

A combined Raman- and FTIR-spectroscopic study of
mixed methanol-water and ethanol-water clusters

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Supplementary Information

Table S1: Experimental FTIR-jet conditions for the mixed methanol-water and for the mixed ethanol-water system. θ denotes the saturator temperature. Also given are the opening times of the mixing valves.

	methanol-water	ethanol-water
$\theta(\text{alcohol})/^\circ\text{C}$	-15	-10
$\text{time}_{\text{open}}(\text{alcohol})/ \text{s}$	0.1	0.4
$\text{time}_{\text{closed}}(\text{alcohol})/ \text{s}$	4.08	2.4
$\theta(\text{water})/^\circ\text{C}$	+5	+5
$\text{time}_{\text{open}}(\text{water})/ \text{s}$	0.92	1.04
$\text{time}_{\text{closed}}(\text{water})/ \text{s}$	1.88	1.8
$\text{time}_{\text{open}}(\text{helium})/ \text{s}$	3.32	2.72
$\text{time}_{\text{closed}}(\text{helium})/ \text{s}$	0.1	0.1

Table S2: Experimental Raman-jet conditions for the mixed methanol-water system.

	overview	dimer region	trimer region			
Roots pumps	$500 \text{ m}^3 \cdot \text{h}^{-1}$	$500 \text{ m}^3 \cdot \text{h}^{-1}$	$500 \text{ m}^3 \cdot \text{h}^{-1}$			
Roots pumps	$250 \text{ m}^3 \cdot \text{h}^{-1}$	$250 \text{ m}^3 \cdot \text{h}^{-1}$	$250 \text{ m}^3 \cdot \text{h}^{-1}$			
Rotary vane pumps	$100 \text{ m}^3 \cdot \text{h}^{-1}$	$100 \text{ m}^3 \cdot \text{h}^{-1}$	$100 \text{ m}^3 \cdot \text{h}^{-1}$			
Dimension of vacuum chamber/ cm^3	60 x 60 x 40 (square footprint)	60 x 60 x 40 (square footprint)	60 x 60 x 40 (square footprint)			
Nozzle distance/ mm	1	3	3			
Objective	Nikon Nikkor ($\varnothing=50 \text{ mm}$, f/1.2)	Nikon Nikkor ($\varnothing=50 \text{ mm}$, f/1.2)	Nikon Nikkor ($\varnothing=50 \text{ mm}$, f/1.2)			
Monochromator slit width/ μm	75	75	75			
Focussing lens	Linos ARB2 ($\varnothing=22.4 \text{ mm}$, f/7)	Linos ARB2 ($\varnothing=22.4 \text{ mm}$, f/7)	Linos ARB2 ($\varnothing=22.4 \text{ mm}$, f/7)			
Monochromator	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)			
			1:0	3:1	1:1	0:1
$\theta(\text{methanol})/^\circ\text{C}$	-25	-28	-28	-25	-28	-
$\text{time}_{\text{open}}(\text{methanol})/ \text{s}$		0.48			2	
$\text{time}_{\text{closed}}(\text{methanol})/ \text{s}$		1.76			3	
$\theta(\text{water})/^\circ\text{C}$	+1	+9.5	-	+1	+7.5	+3
$\text{time}_{\text{open}}(\text{water})/ \text{s}$		2.28			5	
$\text{time}_{\text{closed}}(\text{water})/ \text{s}$		0.1			0.1	
Number of scans	6	6	6	6	6	6
Scan duration/ s	200	300	300	300	300	300

Table S3: Experimental Raman-jet conditions for the mixed deuterated methanol-deuterium oxide system.

Roots pumps	500 m ³ ·h ⁻¹			
Roots pumps	250 m ³ ·h ⁻¹			
Rotary vane pumps	100 m ³ ·h ⁻¹			
Dimension of vacuum chamber/ cm ³	60 x 60 x 40 (square footprint)			
Nozzle distance/ mm	3			
Objective	Nikon Nikkor (\varnothing =50 mm, f/1.2)			
Monochromator slit width/ μ m	75			
Focussing lens	Linos ARB2 (\varnothing =22.4 mm, f/7)			
Monochromator	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)			
	1:0	3:1	1:1	0:1
θ (deuterated methanol)/ °C	-28	-28	-25	-
time _{open} (deuterated methanol)/ s		1.0		
time _{closed} (deuterated methanol)/ s		1.5		
θ (deuterium oxide)/ °C	-	+7.5	+1	+1
time _{open} (deuterium oxide)/ s		2.5		
time _{closed} (deuterium oxide)/ s		0.1		
Number of scans	6			
Scan duration/ s	300			

Table S4: Experimental Raman-jet conditions for the mixed ethanol-water system.

	overview	dimer region	trimer region					
Roots pumps	250 m ³ ·h ⁻¹	250 m ³ ·h ⁻¹	250 m ³ ·h ⁻¹					
Rotary vane pumps	100 m ³ ·h ⁻¹	100 m ³ ·h ⁻¹	100 m ³ ·h ⁻¹					
Dimension of vacuum chamber/ cm ³	22 x 14 x 14 (cylindrical)	60 x 60 x 40 (square footprint)	60 x 60 x 40 (square footprint)					
Nozzle distance/ mm	1	3	2					
Objective	Edmund Optics E32-886 ($\varnothing=50$ mm, f/3)	Nikon Nikkor ($\varnothing=50$ mm, f/1.2)	Nikon Nikkor ($\varnothing=50$ mm, f/1.2)					
Monochromator slit width/ μ m	75	75	100					
Focussing lens	Edmund Optics L45-354 ($\varnothing=50$ mm, f/7)	Edmund Optics L45-354 ($\varnothing=50$ mm, f/7)	Newport PAC087AR.14 ($\varnothing=51$ mm, f/4)					
Monochromator	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)	McPherson 205f (f=500 mm, f/3.2, 1800 gr/mm grating)					
			1:0	5:1	2:1	1:1	1:3	0:1
$\theta(\text{ethanol})/ ^\circ\text{C}$	-8	-8	-10	-8	-10	-21	-24	-
$\theta(\text{water})/ ^\circ\text{C}$	+9	+9	-	-4	+2	+6	+7	+3
Number of scans	5	6	6	6	6	12	12	6
Scan duration/ s	600	600	600	600	600	300	300	600

Table S5: Experimental Raman-jet conditions for the mixed deuterated ethanol-deuterium oxide system.

Roots pumps	500 m ³ ·h ⁻¹
Roots pumps	250 m ³ ·h ⁻¹
Rotary vane pumps	100 m ³ ·h ⁻¹
Dimension of vacuum chamber/ cm ³	60 x 60 x 40 (square footprint)
Nozzle distance/ mm	2
Objective	Nikon Nikkor ($\varnothing=50$ mm, f/1.2)
Monochromator slit width/ μm	75
Focussing lens	Linos ARB2 ($\varnothing=22.4$ mm, f/7)
Monochromator	McPherson 2051 (f=1000 mm, f/8.7, 1200 gr/mm grating)
$\theta(\text{deuterated ethanol})/ \text{ }^\circ\text{C}$	-8
$\theta(\text{deuterium oxide})/ \text{ }^\circ\text{C}$	+9
Number of scans	4
Scan duration/ s	300

Table S6: Differences between the experimental $\tilde{\nu}_{\text{ww}}(\text{exp})$ and the calculated harmonic wavenumber $\omega_{\text{ww}}(\text{th})$ in cm^{-1} for the water and the deuterated water dimer on different levels. For the larger basis sets, the difference approaches twice the expected OH oscillator anharmonic constant, as it should.

$\tilde{\nu}_{\text{ww}}(\text{exp})-\omega_{\text{ww}}(\text{th})$	B3-S	MP2-S	MP2-M	MP2-L
$(\text{H}_2\text{O})_2$	-48	-152	-138	-161
$(\text{D}_2\text{O})_2$	-5	-76	-71	-88

Table S7: Shifted MP2-S/MP2-M average of predicted Raman and IR wavenumbers $\tilde{\nu}$ in cm^{-1} as well as relative Raman and IR intensities (σ_{rel} in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and I_{rel} in $\text{km}\cdot\text{mol}^{-1}$, respectively) for pure and mixed dimers and trimers in the methanol-water system. A methanol mole fraction of $x_{\text{m}}=0.75$ for the Raman and of $x_{\text{m}}=0.50$ for the IR case is assumed. For the scaling procedure, see Section 2.4.

Cluster	Raman		IR	
	$\tilde{\nu}$	σ_{rel}	$\tilde{\nu}$	I_{rel}
ww	3602	9	3602	66
wm	3563	28	3563	82
mw	3615	25	3615	94
mm	3577	79	3577	110
www	3478	2	3529	15
			3540	13
mww	3445	16	3445	18
			3519	39
			3543	42
mmw	3436	49	3436	17
			3505	49
			3539	50
mmm	3438	56	3492	22
			3513	20

Table S8: Shifted MP2-S/MP2-M average of predicted Raman wavenumbers $\tilde{\nu}$ in cm^{-1} as well as relative intensities σ_{rel} in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ for pure and mixed dimers and trimers in the deuterated methanol-deuterium oxide system. A deuterated methanol mole fraction of $x_{\text{m}}=0.75$ is assumed. For the scaling procedure, see Section 2.4.

Cluster	$\tilde{\nu}$	σ_{rel}
ww	2632	6
wm	2607	24
mw	2663	27
mm	2637	72
www	2549	2
mww	2529	15
mmw	2524	41
mmm	2539	50

Table S9: Shifted MP2-S/MP2-M average of predicted Raman and IR wavenumbers $\tilde{\nu}$ in cm^{-1} as well as relative Raman and IR intensities (σ_{rel} in $10^{-36} \cdot \text{m}^2 \cdot \text{sr}^{-1}$ and I_{rel} in $\text{km} \cdot \text{mol}^{-1}$, respectively) for pure and mixed dimers and trimers in the ethanol-water system. An ethanol mole fraction of $x_e=0.50$ for the Raman and of $x_e=0.67$ for the IR case is assumed. For the scaling procedure, see Section 2.4.

Cluster	Raman		IR	
	$\tilde{\nu}$	σ_{rel}	$\tilde{\nu}$	I_{rel}
ww	3602	36	3602	29
we _{g+}	3544	36	3544	70
we _t	3551	34	3551	72
we _{g-}	3557	42	3557	82
e _t w	3601	45	3601	89
e _g w	3599	33	3599	73
e _{g+} e _{g+}	3542	32	3542	169
www	3478	8	3529	4
			3540	4
eww	3428	22	3428	15
			3516	21
			3530	24
eew	3417	27	3417	10
			3473	75
			3524	54
eee	3413	11	3469	56
			3478	57

Table S10: Electronic energies without (E_e) and with zero point energy correction (E_0) in E_h for water, deuterium oxide, methanol, deuterated methanol, and ethanol monomers. Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4 \cdot \text{u}^{-1}$, scattering cross sections (σ) in $10^{-36} \cdot \text{m}^2 \cdot \text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km} \cdot \text{mol}^{-1}$ of the symmetric (*sym*) and asymmetric (*asym*) OH-stretching vibration on different levels are listed.

conformer	E_e	E_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S						
w_{sym}	-76.443809	-76.422595	3763	87	86	0
w_{asym}			3881	43	43	32
$w_{\text{deut,sym}}$		-76.428368	2709	45	76	1
$w_{\text{deut,asym}}$			2847	23	36	21
m	-115.753876	-115.702703	3789	80	79	13
m_{deut}		-115.705938	2759	46	75	11
e_t	-155.081600	-155.001820	3787	117	114	11
e_g	-155.081326	-155.001474	3772	76	75	9
MP2-S						
w_{sym}	-76.244710	-76.223080	3827	83	79	3
w_{asym}			3971	37	33	50
$w_{\text{deut,sym}}$		-76.228965	2755	43	70	3
$w_{\text{deut,asym}}$			2913	20	30	31
m	-115.407363	-115.355145	3850	70	66	22
m_{deut}		-115.358426	2803	39	62	17
e_t	-154.592998	-154.511924	3833	99	95	20
e_g	-154.592769	-154.511308	3824	66	63	16
MP2-M						
w_{sym}	-76.2900916	-76.268685	3833	82	79	12
w_{asym}			3960	33	30	72
$w_{\text{deut,sym}}$		-76.274512	2763	43	70	8
$w_{\text{deut,asym}}$			2901	17	26	43
m	-115.469427	-115.417405	3864	66	62	40
m_{deut}		-115.420687	2813	38	60	28
e_t	-154.676546	-154.595686	3851	95	91	38
e_g	-154.676137	-154.595188	3839	64	62	30
MP2-L						
w_{sym}	-76.3184531	-76.296870	3861	84	79	10
w_{asym}			3989	26	23	76
$w_{\text{deut,sym}}$		-76.302746	2783	44	71	7
$w_{\text{deut,asym}}$			2923	14	21	45
m	-115.5139438	-115.461857	3899	65	60	41
m_{deut}		-115.465151	2839	37	59	28
e_t	-154.7373550	-154.656377	3884	64	88	39
e_g	-154.7370287	-154.656022	3874	65	60	32

Table S11: Dissociation energies without (D_e) and with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for pure and mixed methanol-water dimers. Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the donor (D) and acceptor (A) symmetric (*sym*) and asymmetric (*asym*) OH-stretching vibration on different levels are listed. The S basis set does not predict the correct order.

conformer	D_e	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S							
ww	30.97	19.93	D _{<i>sym</i>}	3650	163	170	301
			A _{<i>sym</i>}	3779	82	81	6
			D _{<i>asym</i>}	3849	57	54	64
			A _{<i>asym</i>}	3889	36	34	60
wm	29.64	20.43	D _{<i>sym</i>}	3624	183	194	376
			A	3801	70	68	26
			D _{<i>asym</i>}	3846	58	55	65
mw	29.70	21.39	D	3669	167	173	374
			A _{<i>sym</i>}	3780	88	86	4
			A _{<i>asym</i>}	3890	38	36	61
mm	28.00	21.71	D	3643	190	199	451
			A	3803	71	69	26
MP2-S							
ww	32.71	21.69	D _{<i>sym</i>}	3754	141	141	238
			A _{<i>sym</i>}	3835	78	74	6
			D _{<i>asym</i>}	3939	47	43	105
			A _{<i>asym</i>}	3969	32	29	80
wm	32.73	23.38	D _{<i>sym</i>}	3722	151	153	304
			A	3855	64	61	35
			D _{<i>asym</i>}	3932	48	44	103
mw	33.00	24.41	D	3765	130	129	345
			A _{<i>sym</i>}	3835	84	80	3
			A _{<i>asym</i>}	3970	33	30	81
mm	32.97	26.35	D	3732	139	140	404
			A	3856	68	65	34

Table S11: continuation

conformer	D_e	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-M							
ww	24.39	15.06	D_{sym}	3740	149	149	287
			A_{sym}	3824	66	63	17
			D_{asym}	3927	44	41	113
			A_{asym}	3944	28	26	98
wm	26.48	18.14	D_{sym}	3695	146	149	351
			A	3852	58	55	53
			D_{asym}	3920	46	43	110
mw	24.56	17.33	D	3754	142	142	404
			A_{sym}	3823	69	67	9
			A_{asym}	3944	29	27	99
mm	26.80	21.20	D	3711	140	142	477
			A	3854	63	60	50
MP2-L							
ww	22.24	13.09	D_{sym}	3763	148	147	297
			A_{sym}	3849	65	62	15
			D_{asym}	3957	39	36	120
			A_{asym}	3973	23	21	99
wm	25.37	17.26	D_{sym}	3721	145	147	374
			A	3887	57	53	54
			D_{asym}	3952	43	39	116
mw	22.44	15.54	D	3778	144	142	424
			A_{sym}	3848	68	65	9
			A_{asym}	3973	24	22	99
mm	25.82	20.32	D	3735	141	142	503
			A	3888	61	57	52

Table S12: Dissociation energies with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for pure and mixed deuterated methanol-deuterium oxide dimers. Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the donor (D) and acceptor (A) symmetric (*sym*) and asymmetric (*asym*) OD-stretching vibration on different levels are listed. The S basis set does not predict the correct order.

conformer	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S						
ww	22.69	D _{sym}	2637	86	150	143
		A _{sym}	2721	43	72	5
		D _{asym}	2814	28	45	59
		A _{asym}	2853	19	29	36
wm	22.41	D _{sym}	2621	92	164	183
		A	2768	39	64	19
		D _{asym}	2810	29	46	63
mw	23.23	D	2671	97	167	216
		A _{sym}	2721	44	74	3
		A _{asym}	2854	20	31	36
mm	22.75	D	2653	103	179	262
		A	2769	40	66	19
MP2-S						
ww	24.42	D _{sym}	2708	73	123	112
		A _{sym}	2761	41	68	6
		D _{asym}	2884	24	37	80
		A _{asym}	2912	17	25	48
wm	25.45	D _{sym}	2687	76	130	144
		A	2807	36	58	24
		D _{asym}	2877	37	24	84
mw	26.34	D	2741	81	134	201
		A _{sym}	2761	37	60	1
		A _{asym}	2913	17	26	48
mm	27.52	D	2718	76	127	233
		A	2808	38	61	23

Table S12: continuation

conformer	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-M						
ww	17.37	D_{sym}	2703	79	134	136
		A_{sym}	2756	34	56	12
		D_{asym}	2871	22	34	85
		A_{asym}	2890	15	22	57
wm	19.97	D_{sym}	2673	75	128	167
		A	2804	33	53	34
		D_{asym}	2864	22	34	87
mw	18.94	D	2733	92	153	231
		A_{sym}	2757	25	42	5
		A_{asym}	2890	15	23	57
mm	22.14	D	2703	76	129	270
		A	2806	36	57	33
MP2-L						
ww	15.36	D_{sym}	2720	79	133	140
		A_{sym}	2774	33	54	11
		D_{asym}	2893	19	29	89
		A_{asym}	2911	12	18	57
wm	19.06	D_{sym}	2692	74	127	178
		A	2830	33	52	35
		D_{asym}	2887	20	31	91
mw	17.08	D	2750	241	396	241
		A_{sym}	2775	24	40	6
		A_{asym}	2911	13	19	56
mm	21.26	D	2721	77	130	286
		A	2831	35	55	33

Table S13: Dissociation energies without (D_e) and with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for pure and mixed methanol-water trimers. Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the OH-stretching vibration on different levels are listed. The S basis set does not predict the correct order.

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S						
$w_d w_d w_u$	90.41	63.54	3503	257	288	29
			3554	38	42	556
			3571	42	45	488
			3859	70	66	54
			3864	65	61	61
$m_u w_d w_d$	87.69	64.43	3494	256	288	171
			3557	78	85	513
			3579	42	46	525
			3864	75	71	61
			3866	81	76	53
$m_d w_d w_u$	87.96	64.57	3493	265	298	131
			3547	52	56	568
			3583	59	64	516
			3857	74	70	59
			3864	72	68	55
$m_d m_d w_u$	84.86	64.84	3501	265	297	144
			3561	96	104	530
			3575	59	64	666
			3858	81	76	58
			3864	72	68	55
$m_d m_u w_d$	84.56	65.02	3510	311	347	26
			3552	58	64	747
			3576	57	61	572
			3863	77	73	58
			3864	72	68	55
$m_d m_d m_u$	81.56	65.37	3515	312	347	43
			3560	83	90	733
			3570	73	79	704

Table S13: continuation

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-S						
$w_d w_d w_u$	93.90	67.82	3636	249	262	20
			3680	27	28	433
			3692	30	30	377
			3935	65	59	67
			3939	50	45	96
$m_u w_d w_d$	93.33	70.09	3613	226	240	157
			3672	73	75	412
			3692	28	28	409
			3933	63	58	84
			3939	66	60	93
$m_d w_d w_u$	93.43	70.42	3608	225	240	171
			3669	65	67	385
			3694	34	35	424
			3929	61	56	87
			3941	60	55	93
$m_d m_d w_u$	92.68	72.75	3604	206	220	208
			3677	99	102	344
			3690	38	38	545
			3927	65	59	86
			3941	60	55	93
$m_d m_u w_d$	91.96	72.66	3612	257	273	89
			3652	55	57	594
			3686	41	42	461
			3935	68	62	89
			3941	60	55	93
$m_d m_d m_u$	91.09	75.08	3606	229	244	150
			3650	72	75	626
			3683	68	70	500

Table S13: continuation

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-M						
$w_d w_d w_u$	73.78	50.18	3609	258	275	15
			3667	29	30	499
			3678	29	30	450
			3911	46	43	117
			3915	44	41	131
$m_u w_d w_d$	75.04	54.57	3916	67	62	70
			3568	219	238	235
			3655	84	87	429
			3683	28	29	484
			3911	57	53	110
$m_d w_d w_u$	75.04	54.33	3915	64	59	101
			3569	228	247	205
			3648	65	68	462
			3683	38	39	492
			3907	54	50	113
$m_d m_d w_u$	76.18	58.76	3915	57	53	99
			3558	239	261	147
			3624	68	72	702
			3677	47	49	516
			3909	61	57	104
$m_d m_u w_d$	75.73	58.59	3567	264	287	90
			3622	49	52	757
			3673	45	47	519
			3912	64	59	101
			3559	266	290	24
$m_d m_d m_u$	77.06	63.03	3623	59	62	773
			3632	52	55	779

Table S13: continuation

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-L						
$w_d w_d w_u$	69.08	46.16	3621	254	269	11
			3685	28	29	518
			3694	28	28	475
			3939	44	40	120
			3943	36	33	140
$m_u w_d w_d$	71.74	51.64	3944	70	64	71
			3584	220	237	213
			3671	76	79	470
			3701	30	30	521
			3941	50	45	121
$m_d w_d w_u$	71.70	51.39	3943	66	60	98
			3585	229	246	183
			3665	59	61	504
			3702	38	39	526
			3937	50	46	119
$m_d m_d w_u$	74.36	56.96	3943	56	51	101
			3574	242	262	122
			3640	60	63	771
			3697	47	48	541
			3940	59	53	108
$m_d m_u w_d$	74.08	56.83	3582	260	281	78
			3641	47	49	796
			3691	45	46	557
			3941	60	55	104
			3573	265	287	16
$m_d m_d m_u$	76.77	62.37	3641	56	58	853
			3650	51	54	787

Table S14: Dissociation energies with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for pure and mixed deuterated methanol-deuterium oxide trimers. Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the OD-stretching vibration on different levels are listed. The B3-S level does not predict the correct order.

conformer	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S					
$w_d w_d w_u$	70.00	2541	146	271	13
		2576	20	36	275
		2586	21	38	243
		2816	31	49	51
		2822	31	50	55
$m_u w_d w_d$	69.50	2535	132	246	101
		2579	45	81	243
		2602	28	51	292
		2819	36	57	57
		2821	37	58	50
$m_d w_d w_u$	69.71	2534	139	258	78
		2570	29	52	286
		2609	38	67	274
		2814	34	54	57
		2821	34	54	50
$m_d m_d w_u$	68.76	2541	127	236	114
		2593	69	125	244
		2604	30	54	381
		2815	38	60	56
$m_d m_u w_d$	68.82	2552	157	290	24
		2581	41	74	401
		2604	31	56	321
		2819	37	59	55
$m_d m_d m_u$	67.92	2564	164	300	43
		2594	49	89	396
		2601	37	66	415

Table S14: continuation

conformer	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-S					
$w_d w_d w_u$	74.02	2631	142	250	8
		2661	13	22	208
		2668	14	25	182
		2876	29	45	52
		2879	22	34	68
		2881	26	40	96
$m_u w_d w_d$	75.49	2618	116	206	91
		2661	44	76	176
		2683	19	32	236
		2874	29	44	73
		2880	31	47	77
$m_d w_d w_u$	75.28	2613	117	208	95
		2655	35	61	187
		2688	25	43	221
		2869	28	44	75
		2881	27	42	76
$m_d m_d w_u$	76.70	2611	100	178	127
		2677	65	111	161
		2688	19	33	311
		2868	30	47	75
$m_d m_u w_d$	76.50	2627	140	248	21
		2652	25	44	354
		2684	24	42	253
		2876	32	50	76
$m_d m_d m_u$	77.74	2630	122	215	95
		2660	38	67	352
		2683	37	64	287

Table S14: continuation

conformer	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-M					
$w_d w_d w_u$	55.87	2614	145	259	7
		2654	14	25	245
		2661	14	25	217
		2856	22	34	89
		2860	24	37	99
		2861	27	42	57
$m_u w_d w_d$	59.06	2588	115	207	124
		2650	47	82	205
		2678	19	33	260
		2853	28	43	88
		2859	29	45	80
$m_d w_d w_u$	58.92	2589	120	216	107
		2643	35	62	229
		2681	25	43	256
		2851	26	40	91
		2859	26	40	77
$m_d m_d w_u$	62.18	2584	118	213	97
		2637	47	82	355
		2678	27	46	284
		2852	29	45	84
$m_d m_u w_d$	61.96	2596	142	256	32
		2631	25	44	426
		2675	26	45	280
		2855	31	48	81
$m_d m_d m_u$	65.31	2597	145	261	17
		2639	31	54	428
		2646	27	48	440

Table S14: continuation

conformer	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-L					
$w_d w_d w_u$	51.68	2624	143	253	6
		2668	14	25	250
		2674	14	24	227
		2876	20	31	92
		2880	22	34	94
		2881	26	39	67
$m_u w_d w_d$	55.98	2598	113	203	122
		2660	44	76	216
		2693	22	37	275
		2872	26	40	91
		2877	28	43	81
$m_d w_d w_u$	55.94	2601	118	211	106
		2656	34	60	240
		2696	26	44	273
		2873	24	37	93
		2880	25	38	79
$m_d m_d w_u$	60.40	2597	119	213	88
		2650	44	76	387
		2693	28	47	299
		2875	28	42	86
$m_d m_u w_d$	60.22	2606	139	249	31
		2644	26	45	444
		2688	26	45	301
		2876	29	45	83
$m_d m_d m_u$	64.77	2607	146	260	13
		2652	30	52	474
		2659	27	47	445

Table S15: Dissociation energies without (D_e) and with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for $\mathbf{m}_3\mathbf{w}$ and \mathbf{m}_4 . Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the OH-stretching vibration on different levels are listed.

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S						
$\mathbf{m}_3\mathbf{w}$	147.40	119.34	3325	398	487	100
			3399	38	45	1555
			3425	59	68	1329
			3457	131	150	372
			3858	78	74	52
\mathbf{m}_4	143.10	119.33	3337	429	521	0
			3416	23	27	1681
			3416	23	27	1681
			3448	194	223	159
MP2-S						
$\mathbf{m}_3\mathbf{w}$	161.39	132.88	3451	372	427	62
			3515	16	17	1455
			3535	72	80	1021
			3579	89	96	421
			3926	70	64	81
\mathbf{m}_4	160.59	136.12	3443	381	440	0
			3517	20	22	1519
			3517	20	22	1519
			3549	157	172	161
MP2-M						
$\mathbf{m}_3\mathbf{w}$	134.68	109.54	3330	362	441	107
			3420	19	22	1775
			3452	74	85	1203
			3519	85	94	564
			3899	67	62	89
\mathbf{m}_4	136.84	115.57	3314	367	451	0
			3421	21	25	1905
			3421	21	25	1905
			3467	147	168	196

Table S16: Dissociation energies without (D_e) and with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ of pure and mixed ethanol-water dimers for dissociation into e_t and w (values for dissociation into e_g and w are given in parentheses). Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the donor (D) and acceptor (A) symmetric (*sym*) and asymmetric (*asym*) OH-stretching vibration on different levels are listed. The S basis set does not predict the correct order.

conformer	D_e	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S							
ww	30.98	19.93	D _{sym}	3650	163	170	301
			A _{sym}	3779	82	81	6
			D _{asym}	3849	57	54	64
			A _{asym}	3889	36	34	60
we _{g+}	29.47	20.22 (21.13)	D _{sym}	3610	168	178	387
			A	3784	68	67	18
			D _{asym}	3845	65	62	60
we _t	29.69	20.51	D _{sym}	3616	171	182	376
			A	3798	98	96	24
			D _{asym}	3845	56	54	63
we _{g-}	28.59	19.98 (20.89)	D _{sym}	3618	207	220	433
			A	3783	66	65	19
			D _{asym}	3845	59	56	68
e _t w	28.99	21.06	D	3667	228	236	400
			A _{sym}	3780	91	89	4
			A _{asym}	3891	39	37	60
e _g w	27.93	19.45 (20.36)	D	3661	171	178	341
			A _{sym}	3780	91	90	4
			A _{asym}	3890	39	37	60
e _{g+} e _{g+}	25.58	19.58 (21.40)	D	3624	188	198	430
			A	3784	71	70	18
e _t e _t	27.03	21.05	D	3636	243	256	485
			A	3799	97	95	23
e _{g-} e _t	26.02	19.67 (20.58)	D	3628	183	193	421
			A	3798	92	90	22
e _{g-} e _{g-}	25.21	19.09 (20.91)	D	3630	221	233	470
			A	3784	64	63	18

Table S16: continuation

conformer	D_e	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-S							
ww	32.71	21.69	D_{sym}	3754	141	141	238
			A_{sym}	3835	78	74	6
			D_{asym}	3939	47	43	105
			A_{asym}	3969	32	29	80
we_{g+}	34.11	23.87 (25.49)	D_{sym}	3699	135	138	290
			A	3831	61	59	25
			D_{asym}	3926	55	51	91
we_t	34.37	24.05	D_{sym}	3711	144	146	300
			A	3836	87	83	31
			D_{asym}	3929	47	43	100
we_{g-}	31.89	22.22 (23.84)	D_{sym}	3716	168	170	347
			A	3831	60	58	27
			D_{asym}	3930	49	45	108
$e_t w$	32.93	24.32	D	3750	171	171	369
			A_{sym}	3834	89	86	4
			A_{asym}	3970	35	31	81
$e_g w$	32.63	23.35 (24.97)	D	3748	126	126	306
			A_{sym}	3831	90	86	3
			A_{asym}	3967	35	31	80
$e_{g+}e_{g+}$	34.57	26.54 (29.78)	D	3695	124	127	358
			A	3829	72	69	25
$e_t e_t$	35.32	27.69	D	3704	172	175	429
			A	3837	90	87	32
$e_{g-}e_t$	35.32	27.36 (28.98)	D	3702	127	129	362
			A	3834	85	82	31
$e_{g-}e_{g-}$	32.00	24.71 (27.95)	D	3708	149	152	401
			A	3831	62	60	26

Table S16: continuation

conformer	D_e	D_0	vibration	ω (th)	A_{Raman}	σ	I_{IR}
MP2-M							
ww	24.39	15.06	D_{sym}	3740	149	149	287
			A_{sym}	3824	66	63	17
			D_{asym}	3927	44	41	113
			A_{asym}	3944	28	26	98
we_{g+}	28.22	19.67 (20.98)	D_{sym}	3680	133	137	341
			A	3831	57	55	39
			D_{asym}	3917	56	52	104
we_t	28.12	19.67	D_{sym}	3681	139	143	349
			A	3837	81	78	48
			D_{asym}	3917	49	46	108
we_{g-}	26.04	17.86 (19.16)	D_{sym}	3688	160	164	393
			A	3829	55	53	40
			D_{asym}	3919	49	45	115
$e_t w$	24.31	17.43	D	3742	188	188	432
			A_{sym}	3823	72	69	10
			A_{asym}	3944	30	27	98
$e_g w$	23.74	16.63	D	3740	138	138	351
			A_{sym}	3820	76	73	10
			A_{asym}	3942	30	28	98
$e_{g+} e_{g+}$	29.12	23.10	D	3678	122	126	403
			A	3828	67	65	37
$e_t e_t$	29.44	23.67	D	3685	172	176	500
			A	3838	90	87	48
$e_{g-} e_t$	29.23	23.32	D	3687	124	127	408
			A	3837	83	79	48
$e_{g-} e_{g-}$	26.02	20.96	D	3703	134	136	407
			A	3832	63	61	39

Table S16: continuation

conformer	D_e	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-L							
ww	22.24	13.09	D_{sym}	3763	148	147	297
			A_{sym}	3849	65	62	15
			D_{asym}	3957	39	36	120
			A_{asym}	3973	23	21	99
$w e_{g+}$	27.38	19.02 (19.95)	D_{sym}	3705	130	133	349
			A	3863	57	54	39
			D_{asym}	3948	53	48	109
$w e_t$	27.12	18.88	D_{sym}	3707	137	139	364
			A	3869	80	75	49
			D_{asym}	3949	45	41	114
$w e_{g-}$	25.22	17.31 (18.24)	D_{sym}	3714	168	171	420
			A	3861	60	57	42
			D_{asym}	3951	49	44	122
$e_t w$	22.15	15.68	D	3765	190	188	454
			A_{sym}	3848	71	68	10
			A_{asym}	3973	25	22	98
$e_g w$	22.72	15.17 (16.10)	D	3762	139	138	373
			A_{sym}	3846	74	71	10
			A_{asym}	3971	25	23	97
$e_{g+} e_{g+}$	30.72	23.22 (25.09)	D	3704	118	120	406
			A	3860	67	63	38
$e_t e_t$	28.69	23.25	D	3711	167	170	506
			A	3872	67	81	49
$e_{g-} e_t$	28.83	23.15 (25.02)	D	3712	120	122	416
			A	3871	82	78	49
$e_{g-} e_{g-}$	26.86	19.62 (21.48)	D	3678	133	137	412
			A	3804	63	62	39

Table S17: Dissociation energies with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for pure and mixed deuterated ethanol-deuterium oxide dimers for dissociation into e_t and w (values for dissociation into e_g and w are given in parentheses). Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the donor (D) and acceptor (A) symmetric (*sym*) and asymmetric (*asym*) OD-stretching vibration on different levels are listed. Only the L basis set does predict the correct order.

conformer	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S						
ww	22.69	D_{sym}	2637	86	150	143
		A_{sym}	2721	43	72	5
		D_{asym}	2814	28	45	59
		A_{asym}	2853	19	29	36
$w e_{g+}$	22.19	D_{sym}	2611	87	154	188
	(23.10)	A	2754	41	67	13
		D_{asym}	2809	30	48	59
$w e_t$	22.49	D_{sym}	2616	87	155	183
		A	2764	50	82	17
		D_{asym}	2809	28	44	61
$e_{g+} e_{g+}$	20.54	D	2640	103	180	247
	(22.36)	A	2755	43	71	13
MP2-S						
ww	24.42	D_{sym}	2708	73	123	112
		A_{sym}	2761	41	68	6
		D_{asym}	2884	24	37	80
		A_{asym}	2912	17	25	48
$w e_{g+}$	26.06	D_{sym}	2672	71	122	137
	(27.50)	A	2789	36	59	18
		D_{asym}	2872	26	40	77
$w e_t$	26.28	D_{sym}	2681	73	126	143
		A	2793	45	72	22
		D_{asym}	2874	23	36	82
$e_{g+} e_{g+}$	27.90	D	2691	69	118	206
	(30.76)	A	2788	42	68	18

Table S17: continuation

conformer	D_0	vibration	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-M						
ww	17.37	D_{sym}	2703	79	134	136
		A_{sym}	2756	34	56	12
		D_{asym}	2871	22	34	85
		A_{asym}	2890	15	22	57
we_{g^+}	21.48 (22.74)	D_{sym}	2663	71	123	163
		A	2788	35	56	26
		D_{asym}	2861	26	40	84
we_t	21.50	D_{sym}	2664	73	126	167
		A	2794	42	68	31
		D_{asym}	2861	23	36	86
$\text{e}_{g^+}\text{e}_{g^+}$	23.99 (26.52)	D	2679	69	119	229
		A	2786	41	66	24
MP2-L						
ww	15.36	D_{sym}	2720	79	133	140
		A_{sym}	2774	33	54	11
		D_{asym}	2893	19	29	89
		A_{asym}	2911	12	18	57
we_{g^+}	20.78 (21.72)	D_{sym}	2682	70	119	167
		A	2812	35	56	26
		D_{asym}	2883	24	37	87
we_t	20.67	D_{sym}	2683	72	123	175
		A	2817	42	66	32
		D_{asym}	2884	21	32	89
$\text{e}_{g^+}\text{e}_{g^+}$	24.03 (25.92)	D	2698	68	115	231
		A	2810	41	66	25

Table S18: Dissociation energies without (D_e) and with zero point energy correction (D_0) in $\text{kJ}\cdot\text{mol}^{-1}$ for pure and mixed ethanol-water trimers (*trans* conformation and equal molecules pointing in the same direction). Also, calculated wavenumbers ($\omega(\text{th})$) in cm^{-1} , scattering activities (A_{Raman}) in $\text{\AA}^4\cdot\text{u}^{-1}$, scattering cross sections (σ) in $10^{-36}\cdot\text{m}^2\cdot\text{sr}^{-1}$ and IR intensities (I_{IR}) in $\text{km}\cdot\text{mol}^{-1}$ of the OH-stretching vibration on different levels are listed.

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
B3-S						
www	90.41	63.54	3503	257	288	29
			3554	38	42	556
			3571	42	45	488
			3859	70	66	54
			3864	65	61	61
eww	86.61	63.96	3489	266	300	228
			3557	105	114	481
			3581	56	60	553
			3862	73	69	60
			3866	89	84	53
eew	82.57	63.60	3498	287	323	184
			3562	165	180	519
			3576	79	85	737
			3857	83	79	59
eee	77.79	63.24	3516	424	472	54
			3559	124	135	818
			3571	110	120	769

Table S18: continuation

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-S						
www	93.90	67.82	3636	249	262	20
			3680	27	28	433
			3692	30	30	377
			3935	65	59	67
			3939	50	45	96
eww	93.66	70.61	3943	56	51	101
			3599	225	241	218
			3667	105	108	391
			3689	27	28	396
			3929	62	57	86
eew	92.93	73.13	3939	75	68	89
			3593	278	298	57
			3635	61	64	611
			3668	56	58	484
eee	91.79	75.91	3924	75	69	89
			3582	334	360	18
			3627	80	85	686
			3635	77	81	723
MP2-M						
www	73.78	50.18	3609	258	275	15
			3667	29	30	499
			3678	29	30	450
			3911	46	43	117
			3915	44	41	131
eww	75.59	55.49	3916	67	62	70
			3547	209	229	324
			3654	119	123	362
			3682	30	31	481
			3908	58	53	107
eew	77.95	61.19	3915	71	66	102
			3542	255	281	125
			3600	62	66	731
			3669	64	67	481
eee	79.75	67.08	3905	74	68	105
			3535	328	361	20
			3600	72	77	824
			3610	79	84	823

Table S18: continuation

conformer	D_e	D_0	$\omega(\text{th})$	A_{Raman}	σ	I_{IR}
MP2-L						
www	69.08	46.16	3621	269	254	11
			3685	29	28	518
			3694	28	28	475
			3939	40	44	120
			3943	33	36	140
			3944	64	70	71
eww	72.25	52.80	3566	227	209	304
			3671	114	110	402
			3700	33	32	518
			3939	48	53	113
			3944	64	70	104
eew	76.05	59.75	3936			109
			3689			497
			3617			771
			3557			118

Table S19: Experimental Raman-jet band positions $\tilde{\nu}$ in cm^{-1} , modified red shifts $\delta\tilde{\nu}$ in cm^{-1} and Iogansen enthalpies ΔH_{Iog} in $\text{kJ}\cdot\text{mol}^{-1}$ for the mixed (undeuterated and deuterated) methanol-water system. In case of the water monomer an average of the symmetric and antisymmetric stretching vibration position [G. Avila *et al.*, *J. Mol. Spectrosc.* (2004) 228:38-65] was used for the Iogansen analysis.

Assignment	$\tilde{\nu}$	$\delta\tilde{\nu}$	ΔH_{Iog}
w_{sym}	3658		
w_{asym}	3756		
m	3686		
ww	3602	82	-11.8
wm	3567	123	-14.4
mm	3577	109	-13.6
www	3491	205	-18.6
mww	3440	254	-20.7
mmw	3425	265	-21.2
mmm	3414	272	-21.4
w_4	3341	360	-24.7
m_3w	3239	451	-27.6
m_4	3212	474	-28.3
w_5	3311	390	-25.7
m_4w	3191	498	-29.0
m_5	3167	519	-29.6
w_{sym} (deuterated)	2672		
w_{asym} (deuterated)	2788		
m (deuterated)	2719		
ww (deuterated)	2632	64	-10.4
wm (deuterated)	2611	91	-12.4
mm (deuterated)	2637	82	-11.8
www (deuterated)	2557	154	-16.1
mww, mmw (deuterated)	2526	188	-17.8
mmm (deuterated)	2530	189	-17.9

Table S20: Experimental Raman-jet band positions $\tilde{\nu}$ in cm^{-1} , modified red shifts $\delta\tilde{\nu}$ in cm^{-1} and Iogansen enthalpies ΔH_{Iog} in $\text{kJ}\cdot\text{mol}^{-1}$ for the mixed (undeuterated and deuterated) ethanol-water system. In the case of the water monomer an average of the symmetric and antisymmetric stretching vibration position [G. Avila *et al.*, *J. Mol. Spectrosc.* (2004) 228:38-65] was used for the Iogansen analysis.

Assignment	$\tilde{\nu}$	$\delta\tilde{\nu}$	ΔH_{Iog}
w_{sym}	3657		
w_{asym}	3756		
e_{g+}	3661		
e_t	3678		
ww	3602	82	-11.8
$w_{e_{g+}}$	3548	144	-15.6
w_{e_t}	3551	140	-15.4
$e_{g+}e_{g+}$	3532	129	-14.8
$e_{g-}e_t$	3548	113	-13.8
www	3491	205	-18.6
eww	3427	264	-21.1
eew	3409	276	-21.6
eee	3414	292	-22.2
w_{sym} (deuterated)	2672		
w_{sym} (deuterated)	2788		
e_{g+} (deuterated)	2700		
e_t (deuterated)	2714		
ww (deuterated)	2632	64	-10.4
$w_{e_{g+}}$ (deuterated)	2601	103	-13.2
w_{e_t} (deuterated)	2602	102	-13.1
$e_{g+}e_{g+}$ (deuterated)	2609	91	-12.4
$e_{g-}e_t$ (deuterated)	2621	79	-11.6