Supplementary Information

pH-dependent Reactivity of Water at MgO(100) and MgO(111) Surfaces

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S1. Surface Complexation Model parameters

Table S1: Surface Complexation Model parameter values

Triple Layer Model parameters	MgO 100	MgO 111
Protonation constants ($logK_1$, $logK_2$)	7, 16	7, 16
Ion affinities ($logK_C$, $logK_A$)	3.0, 3.0	3.0, 3.0
Surface Site Density Ns (sites/nm^2)	22	13
Capacitances of TLM model: c_1, c_2 (F/m^2)	0.6, 0.2	0.6, 0.2

S2. Fitting Parameters for the MgO(100)/D_2O Interface vSFG Spectra

Table S2: Fitting parameters for the vSFG spectra at pH 7-2 of MgO(100)/D_2O interface

	pH7		**pH6**		**pH5**		**pH4**		**pH3**		**pH2**	
Parameters	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error
y_0	2.54	0.63	3.55	0.56	3.51	0.50	3.19	0.56	3.44	0.74	2.04	1.28
x_{c1}	2484.51	8.48	2485.54	7.83	2493.54	7.46	2497.29	8.91	2519.98	8.12	2492.86	5.87
w_1	109.69	17.61	96.86	15.53	95.39	14.70	108.34	18.30	116.40	17.02	150.72	14.17
A_1	397.45	61.17	341.83	51.37	330.26	47.60	369.09	59.75	493.90	70.49	920.70	88.47
x_{c2}	2681.86	3.32	2679.65	3.51	2678.57	3.27	2680.90	3.82	2682.89	7.73	2709.05	24.70
w_2	13.72	4.40	12.21	4.34	12.11	4.12	14.84	5.29	13.27	10.73	10.00	27.20
A_2	55.93	15.99	46.40	14.28	45.57	13.29	54.01	17.54	37.68	25.83	20.00	47.78
x_{c3}	2744.71	0.94	2745.76	0.95	2746.36	0.91	2746.68	1.07	2755.39	1.04	2755.20	2.17
w_3	34.55	1.61	37.11	1.64	38.04	1.57	38.07	1.82	34.94	1.80	25.07	3.62
A_3	326.72	13.42	335.81	13.00	336.76	12.17	332.80	14.27	317.39	14.12	199.00	25.11
Red. c^2	9.220		8.385		7.030		7.586		12.355		23.964	
Adj. R^2	0.975		0.974		0.977		0.974		0.962		0.900	

Table S3: Fitting parameters for the vSFG spectra at pH 7-13 of MgO(100)/D_2O interface

	pH7		pH8		pH9		pH10		pH11		pH12		pH13	
Parameters	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error
y_0	2.55	0.61	3.19	0.51	2.95	0.47	2.56	0.44	3.24	0.37	4.44	0.33	4.73502	0.32085
x_{c1}	2487.35	7.73	2491.73	7.79	2489.74	7.42	2520.33	8.08	2527.79	11.96	2522.35	20.24	2509.521	17.60301
w_1	104.48	15.57	94.76	15.21	98.32	14.70	82.70	15.12	59.63	21.00	56.80	35.27	67.33831	31.69691
A_1	393.89	55.69	325.02	48.71	332.12	46.71	264.07	44.61	139.56	43.66	96.48	53.55	123.6466	53.08549
x_{c2}	2680.14	3.77	2678.35	4.01	2677.85	3.47	2681.49	4.18	2674.02	3.04	2679.75	2.66	2682.732	2.39427
w_2	10.31	4.07	11.09	4.83	13.70	4.71	20.34	6.13	21.67	4.60	30.47	3.71	33.00602	3.11702
A_2	39.23	13.47	38.40	14.50	48.83	15.26	74.45	23.80	90.07	19.16	152.07	19.86	179.7426	18.94752
x_{c3}	2740.58	0.95	2741.04	0.95	2741.77	0.91	2741.49	1.18	2741.50	0.96	2745.56	0.82	2746.321	0.70725
w_3	36.42	1.63	38.35	1.62	39.20	1.54	39.18	1.82	38.77	1.56	31.42	1.35	29.74382	1.18014
A_3	343.63	13.52	346.76	12.95	355.30	12.55	361.79	16.15	362.22	13.59	299.46	12.50	297.6894	11.7703
Red. c^2	9.503		7.421		5.963		6.217		5.914		4.869		4.142	
Adj. R^2	0.975		0.978		0.983		0.984		0.986		0.989		0.992	

S3. Normalized vSFG Spectra of MgO(100)/D_2O Interface for Acidic and Alkaline pH Series

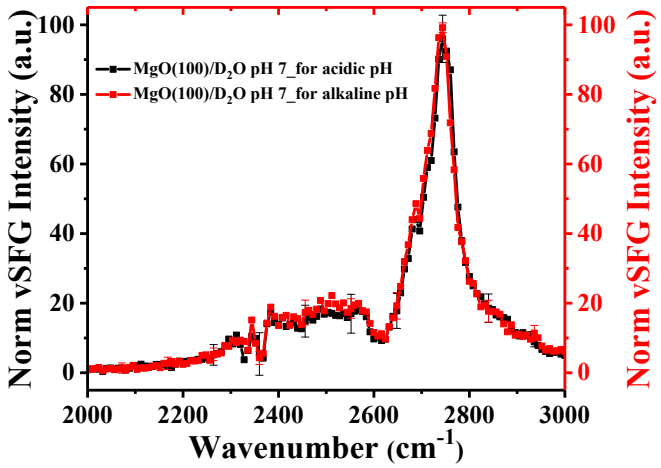

Figure S1: Normalized vSFG spectra of the MgO(100)/D_2O interfaces at pH 7 for acidic and alkaline pH experiment.

S4. Deconvolution of the Molecular Water Peak at the MgO(100)/D_2O Interface

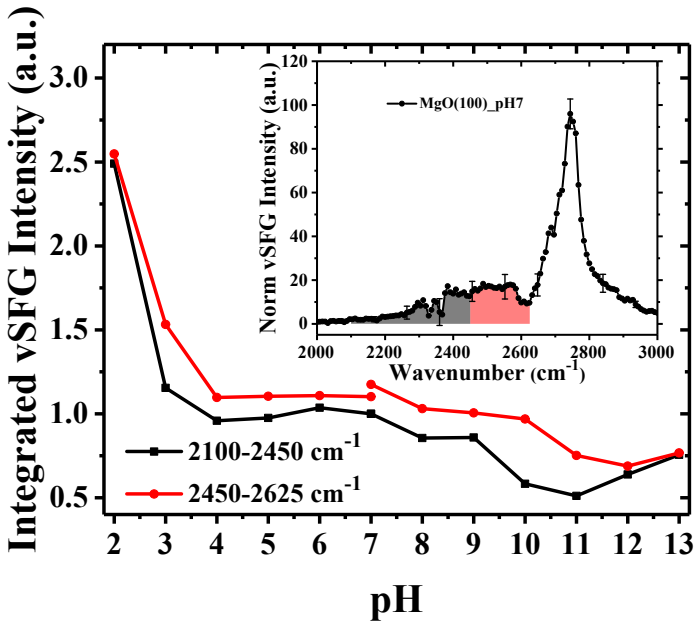

Figure S2: Variation of the integrated vSFG intensity of the strongly H-bonded OD group and weakly H-bonded OD group of the D_2O molecule at the MgO(100)/D_2O interface. The inset shows the strongly H-bonded and weakly H-bonded OD group region in the MgO(100)/D_2O spectra at pH 7.

S5. Variation of the Surface Charge Density as a Function of pH at the MgO/water Interface

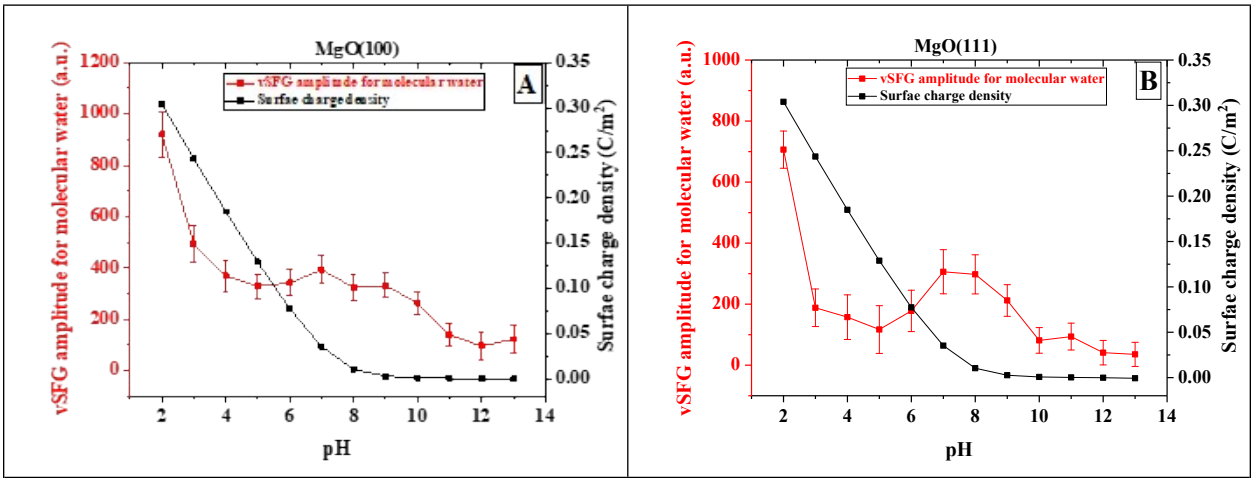

Figure S3: The variation of experimental vSFG amplitude for the molecular water peak and calculated surface charge density as a function of pH of water at the MgO(100) (A) and MgO(111) (B) surface.

S6. The vSFG spectra at the MgO(100)/D_2O Interface with and without Background Electrolytes

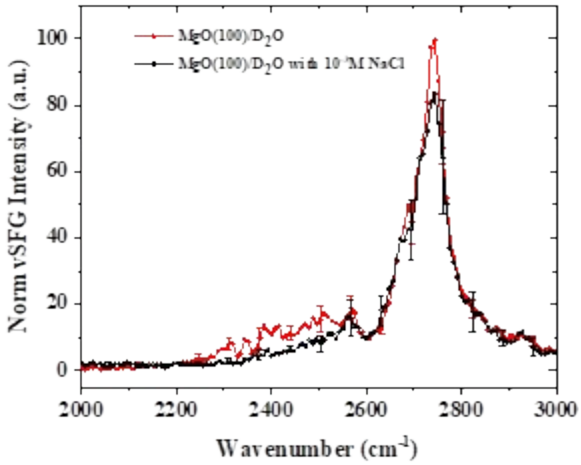

Figure S4: The comparison of the vSFG spectra of the MgO(100)/D_2O interface without any electrolytes (red spectra) and with 10^{-3}M NaCl as a background electrolyte (black spectra) at neutral pH. The addition of the NaCl reduced the vSFG intensity from the molecular water.

S7. Fitting Parameters for the MgO(111)/D_2O Interface vSFG Spectra

Table S4: Fitting parameters for the vSFG spectra at pH 7-2 of MgO(111)/D_2O interface

Parameters	pH7		pH6		pH5		pH4		pH3		pH2	
	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error
y_0	4.32	0.73	4.14	0.56	4.36	0.51	3.98	0.51	3.27	0.52	1.82	1.13
x_{c1}	2482.41	16.56	2496.35	16.88	2501.32	27.33	2489.86	21.00	2475.29	14.93	2447.81	4.70
w_1	87.92	32.36	74.21	31.32	65.00	48.99	76.73	39.33	78.54	28.15	112.43	10.02
A_1	242.95	82.77	178.08	67.80	117.02	78.26	157.41	73.13	188.19	61.53	706.53	60.99
x_{c2}	2691.11	6.18	2688.68	5.39	2693.61	6.60	2688.83	5.42	2686.28	6.88	2706.66	15.23
w_2	15.85	8.56	14.39	7.15	19.42	9.50	14.64	7.22	14.55	9.21	10.00	17.47
A_2	53.27	23.41	47.04	18.70	58.76	24.28	45.21	17.83	39.19	20.30	25.00	34.45
x_{c3}	2768.49	0.94	2768.69	0.95	2767.25	1.01	2767.96	0.97	2765.54	1.28	2761.68	1.88
w_3	24.06	1.49	25.39	1.51	22.42	1.61	24.16	1.52	30.93	2.14	21.51	3.04
A_3	221.15	11.22	212.38	10.32	180.97	10.76	188.17	9.65	217.95	12.69	164.68	19.11
Red. c^2	16.497		11.656		11.007		9.345		8.623		28.493	
Adj. R^2	0.933		0.935		0.924		0.928		0.919		0.863	

Table S5: Fitting parameters for the vSFG spectra at pH 7-13 of MgO(111)/D_2O interface

	pH7		pH8		pH9		pH10		pH11		pH12		pH13	
Parameters	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error	Value	Std. Error
y_0	4.02	0.77	3.26	0.63	2.90	0.44	1.96	0.28	2.71	0.33	2.78	0.25	2.94	0.24
x_{c1}	2475.21	11.69	2470.47	10.84	2482.15	11.42	2502.75	17.93	2472.09	16.64	2482.14	25.29	2496.35	27.00
w_1	91.27	23.12	94.26	21.65	81.59	21.77	50.98	30.42	52.55	28.39	34.07	39.75	30.82	41.65
A_1	306.28	72.24	297.88	64.03	212.19	51.76	81.40	41.95	93.88	44.01	41.28	40.05	35.56	39.56
x_{c2}	2689.97	6.14	2684.98	6.42	2690.13	4.95	2690.19	4.83	2691.72	3.58	2687.80	2.33	2687.18	2.12
w_2	14.38	8.20	8.68	7.60	16.43	6.88	20.15	6.97	22.07	5.18	17.34	3.21	19.63	3.01
A_2	48.69	22.16	26.03	16.36	49.14	16.59	54.40	15.85	75.34	14.97	64.27	9.54	77.53	9.66
x_{c3}	2767.56	0.93	2767.21	0.85	2767.05	0.71	2767.13	0.79	2766.10	0.72	2765.97	0.58	2763.99	0.56
w_3	23.68	1.46	22.35	1.27	19.88	1.06	23.21	1.26	19.61	1.11	18.39	0.85	15.97	0.80
A_3	218.98	11.03	189.44	8.65	162.67	6.98	162.15	7.27	151.16	7.00	140.36	5.12	123.30	4.81
Red. c^2	17.333		11.545		6.690		3.735		4.952		3.531		3.569	
Adj. R^2	0.930		0.930		0.949		0.954		0.954		0.964		0.962	

S8. Deconvolution of the Molecular Water Peak at the MgO(100)/D_2O Interface

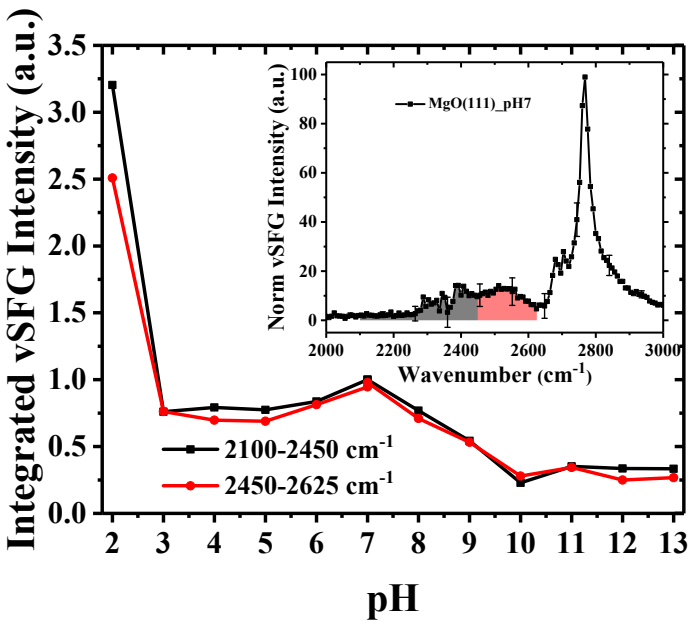

Figure S5: Variation of the integrated vSFG intensity of the strongly H-bonded OD group and weakly H-bonded OD group of the D_2O molecule at the MgO(100)/D_2O interface. The inset shows the strongly H-bonded and weakly H-bonded OD group region in the MgO(100)/D_2O spectra at pH 7.