Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

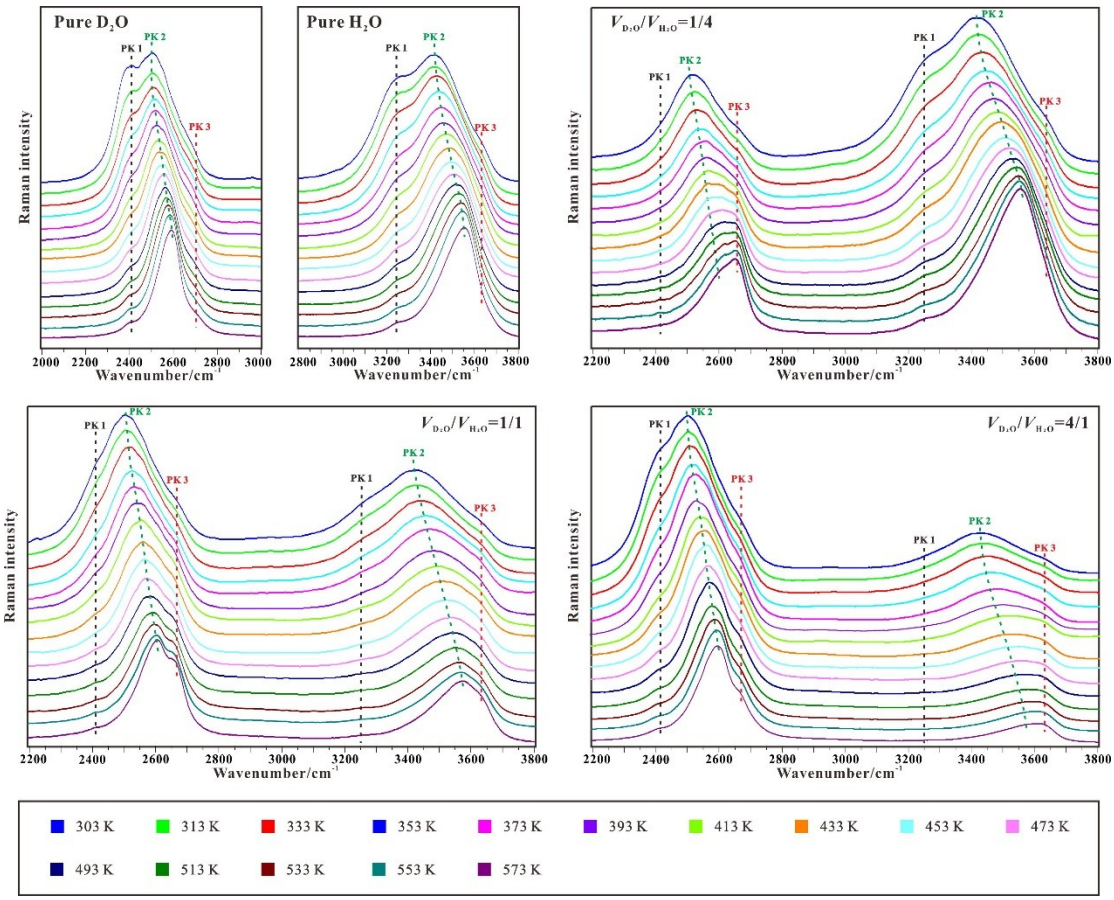

Fig. S1 OD/OH stretch bands of isotopic substitution water at temperatures from 303 to 573 K. The three peaks are denoted as “PK 1”, “PK 2” and ““PK 3”.

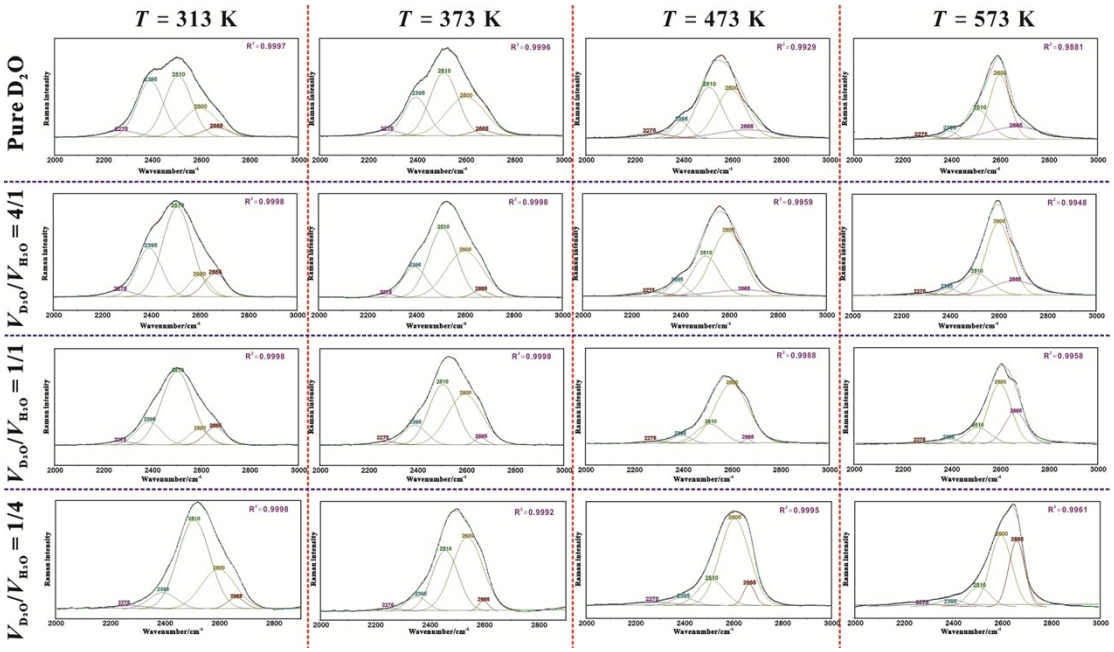

Fig. S2 Gaussian fitting of OD stretch bands for isotopic substitution water. The square dotted line represents the smoothed line of the raw spectral data, and the superposed contour is the fitted line by the five Gaussian components.

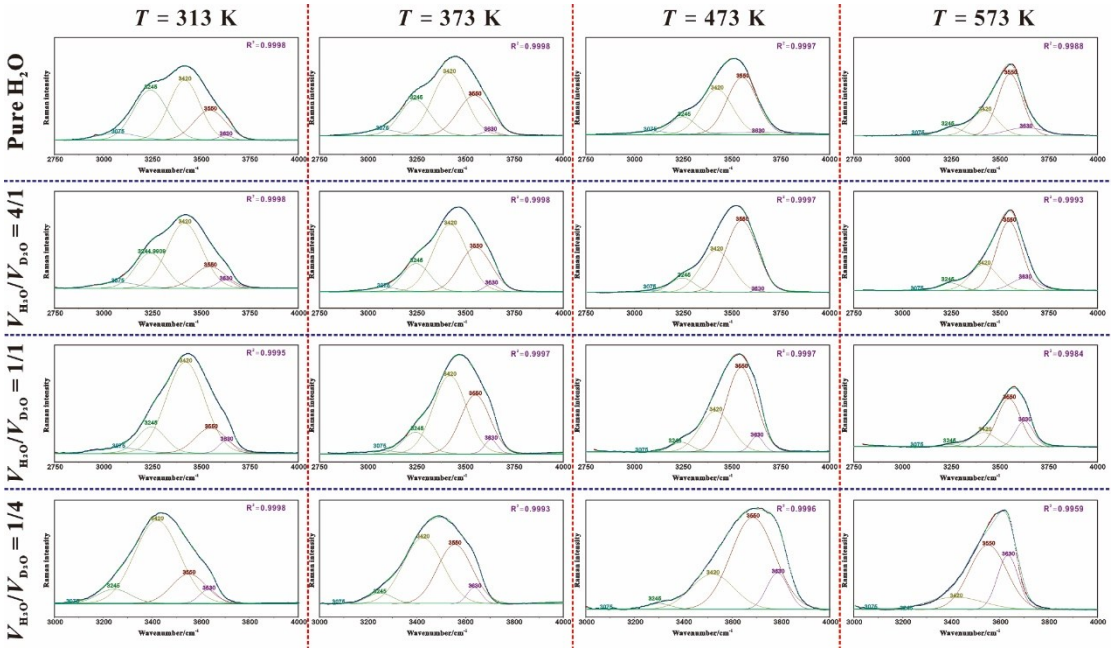

Fig. S3 Gaussian fitting of OH stretch bands for isotopic substitution water. The square dotted line represents the smoothed line of the raw spectral data, and the superposed contour is the fitted line by the five Gaussian components.

Table S1. The estimated relative amounts of hydrogen bonding configurations: two kinds of tetrahedral (FHW_1, FHW_2), single donor (SD) HB configuration, single hydrogen-bonded water (SHW), and free water (FW). Average number of H···O–H/D···O–D bonds ($n_{HBs,HOH}$/$n_{HBs,DOD}$) and average number of hydrogen bonds (n_{HBs}) in isotopic substitution water are listed.

$V_{D2O/VH2O}$	T	D2O						H2O					
	(K)	FHW1	FHW2	SD	SHW	FW	$n_{HBs,DOD}$	FHW1	FHW2	SD	SHW	FW	$n_{HBs,HOH}$
1/0 (left) 0/1 (right)	**303**	3.9	40	32	23	1.3	2.6	4.9	35	39	19	2.6	2.5
	313	3.9	35	38	18	5.8	2.5	4.6	33	40	20	3.1	2.5
	333	3.8	31	40	19	6.2	2.4	4.5	30	41	21	3.4	2.4
	353	3.8	27	42	22	5.8	2.3	4.2	27	42	24	3.5	2.3
	373	3.7	25	42	26	3.8	2.3	3.9	24	42	27	3.1	2.2
	393	3.7	23	42	31	1.5	2.2	3.6	22	42	31	2.3	2.2
	413	3.6	20	41	34	1.6	2.1	3.3	20	41	35	1.3	2.1
	433	3.7	18	41	34	3.2	2.0	3.1	18	40	40	0.3	2.0
	453	3.6	15	41	36	5.0	1.9	2.9	16	38	42	0.9	1.9
	473	3.5	13	40	38	6.3	1.8	2.7	14	36	46	1.5	1.8
	493	3.3	11	37	41	7.3	1.7	2.4	13	34	49	1.9	1.8
	513	3.1	9.8	35	44	8.0	1.7	2.0	11	32	53	2.6	1.7
	533	2.9	8.6	32	48	8.8	1.6	1.7	9.9	29	55	3.6	1.6
	553	2.7	7.7	29	52	9.5	1.5	1.5	9.0	26	58	5.3	1.5
	573	2.4	6.8	25	56	10	1.4	1.2	8.1	24	59	7.7	1.4
1/4	**303**	1.9	10	59	21	7.7	2.3	4.5	28	48	14	6.0	2.4
	313	2.1	10	56	25	7.0	2.2	4.3	26	48	16	6.0	2.3
	333	2.2	10	48	35	4.8	2.1	3.9	23	47	20	5.7	2.2
	353	1.7	9.3	43	40	6.1	2.1	3.4	21	46	25	5.2	2.1
	373	1.7	9.0	38	46	6.2	2.0	3.0	19	44	29	4.9	2.0
	393	1.8	8.1	32	51	7.0	2.0	2.8	17	42	34	4.1	2.0
	413	1.6	7.6	27	56	8.6	1.9	2.3	15	40	40	3.6	1.9
	433	1.7	7.0	21	59	11	1.9	2.3	14	38	44	2.9	1.8
	453	2.2	6.1	16	63	13	1.8	1.9	12	35	49	2.4	1.7
	473	2.0	5.1	17	56	20	1.7	1.7	11	32	54	1.7	1.7
	493	2.1	5.0	14	54	25	1.6	1.2	9.7	28	59	1.5	1.6
	513	1.5	4.1	14	50	31	1.5	1.0	8.5	27	59	5.1	1.5
	533	1.5	4.4	11	48	35	1.4	0.7	7.6	25	59	8.2	1.4
	553	1.7	4.4	12	44	37	1.3	0.7	7.1	24	59	9.5	1.4
	573	1.5	4.2	12	43	40	1.3	0.4	6.6	23	60	11	1.3
1/1	**303**	3.2	18	58	8.1	13	2.1	4.3	17	59	12	8.0	2.1
	313	2.7	17	55	12	13	2.0	3.5	16	57	16	7.8	2.1
	333	2.7	16	52	18	11	2.0	3.0	15	52	23	7.5	2.0
	353	2.4	14	48	28	7.0	1.9	2.1	13	49	28	8.1	1.9
	373	2.5	14	43	36	5.1	1.9	1.6	12	45	34	7.9	1.8
	393	2.8	13	38	42	4.3	1.8	1.5	11	41	39	7.4	1.7
	413	2.3	11.5	34	48	4.1	1.7	1.1	10	37	44	7.6	1.6

	433	2.3	10.6	30	53	4.3	1.6	0.6	8.0	34	49	8.5	1.5
	453	2.1	9.3	26	58	4.8	1.6	0.1	7.3	31	53	9.3	1.4
	473	2.4	8.5	21	63	5.2	1.5	0.4	6.4	27	56	10	1.4
	493	1.9	7.6	16	68	6.4	1.4	0.4	5.8	26	55	13	1.3
	513	1.9	6.4	10	74	7.8	1.3	0.7	4.5	24	53	19	1.2
	533	2.1	5.1	11	70	11	1.2	1.7	3.3	19	57	20	1.1
	553	1.2	4.6	15	57	22	1.1	0.3	3.9	19	53	24	1.1
	573	1.0	4.4	14	53	28	1.0	0.8	2.9	16	52	28	1.0
	303	3.5	29	46	11	12	1.9	1.6	10	61	16	11	1.9
	313	3.4	26	48	11	12	1.9	0.5	10	59	21	9.8	1.8
	333	3.1	22	49	13	13	1.8	1.3	8.9	53	27	9.6	1.7
	353	3.0	21	47	21	7.7	1.7	0.8	7.8	48	33	9.9	1.6
	373	2.4	19	44	30	4.7	1.6	0.2	7.1	43	39	11	1.5
	393	2.6	18	41	36	2.7	1.5	0.0	5.5	37	46	12	1.4
	413	3.0	16	39	41	1.7	1.5	2.8	2.1	32	51	13	1.3
	433	2.8	14	37	45	1.8	1.4	0.5	4.9	28	51	15	1.3
	453	2.8	12	34	48	2.4	1.3	1.1	1.5	26	54	18	1.2
	473	3.1	11	31	50	4.6	1.2	0.5	3.5	21	54	21	1.1
	493	2.6	9.5	28	55	5.1	1.1	0.9	2.6	19	53	25	1.0
	513	2.5	8.3	25	58	6.2	1.0	0.9	2.5	17	51	29	1.0
	533	2.3	7.1	21	62	7.7	0.9	0.7	2.1	15	49	33	0.9
	553	2.0	6.1	19	63	10	0.9	1.0	0.0	10	51	38	0.8
	573	1.8	5.7	18	62	12	0.9	0.9	0.0	9.4	49	41	0.7
4/1	**303**	3.5	28	46	11	12	1.9	1.6	10	61	16	11	1.9
	313	3.4	26	48	11	12	1.9	0.5	10	59	21	9.8	1.8
	333	3.1	22	49	13	13	1.8	1.3	8.9	53	27	9.6	1.7
	353	3.0	21	47	21	7.7	1.7	0.8	7.8	48	33	9.9	1.6
	373	2.4	19	44	30	4.7	1.6	0.2	7.1	43	39	11	1.5
	393	2.6	18	41	36	2.7	1.5	0.0	5.5	37	46	12	1.4
	413	3.0	16	39	41	1.7	1.5	2.8	2.1	32	51	13	1.3
	433	2.8	14	37	45	1.8	1.4	0.5	4.9	28	51	15	1.3
	453	2.8	12	34	48	2.4	1.3	1.1	1.5	26	54	18	1.2
	473	3.1	11	31	50	4.6	1.2	0.5	3.5	21	54	21	1.1
	493	2.6	9.5	29	55	5.1	1.1	0.9	2.6	19	53	25	1.0
	513	2.5	8.3	25	58	6.2	1.0	0.9	2.5	17	51	29	1.0
	533	2.3	7.1	21	62	7.7	0.9	0.7	2.1	15	49	33	0.9
	553	2.0	6.1	19	63	10	0.9	1.0	0.0	10	51	38	0.8
	573	1.8	5.7	18	62	12	0.9	0.9	0.0	9.4	49	41	0.7