which interaction are responsible for each sub peak. These two interactions are located rather close to each other which are in line with the fact that there is no severe separation within the anionic parts of spectra from previous investigations.[94-110] If the peak locations of these two spectra is compared to the peak location of bulk water at 2509 cm^{-1}, the following hypothesis could be set: As the O-D oscillator engaged in a TeO(H)-HOD interaction (No 1 in Figure S3) is further from the central atom than an O-D oscillator engaged in a TeO(H)-DOH interaction (No 2 in Figure S3), it should have properties more similar to bulk water. As the peak of 2474 cm^{-1} is the one closest to bulk water O-D stretching frequency, this peak is assigned to O-D oscillators engaged in TeO(H)-HOD interactions. By exclusion, the peak at 2564 cm^{-1} is assigned to O-D oscillators engaged in TeO(H)-DOH interactions. It can be seen in figure S3 that this assignment is also compatible with a possible alternating pattern of increased(+) and decreased(-) bond energy for covalent and electrostatic interactions, measured as dislocation of affected spectrum peaks. This reasoning is in line with the suggested preference of hydration at the hydrogen side of acidic hydroxyl groups, as discussed in the main article.

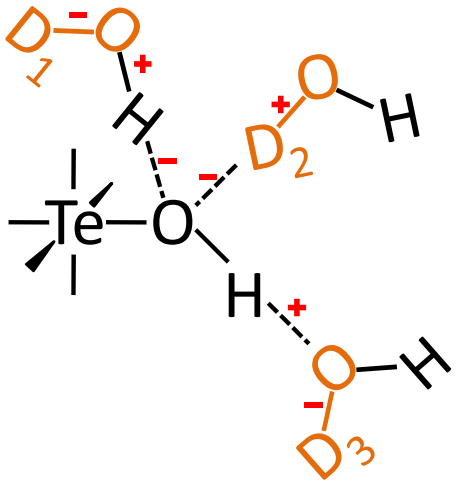

Figure S7: Possible occurrence of HDO in the hydration shell of telluric acid. An O-D oscillator can be described to have either higher (+) or lower (-) energy compared to one in bulk solvent and this is measured by the position of its affected spectrum peak relative to the affected spectrum of bulk solvent. If the energy of one covalent or electrostatic interaction is changed, the energy of a neighboring interaction should change in the opposite direction. Oscillator suffixes 1, 2 and 3 are referred to in the text..

Table S9: *The affected spectrum of $Te(OH)_6$(aq), assuming that the alternative interpretation mention above is correct. Peaks for which a weighted average is given are Gaussian combinations of below standing italic marked peaks. Other peaks have Gaussian shape.*

	Center cm^{-1}	Weighted cm^{-1}	Assignment
$Te(OH)_6$	2511	2449	Affected spect.
(N=9.7)	2533	2513	TeO-bonded HDO
	2564		*TeO(H)-DOH*
	2474		*TeO(H)-HOD*
	2340		Mainly Te(O)H-OHD

Appendix 5 – Affected spectrum for arsenous acid, $As(OH)_3$

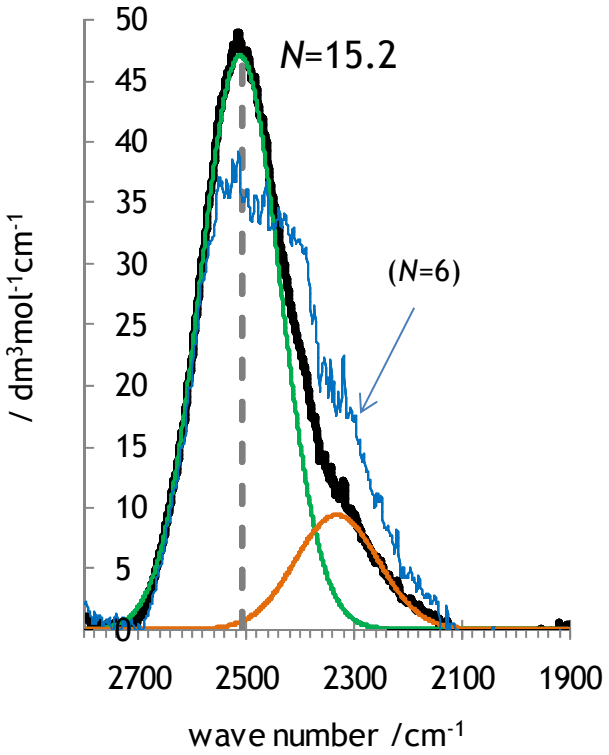

Figure S8: Affected spectrum of $As(OH)_3(aq)$ for N=6. The spectrum is modeled from two contributions of Gaussian character. The peak at 2331 cm^{-1} (orange) is considered to be due to interactions with the hydroxyl hydrogen, while the peak at 2511 is due to interactions with the hydroxyl oxygen. The noisy blue line is an alternative affected spectrum for N=6, shown for comparison. The position of bulk water at 2509 cm^{-1} is shown as a grey dashed line.

Appendix 6 – Distances in homoleptic complexes $As(OL)_3$

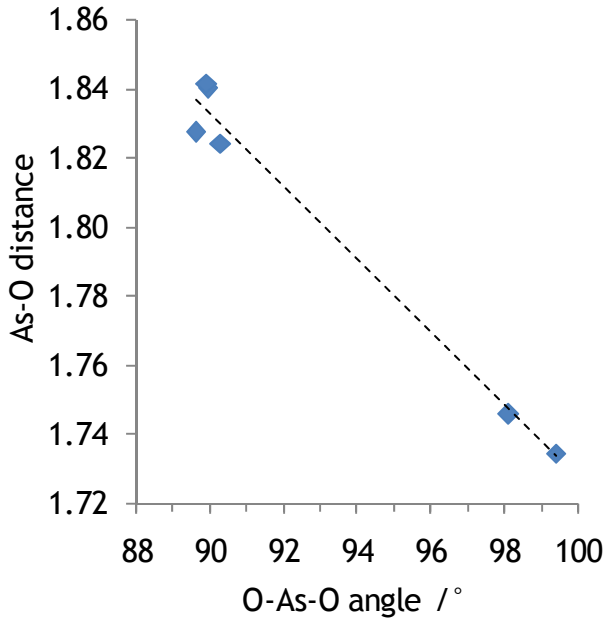

Figure S9 A possible relationship between As-O bond length and O-As-O angle is indicated with a dashed line for a number of homoleptic complexes $As(OL)_3$; trifluoroacetate,[111] acetate[112],[113] and 2,2-dimethylpropionate.[114] Also compounds with space demanding phenyl substituted ligands ($As(OSn(Ph)_3)_3$ and $As(OSi(Ph)_3)_3$).[115],[116]

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