DFT analysis of molybdenum isotope fractionation

Supplementary Information

Colin L. Weeks,[a] Ariel D. Anbar,[b, c] Laura E. Wasylenki[b] and Thomas G. Spiro*[a]

[a]Department of Chemistry, Princeton University, Princeton, NJ, 08544

[b]School of Earth & Space Exploration, Arizona State University, Tempe, AZ, 85287

[c]Department of Chemistry & Biochemistry, Arizona State University, Tempe, AZ, 85287

*Address correspondence to: Thomas G. Spiro, Department of Chemistry, Princeton University, Princeton, NJ, 08544, Tel: +1-609-258-3907, Fax: +1-609-258-0348, E-mail: spiro@princeton.edu

Table S1 Frequencies for $MoO_3(H_2O)$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
69	1.000255	$\rho_t H_2O$
113	1.001013	$\rho_r H_2O + \delta MoO$
135	1.000868	$\rho_w H_2O + \delta MoO$
233	1.001177	$\delta_s MoO$
317	1.000357	$\rho_w H_2O + \delta MoO$
330	1.000962	$\delta_{as} MoO$
340	1.00065	$\rho_w H_2O + \delta MoO$
395	1.002567	νMoO(aqua)
610	1.00003	$\rho_r H_2O$
964	1.002142	$\nu_{as} MoO$(oxo)
969	1.002031	$\nu_{as} MoO$(oxo)
985	1.000598	$\nu_s MoO$(oxo)
1628	1.000000	δH_2O
3775	1.000000	$\nu_s OH$
3864	1.000000	$\nu_{as} OH$

Table S2 Frequencies for $MoO_3(H_2O)_2$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
57	1.001409	$\rho_r H_2O + \delta MoO$
73	1.00028	$\rho_r H_2O$
123	1.001108	$\rho_r H_2O + \rho_w H_2O$
162	1.000547	$\rho_w H_2O + \delta MoO(aqua)$
224	1.000042	$\delta MoO(aqua)$
248	1.00016	$\rho_w H_2O + \rho_t H_2O$
265	1.000588	$\nu MoO(aqua) + \rho_t H_2O$
289	1.000159	$\rho_t H_2O$
331	1.000831	$\delta MoO(oxo)$
335	1.000927	$\rho_t H_2O + \delta MoO(oxo)$
389	1.002796	$\nu MoO(aqua)$
420	1.000169	$\rho_t H_2O$
497	1.000069	$\rho_w H_2O$
528	1.000042	$\rho_w H_2O$
633	1.000028	$\rho_t H_2O$
952	1.002075	$\nu_{as} MoO(oxo)$
962	1.001837	$\nu_{as} MoO(oxo)$
979	1.00091	$\nu_s MoO(oxo)$
1561	1.000000	δH_2O
1649	1.000000	δH_2O
3740	1.000000	$\nu_s OH$
3759	1.000000	$\nu_s OH$
3829	1.000000	$\nu_{as} OH$
3879	1.000000	$\nu_{as} OH$

Table S3 Frequencies for $MoO_3(H_2O)_3$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

Gas Phase			PCM Solvent Model		
$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment	$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
45	1.000399	$\rho_r H_2O$	115	1.000004	$\rho_t H_2O + \delta MoO(aqua)$
65	1.000646	$\rho_r H_2O + \delta MoO$	131	1.000006	$\rho_w H_2O + \delta MoO(aqua)$
87	1.000046	$\rho_t H_2O + \delta MoO$	138	1.000075	$\rho_w H_2O + \delta MoO(aqua)$
123	1.000842	$\delta MoO(aqua)$	148	1.000510	$\rho_t H_2O + \rho_r H_2O$
141	1.001058	δMoO	163	1.001788	$\delta MoO(aqua)$
143	1.000991	δMoO	177	1.000302	$\rho_r H_2O$
220	1.000093	$\rho_r H_2O + \delta MoO(aqua)$	182	1.001488	δMoO
226	1.000042	$\rho_r H_2O + \nu MoO(aqua)$	195	1.000460	$\rho_t H_2O + \delta MoO(aqua)$
241	1.000128	$\rho_r H_2O + \nu MoO(aqua)$	245	1.000165	$\rho_t H_2O + \nu MoO(aqua)$
244	1.000121	$\rho_r H_2O + \nu MoO(aqua)$	253	1.000011	$\nu MoO(aqua) + \rho_t H_2O$
252	1.000026	$\nu_s MoO(aqua)$	260	1.000037	$\nu MoO(aqua) + \rho_r H_2O$
306	1.000339	$\rho_t H_2O$	278	1.000033	$\rho_w H_2O$
330	1.000929	$\delta_{as} MoO(oxo)$	289	1.000070	$\rho_w H_2O$
331	1.000936	$\delta_{as} MoO(oxo)$	323	1.000474	$\rho_w H_2O$
352	1.003480	$\delta_s MoO(oxo)$	346	1.000846	$\delta_{as} MoO(oxo) + \rho_w H_2O$
513	1.000072	$\rho_w H_2O$	348	1.000759	$\delta_{as} MoO(oxo) + \rho_w H_2O$
515	1.000064	$\rho_w H_2O$	376	1.002923	$\delta_s MoO(oxo) + \rho_w H_2O$
526	1.000019	$\rho_w H_2O$	434	1.000136	$\rho_w H_2O$
579	1.000035	$\rho_t H_2O$	562	1.000033	$\rho_r H_2O$
581	1.000029	$\rho_t H_2O$	581	1.000032	$\rho_r H_2O$
599	1.000047	$\rho_t H_2O$	590	1.000033	$\rho_r H_2O$
948	1.002122	$\nu_{as} MoO(oxo)$	868	1.002093	$\nu_{as} MoO(oxo)$
949	1.002122	$\nu_{as} MoO(oxo)$	869	1.002110	$\nu_{as} MoO(oxo)$
964	1.000598	$\nu_s MoO(oxo)$	947	1.000648	$\nu_s MoO(oxo)$

1595	1.000000	δOH	1549	1.000000	δH_2O
1606	1.000000	δOH	1561	1.000000	δH_2O
1607	1.000000	δOH	1562	1.000000	δH_2O
3766	1.000000	$\nu_s OH$	3517	1.000000	$\nu_s OH$
3767	1.000000	$\nu_s OH$	3524	1.000000	$\nu_s OH$
3768	1.000000	$\nu_s OH$	3532	1.000000	$\nu_s OH$
3868	1.000000	$\nu_{as} OH$	3568	1.000000	$\nu_{as} OH$
3868	1.000000	$\nu_{as} OH$	3587	1.000000	$\nu_{as} OH$
3869	1.000000	$\nu_{as} OH$	3589	1.000000	$\nu_{as} OH$

Table S4. Frequencies for $MoO_2(OH)_2$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
196	1.000790	δMoO(hydroxo) + ρ_tOH
226	1.000215	ρ_tOH + δMoO
228	1.001981	ρ_tOH + δMoO
265	1.001733	δMoO
278	1.000134	ρ_tOH + δMoO
305	1.000348	ρ_tOH
358	1.000853	δMoO(oxo) + ρ_tOH
655	1.000226	ν_{as}MoO(hydroxo) + δMoOH
667	1.000102	ν_sMoO(hydroxo) + δMoOH
726	1.001025	ν_sMoO(hydroxo) + δMoOH
743	1.002123	ν_{as}MoO(hydroxo) + δMoOH
1010	1.002085	ν_{as}MoO(oxo)
1019	1.001135	ν_sMoO(oxo)
3833	1.000000	ν_{as}OH
3838	1.000000	ν_sOH

Table S5 Frequencies for $MoO_2(OH)_2(H_2O)$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
102	1.000576	$\rho_w H_2O + \delta MoO$
127	1.000835	$\delta MoO + \nu MoO(aqua)$
156	1.000954	$\delta MoO(aqua/hydroxo)$
202	1.001200	$\delta MoO(aqua/hydroxo)$
233	1.000146	$\rho_r H_2O$
253	1.000641	δMoO
266	1.000320	$\rho_r H_2O + \delta MoO$
273	1.001554	$\delta MoO + \rho_r H_2O$
325	1.000410	$\rho_t OH + \delta MoO(oxo)$
368	1.000637	$\rho_t OH + \delta MoO(oxo)$
426	1.000031	$\rho_t OH + \rho_t H_2O$
461	1.000080	$\rho_w H_2O$
487	1.000003	$\rho_t H_2O + \rho_t OH$
679	1.001460	$\nu MoO(hydroxo) + \delta MoOH$
712	1.001388	$\nu MoO(hydroxo) + \delta MoOH$
747	1.000486	$\delta MoOH + \nu MoO(hydroxo)$
785	1.000154	$\delta MoOH$
995	1.001743	$\nu_{as} MoO(oxo)$
1018	1.001471	$\nu_s MoO(oxo)$
1633	1.000000	δH_2O
3774	1.000000	$\nu_s OH(aqua)$
3798	1.000000	$\nu OH(hydroxo)$
3837	1.000000	$\nu OH(hydroxo)$
3870	1.000000	$\nu_{as} OH(aqua)$

Table S6 Frequencies for $MoO_2(OH)_2(H_2O)_2$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

Gas Phase			PCM Solvent Model		
$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment	$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
70	1.000084	δMoO(aqua)	34	1.000256	$\rho_r H_2O + \rho_t OH$
91	1.000333	$\rho_r H_2O$	68	0.999932	δMoO(aqua)
107	1.000271	δMoO	94	0.999817	$\rho_t OH$ + δMoO
126	1.001096	δMoO	117	1.000130	$\rho_r H_2O$ + δMoO
152	1.001345	νMoO(aqua) + $\rho_r H_2O$	150	1.000116	$\rho_r H_2O + \rho_t OH$
180	1.001391	νMoO(aqua)	180	1.001682	νMoO(aqua) + $\rho_r H_2O$
224	1.000238	$\rho_r H_2O + \rho_t OH$	194	1.002167	νMoO(aqua)
236	1.000319	$\rho_r H_2O$ + δMoO	203	1.000358	$\rho_t OH$ + δMoO
256	1.000184	δMoO	214	1.000606	$\rho_t OH$ + δMoO
264	1.000607	δMoO	241	1.000254	$\rho_r H_2O + \rho_t OH$
282	1.000734	$\rho_r H_2O$ + δMoO	260	1.000476	$\rho_t OH + \rho_r H_2O$
297	1.000853	δMoO	270	1.000538	δMoO
346	1.000470	$\rho_t OH$ + δMoO(oxo)	292	1.000665	δMoO + $\rho_t OH$
369	1.000748	$\rho_t OH$ + δMoO(oxo)	318	1.000484	δMoO + $\rho_t OH$
401	1.000018	$\rho_t OH + \rho_t H_2O$	349	1.000980	$\rho_w H_2O$ + δMoO(oxo)
436	1.000151	$\rho_w H_2O$	381	1.000279	$\rho_w H_2O$ + δMoO(oxo)
480	1.000054	$\rho_w H_2O$	482	1.000049	$\rho_w H_2O$
515	1.000025	$\rho_t H_2O + \rho_t OH$	540	1.000006	$\rho_t H_2O$
567	1.000007	$\rho_t H_2O$	557	1.000028	$\rho_t H_2O$
615	1.001300	νMoO(hydroxo)	609	1.002142	ν_{as}MoO(hydroxo) + δMoOH
674	1.001784	νMoO(hydroxo) + δMoOH	619	1.000765	ν_sMoO(hydroxo) + δMoOH
772	1.000158	δMoOH	767	1.000182	δMoOH
816	1.000141	δMoOH	779	1.000089	δMoOH
990	1.001802	ν_{as}MoO(oxo)	926	1.001968	ν_{as}MoO(oxo)

1007	1.001356	ν_sMoO(oxo)	966	1.001106	ν_sMoO(oxo)
1589	1.000000	δH_2O	1554	1.000000	δH_2O
1641	1.000000	δH_2O	1562	1.000000	δH_2O
3753	1.000000	ν_sOH(aqua)	3419	1.000000	νOH(hydroxo)
3786	1.000000	ν_sOH(aqua)	3512	1.000000	νOH(hydroxo)
3811	1.000000	νOH(hydroxo)	3542	1.000000	ν_sOH(aqua)
3835	1.000000	νOH(hydroxo)	3548	1.000000	ν_sOH(aqua)
3859	1.000000	ν_{as}OH(aqua)	3596	1.000000	ν_{as}OH(aqua)
3895	1.000000	ν_{as}OH(aqua)	3610	1.000000	ν_{as}OH(aqua)

In the calculations with the PCM solvent model the second and third modes had higher frequencies for the ^{97}Mo isotopomer, which should not be the case. This is not due to a rounding error, the frequencies given to four decimal places were used in determining $^{95}\nu/^{97}\nu$.

Table S7 Frequencies for $MoO(OH)_4$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
72	1.000075	ρ_tOH + δMoO
100	1.000123	ρ_tOH + δMoO
217	1.000788	ρ_tOH + δMoO
239	1.001656	ρ_tOH + δMoO
251	1.000683	δMoO
266	1.002172	δMoO
294	1.00108	δMoO + ρ_tOH
330	1.000509	ρ_tOH + δMoO
402	1.000224	ρ_tOH + δMoO
470	1.000057	ρ_tOH
561	1.000151	ν_{as}MoO(hydroxo)
601	1.000031	ρ_tOH
647	1.000912	νMoO(hydroxo) + δMoOH
662	1.001163	νMoO(hydroxo) + δMoOH
706	1.00079	ν_sMoO(hydroxo) + δMoOH
735	1.001484	νMoO(hydroxo) + δMoOH
792	1.000363	δMoOH
804	1.000465	δMoOH
979	1.000152	δMoOH
1020	1.001659	νMoO(oxo)
3796	1.000000	νOH
3805	1.000000	νOH
3824	1.000000	νOH
3831	1.000000	νOH

Table S8 Frequencies for $MoO(OH)_4(H_2O)$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
65	1.000898	ρ_tOH + δMoO
97	1.000072	ρ_tOH + δMoO
127	1.000306	δMoO + νMoO(aqua)
156	1.000754	δMoO
162	1.001092	νMoO(aqua) + δMoO
244	1.001115	$\rho_r H_2O$ + δMoO
247	1.000043	$\rho_r H_2O$ + ρ_tOH
263	1.001052	δMoO + $\rho_r H_2O$
281	1.001333	δMoO + ρ_tOH
293	1.001115	δMoO
319	1.000227	δMoO + ρ_tOH
369	1.000082	ρ_tOH
391	1.000288	ρ_tOH + $\rho_t H_2O$
476	1.000064	ρ_tOH + $\rho_t H_2O$
519	1.000018	δMoOH + ρ_tOH
538	1.000163	ν_{as}MoO(hydroxo)
569	1.000027	ρ_tOH
579	1.000085	ρ_tOH + $\rho_t H_2O$
635	1.001571	ν_sMoO(hydroxo)
679	1.001601	νMoO(hydroxo) + δMoOH
709	1.001042	νMoO(hydroxo) + δMoOH
760	1.000152	δMoOH
794	1.000372	δMoOH
829	1.000317	δMoOH
940	1.000140	δMoOH
1027	1.001658	νMoO(oxo)
1639	1.000000	δH_2O
3756	1.000000	ν_sOH(aqua)
3789	1.000000	νOH(hydroxo)
3811	1.000000	νOH(hydroxo)
3814	1.000000	νOH(hydroxo)
3816	1.000000	νOH(hydroxo)
3863	1.000000	ν_{as}OH(aqua)

Table S9 Frequencies for $Mo(OH)_6$ and frequency ratios for the ^{95}Mo and ^{97}Mo isotopomers in the gas phase. Calculations with B3LYP theory and the LANL2DZ ECP basis set for Mo and the 6-311+G(2df,p) basis set for O and H

$^{95}\nu$	$^{95}\nu/^{97}\nu$	Assignment
137	1.000056	δMoO
142	1.000146	δMoO
143	1.000146	δMoO
221	1.002771	δMoO
241	1.001998	δMoO
242	1.002002	δMoO
314	1.000574	δMoO
315	1.000568	δMoO
368	1.000047	δMoO
480	1.000041	ρ_tOH
483	1.000036	ρ_tOH
534	1.000064	ρ_tOH
535	1.000062	ρ_tOH
550	1.000022	ρ_tOH
557	1.000107	ρ_tOH
559	1.000099	νMoO(hydroxo) + ρ_tOH
618	1.000091	ρ_tOH + νMoO(hydroxo)
642	1.001686	νMoO(hydroxo) + ρ_tOH
701	1.001309	νMoO(hydroxo) + δMoOH
702	1.001325	νMoO(hydroxo) + δMoOH
722	1.000355	νMoO(hydroxo)
779	1.000063	δMoOH
817	1.000871	δMoOH
818	1.000828	δMoOH
894	1.000366	δMoOH
899	1.000236	δMoOH
968	1.000295	δMoOH
3791	1.000000	νOH
3792	1.000000	νOH
3796	1.000000	νOH
3805	1.000000	νOH
3806	1.000000	νOH
3807	1.000000	νOH