Supporting information for:

Improved methods for Feynman Path Integral Calculations Vibrational-Rotational Free Energies and Application to Isotopic Fractionation of hydrated Chloride Ions

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1. Overview

Section 2 outlines the calculation of the statistical uncertainties. Tables S1, S2, and S3 provide vibrational harmonic frequencies for the two conformers of $Cl(HDO)^-$ and for $Cl(D_2O)^-$. Tables S4, S5, and S5 list harmonic frequencies for H_2O, HDO, and D_2O. Table S7 lists optimized geometries for H_2O. Tables S8 and S9 are versions of Tables 7 and 8 without the MP2/E4 calculation and with more significant figures. Table S10 provides absolute energies for the various electronic structure calculations as well as binding energies.

2. Statistical error analysis

The contributions to $Q^{[P]}$ from each strata are uncorrelated with each other, so we have

$$Q^{[P]} = \sum_{k=1}^{N^{\text{strata}}} Q_k^{[P]}(T) \tag{S1}$$

and

$$\sigma^2 = \sum_{k=1}^{N^{\text{strata}}} \sigma_k^2 , \tag{S2}$$

where N^{strata} is the number of strata, σ^2 is the variance for the entire calculation, and σ_k^2 is the variance of the samples that fall within stratum *k*. Within each stratum we can express the results as a product of two components that have separately calculated Monte Carlo uncertainties:

$$Q_k^{[P]} = \alpha_k q_k , \tag{S3}$$

where α_k is given by eq 22 and the q_k are given by

$$q_k = \frac{1}{N_k^{\text{centroids}}} \sum_{j=1}^{N_k^{\text{centroids}}} \tilde{q}_{j;k} , \tag{S4}$$

which is the average of statistically independent contributions from the N_k^{centroid} centroid samples from within stratum *k*. Each of the $\tilde{q}_{j;k}$ is an average over all the paths at a given centroid sample *j* at centroid position $\mathbf{x}_{\text{C}}$

$$\tilde{q}_{j;k} = \frac{Q^{\text{fp}}(T)\langle f \rangle}{\sigma_{\text{sym}} N^{\text{paths}} f(\mathbf{x}_{\text{C}})} \sum_{i=1}^{N^{\text{paths}}} \left\langle \exp\left\{ \frac{-\beta}{P} \sum_{l=1}^{P} V(\mathbf{x}_l) \right\} \right\rangle_{\text{fp},f(\mathbf{x}_{\text{C}});k} . \tag{S5}$$

We then have

$$\frac{\sigma_k^2}{\left[Q_k^{[P]}\right]^2} = \frac{\sigma_k^2(\alpha_k)}{\alpha_k^2} + \frac{\sigma_k^2(q_k)}{q_k^2} \tag{S6}$$

where

$$\sigma_k^2(q_k) = \frac{1}{N_k^{\text{centroids}}} \left[\frac{1}{N_k^{\text{centroids}}} \left(\sum_{j=1}^{N_k^{\text{centroids}}} \tilde{q}_{j;k}^2 \right) - q_k \right] \tag{S7}$$

and

$$\sigma_k^2(\alpha_k) = \frac{\alpha_k - \alpha_k^2}{N^{\text{candidates}}} \tag{S8}$$

where $N^{\text{candidates}}$ is the total number of candidate centroids examined during the calculation. The first term on the right hand side of eq S6 is bounded from above by $1/N_k^{\text{centroids}}$ so we can see that in the calculations presented here, this term contributes negligibly to the final uncertainty.

Table S1. Harmonic frequencies (in cm^{-1}) for $[Cl...HOD]^-$ for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
DWX PES	3491.39	2849.38	1645.82	329.64	185.95	810.50
MDWX PES	3359.71	2737.13	1578.18	353.26	212.62	855.14
RB PES	3393.28	2800.70	1550.49	298.80	196.30	719.88
mPW1PW/aug-cc-pVTZ	3330.94	2848.00	1521.42	298.84	194.14	746.89
MP2/aug-cc-pVTZ	3344.50	2825.37	1515.79	296.82	197.50	749.40
MP2/aug-cc-pV(T+d)Z	3342.79	2825.33	1515.77	297.02	197.48	749.78
MP2/aug-cc-pV(Q+d)Z	3360.68	2838.48	1518.80	291.76	197.08	746.87
MP2/aug-cc-pV(5+d)Z	3360.99	2840.77	1518.30	290.10	196.94	746.02
CCSD(T)/aug-cc-pVTZ	3393.97	2807.31	1530.12	291.19	194.77	738.18
CCSD(T)/aug-cc-pV(T+d)Z	3392.74	2807.37	1530.24	292.51	194.96	739.15
CCSD(T)/aug-cc-pV(Q+d)Z	3419.94	2822.70	1533.22	284.28	193.04	731.43
icMRCI+Q/aug-cc-pVTZ	3419.03	2810.65	1535.68	290.16	191.93	735.48
icMRCI+Q/aug-cc-pV(T+d)Z	3417.88	2810.61	1535.70	290.38	191.93	736.08
icMRCI+Q/aug-cc-pV(Q+d)Z	3447.96	2827.00	1539.03	281.93	189.71	729.50

Table S2. Harmonic frequencies (in cm^{-1}) for $[Cl...DOH]^-$ for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
DWX PES	3921.46	2539.60	1542.23	340.89	188.55	599.03
MDWX PES	3766.58	2445.19	1453.36	369.18	216.87	628.68
RB PES	3856.25	2466.58	1449.46	310.79	198.19	527.63
mPW1PW/aug-cc-pVTZ	3919.91	2423.06	1421.97	311.96	195.20	547.16
MP2/aug-cc-pVTZ	3891.24	2430.94	1413.80	309.81	199.06	548.13
MP2/aug-cc-pV(T+d)Z	3891.20	2429.71	1413.67	310.07	199.03	548.37
MP2/aug-cc-pV(Q+d)Z	3909.15	2442.76	1419.11	303.96	198.71	547.37
MP2/aug-cc-pV(5+d)Z	3912.42	2442.96	1419.01	302.24	198.49	546.85
CCSD(T)/aug-cc-pVTZ	3864.20	2467.69	1431.53	302.39	196.77	541.20
CCSD(T)/aug-cc-pV(T+d)Z	3864.29	2466.81	1431.52	303.94	196.86	541.79
CCSD(T)/aug-cc-pV(Q+d)Z	3885.27	2486.58	1438.01	294.51	195.05	538.00
icMRCI+Q/aug-cc-pVTZ	3868.54	2485.97	1438.20	301.49	193.60	539.51
icMRCI+Q/aug-cc-pV(T+d)Z	3868.50	2485.16	1438.16	301.77	193.58	539.86
icMRCI+Q/aug-cc-pV(Q+d)Z	3890.92	2507.02	1445.00	292.22	191.48	536.79

Table S3. Harmonic frequencies (in cm^{-1}) for $Cl(D_2O)^-$ for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
DWX PES	2859.93	2534.06	1324.85	292.44	183.08	590.81
MDWX PES	2747.61	2439.69	1258.60	316.14	209.30	621.78
RB PES	2809.37	2460.67	1248.39	265.49	193.19	522.74
mPW1PW/aug-cc-pVTZ	2853.22	2418.90	1225.16	265.55	190.97	542.22
MP2/aug-cc-pVTZ	2833.77	2425.13	1219.35	264.08	194.30	543.63
MP2/aug-cc-pV(T+d)Z	2833.72	2423.91	1219.28	264.27	194.28	543.89
MP2/aug-cc-pV(Q+d)Z	2846.79	2436.96	1223.02	259.30	193.91	542.30
MP2/aug-cc-pV(5+d)Z	2849.20	2437.12	1222.85	257.77	193.77	541.73
CCSD(T)/aug-cc-pVTZ	2813.81	2462.20	1232.84	258.65	191.66	536.11
CCSD(T)/aug-cc-pV(T+d)Z	2813.86	2461.32	1232.88	259.83	191.84	536.77
CCSD(T)/aug-cc-pV(Q+d)Z	2829.21	2481.00	1237.11	252.13	189.97	532.02
icMRCI+Q/aug-cc-pVTZ	2817.05	2480.32	1237.97	257.60	188.87	534.27
icMRCI+Q/aug-cc-pV(T+d)Z	2817.01	2479.51	1237.95	257.79	188.87	534.68
icMRCI+Q/aug-cc-pV(Q+d)Z	2818.01	2501.08	1242.30	247.85	186.27	529.89

Table S4. Harmonic frequencies (in cm^{-1}) for H_2O for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3
PS PES	3832.72	1649.08	3944.28
RRK2 PES	3817.36	1639.60	3922.15
mPW1PW/aug-cc-pVTZ	3861.12	1637.49	3966.41
MP2/aug-cc-pVTZ	3821.95	1628.13	3947.77
MP2/aug-cc-pVQZ	3839.78	1632.18	3965.58
MP2/aug-cc-pV5Z	3842.69	1631.91	3969.31
CCSD(T)/aug-cc-pVTZ	3810.69	1645.18	3919.78
CCSD(T)/aug-cc-pVQZ	3831.10	1649.41	3940.52
icMRCI+Q/aug-cc-pVTZ	3813.58	1651.14	3920.46
icMRCI+Q/aug-cc-pV(T+d)Z	3813.56	1651.17	3920.44
icMRCI+Q/aug-cc-pV(Q+d)Z	3835.24	1655.73	3942.20

Table S5. Harmonic frequencies (in cm^{-1}) for HDO for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3
PS PES	2824.27	1445.56	3890.76
RRK2 PES	2816.03	1434.40	3872.41
mPW1PW/aug-cc-pVTZ	2843.01	1435.42	3915.81
MP2/aug-cc-pVTZ	2820.90	1427.14	3887.78
MP2/aug-cc-pVQZ	2833.90	1430.69	3905.62
MP2/aug-cc-pV5Z	2836.27	1430.47	3908.99
CCSD(T)/aug-cc-pVTZ	2807.42	1442.07	3867.36
CCSD(T)/aug-cc-pVQZ	2822.41	1445.79	3887.98
icMRCI+Q/aug-cc-pVTZ	2808.78	1447.35	3869.13
icMRCI+Q/aug-cc-pV(T+d)Z	2808.75	1447.38	3869.13
icMRCI+Q/aug-cc-pV(Q+d)Z	2824.58	1451.38	3890.88

Table S6. Harmonic frequencies (in cm^{-1}) for D_2O for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3
PS PES	2762.71	1207.03	2890.04
RRK2 PES	2763.18	1195.08	2873.84
mPW1PW/aug-cc-pVTZ	2783.04	1198.62	2906.79
MP2/aug-cc-pVTZ	2755.18	1191.60	2892.11
MP2/aug-cc-pVQZ	2768.00	1194.58	2905.35
MP2/aug-cc-pV5Z	2770.01	1194.41	2908.18
CCSD(T)/aug-cc-pVTZ	2747.12	1204.10	2871.66
CCSD(T)/aug-cc-pVQZ	2761.77	1207.23	2887.09
icMRCI+Q/aug-cc-pVTZ	2749.36	1208.37	2871.99
icMRCI+Q/aug-cc-pV(T+d)Z	2749.34	1208.40	2871.97
icMRCI+Q/aug-cc-pV(Q+d)Z	2764.90	1211.76	2888.14

Table S7. Optimized configurations for H_2O for the analytical surfaces and various electronic structure methods. The OH distance is in Å and the HOH angle is in degrees

Method	R(OH)	θ(HOH)
PS PES	0.9578	104.51
RRK2 PES	0.9572	104.52
mPW1PW/aug-cc-pVTZ	0.9579	104.94
MP2/aug-cc-pVTZ	0.9614	104.11
MP2/aug-cc-pVQZ	0.9589	104.27
MP2/aug-cc-pV5Z	0.9584	104.34
CCSD(T)/aug-cc-pVTZ	0.9616	104.18
CCSD(T)/aug-cc-pVQZ	0.9590	104.37
icMRCI+Q/aug-cc-pVTZ[a]	0.9613	103.99
icMRCI+Q/aug-cc-pV(T+d)Z[a]	0.9613	103.99
icMRCI+Q/aug-cc-pV(Q+d)Z[a]	0.9586	104.18

[a]Supermolecule calculations with Cl^-

Table S8. Equilibrium configuration of the global minimum of $Cl(H_2O)^-$ as predicted by a variety of methods. Distances are in Å and angles are in degrees; the dihedral angle is 0° in all cases

Method	R(OH)	R(OH′)	θ(HOH′)	R(Cl⁻H)	θ(Cl⁻HO)
DWX PES	0.9869	0.9541	99.40	2.1635	165.56
MDWX PES	0.9916	0.9536	99.03	2.1184	167.16
RB PES	0.9878	0.9615	100.76	2.1350	168.18
mPW1PW/aug-cc-pVTZ	0.9892	0.9569	101.39	2.1226	168.39
MP2/aug-cc-pVTZ	0.9908	0.9607	100.63	2.1160	168.90
MP2/aug-cc-pV(T+d)Z	0.9909	0.9607	100.64	2.1151	168.93
MP2/aug-cc-pV(Q+d)Z	0.9882	0.9582	100.71	2.1165	168.19
MP2/aug-cc-pV(5+d)Z	0.9879	0.9577	100.75	2.1149	168.12
CCSD(T)/aug-cc-pVTZ	0.9879	0.9612	100.75	2.1377	168.06
CCSD(T)/aug-cc-pV(T+d)Z	0.9880	0.9612	100.75	2.1369	168.08
CCSD(T)/aug-cc-pV(Q+d)Z	0.9848	0.9585	100.81	2.1435	166.99
icMRCI+Q/aug-cc-pVTZ	0.9864	0.9607	100.63	2.1485	167.98
icMRCI+Q/aug-cc-pV(T+d)Z	0.9864	0.9607	100.63	2.1478	167.99
icMRCI+Q/aug-cc-pV(Q+d)Z	0.9831	0.9580	100.70	2.1560	166.89

Table S9. Harmonic frequencies (in cm^{-1}) for $Cl(H_2O)^-$ for the analytical surfaces and various electronic structure methods

Method	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
DWX PES	3924.91	3483.06	1818.55	403.55	191.93	816.52
MDWX PES	3770.24	3351.02	1729.73	433.41	220.74	860.17
RB PES	3859.53	3387.15	1709.84	367.15	201.87	723.44
mPW1PW/aug-cc-pVTZ	3921.73	3327.84	1677.08	368.42	198.99	750.48
MP2/aug-cc-pVTZ	3894.34	3338.48	1669.42	365.51	202.84	752.67
MP2/aug-cc-pV(T+d)Z	3894.29	3336.76	1669.33	365.80	202.81	753.04
MP2/aug-cc-pV(Q+d)Z	3912.18	3354.81	1674.17	358.90	202.49	750.55
MP2/aug-cc-pV(5+d)Z	3915.46	3355.03	1673.82	356.91	202.28	749.74
CCSD(T)/aug-cc-pVTZ	3866.94	3389.93	1687.84	357.40	200.42	741.88
CCSD(T)/aug-cc-pV(T+d)Z	3867.03	3388.70	1687.85	359.22	200.51	742.80
CCSD(T)/aug-cc-pV(Q+d)Z	3887.99	3416.01	1693.27	348.53	198.66	735.79
icMRCI+Q/aug-cc-pVTZ	3871.39	3415.21	1694.82	357.05	197.25	739.53
icMRCI+Q/aug-cc-pV(T+d)Z	3871.34	3414.06	1694.81	357.33	197.24	740.00
icMRCI+Q/aug-cc-pV(Q+d)Z	3893.66	3444.19	1700.61	345.86	195.03	733.92

Table S10. Total energies (in E_h) and ΔE (in kcal/mol) for the various electronic structure methods considered (n/a denotes not applicable)

Method	$Cl(H_2O)^-$	H_2O	$Cl^- + H_2O$[a]	Cl^-	ΔE
mPW1PW/aug-cc-pVTZ	−536.776404	−76.442674	n/a	−460.310427	−14.62
MP2/aug-cc-pVTZ	−536.134391	−76.328992	n/a	−459.780792	−15.44
MP2/aug-cc-pV(T+d)Z	−536.135147	−76.328992	n/a	−459.781540	−15.45
MP2/aug-cc-pV(Q+d)Z	−536.179432	−76.351919	n/a	−459.803084	−15.33
MP2/aug-cc-pV(5+d)Z	−536.196159	−76.360228	n/a	−459.811568	−15.29
CCSD(T)/aug-cc-pVTZ	−536.171682	−76.342326	n/a	−459.805042	−15.26
CCSD(T)/aug-cc-pV(T+d)Z	−536.173272	−76.342326	n/a	−459.806626	−15.26
CCSD(T)/aug-cc-pV(Q+d)Z	−536.215961	−76.363588	n/a	−459.828395	−15.05
icMRCI+Q/aug-cc-pVTZ	−536.161107	n/a	−536.137456	n/a	−14.84
icMRCI+Q/aug-cc-pV(T+d)Z	−536.162392	n/a	−536.138738	n/a	−14.84
icMRCI+Q/aug-cc-pV(Q+d)Z	−536.203474	n/a	−536.180173	n/a	−14.62

[a]Supermolecule calculations