# Supporting information: Attenuated Deuterium Stabilization of Hydrogen Bound Complexes at Room Temperature

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## References

## S1 Theory and Computations

## S1.1 Methanol Complexes

Table S1: Electronic energies ( $\Delta E$ ), zero-point vibrational energy ( $\Delta ZPVE$ ), enthalpy-( $\Delta H^{\circ}$ ) and Gibbs energy of complex formation ( $\Delta G^{\circ}$ ) in kJ/mol, entropy of complex formation ( $\Delta S^{\circ}$ ) in J/(mol·K), at T = 298 K. 2D+2D LMPT and 4D LM calculated fundamental OH- and OD-stretching transition frequency ( $\tilde{\nu}_{calc}$ ) in cm<sup>-1</sup> and associated oscillator strength ( $f_{calc}$ ). Conformers of a complex is labeled with an integer, starting at 1 for the lowest energy conformer. Label is omitted if only one conformer is found. The dash "-" indicate that the value was not calculated.

Complex	$\Delta \mathbf{E}^{a}$	$\Delta ZPVE^{a}$	$\Delta \mathbf{H}^{\diamond a}$	$\Delta \mathbf{G}^{\diamond a}$	$\Delta S^{\oplus a}$	$\tilde{\nu}_{calc}$	$f_{calc} \times 10^{-5}$	$\tilde{\nu}_{calc}$	$f_{calc} \times 10^{-5}$
$\underline{B3LYP}-\underline{D3^{b}}$						2D+	-2D LMPT		4D LM
$MeOH \cdot DME-1$	-26.9	5.2	-20.0	6.9	-90.3	3485	10.4	3481	10.3
$MeOH \cdot DME-2$	-26.3	4.9	-19.7	6.5	-88.1	3488	7.90	3485	8.07
$MeOD-d_1 \cdot DME-1$	-26.9	4.4	-20.7	6.6	-91.5	2570	5.72	2567	5.50
MeOD- $d_1$ ·DME-2	-26.3	4.2	-20.4	6.2	-89.3	2575	4.27	2571	4.30
$MeOD-d_4 \cdot DME-1$	-26.9	4.4	-20.6	6.6	-91.1	2567	5.78	2567	5.50
$MeOD-d_4 \cdot DME-2$	-26.3	4.2	-20.2	6.1	-88.3	2573	4.31	2571	4.30
MeOH·TMA	-37.3	5.8	-30.4	2.8	-111.2	3236	17.7	3242	17.1
$MeOD-d_1 \cdot TMA$	-37.3	5.0	-31.1	2.6	-112.9	2393	10.2	2398	9.15
DOTY DA									
$\omega B97X-D^{\circ}$				110					
MeOH·DME-1	-25.0	6.3	-17.7	14.3	-107	3599	7.21	-	-
MeOH·DME-2	-25.0	7.4	-17.2	18.7	-120	3591	9.36	-	-
$MeOD-d_1 \cdot DME-1$	-25.0	5.7	-18.3	14.2	-109	2653	3.94	-	-
MeOD- $d_1$ ·DME-2	-25.0	6.8	-17.8	18.6	-122	2644	5.12	-	-
$MeOD-d_4 \cdot DME-1$	-25.0	5.5	-18.2	13.9	-108	2650	3.99	-	-
$MeOD-d_4 \cdot DME-2$	-25.0	6.5	-17.8	18.5	-122	2642	5.18	-	-
MeOH·TMA	-35.8	6.3	-28.6	5.3	-114	3358	16.6	-	-
MeOD- $d_1$ ·TMA	-35.8	5.7	-29.3	5.4	-116	2481	9.04	-	-
CCSD(T)-F12a <sup>c</sup>									
MeOH·DME	-25.4	4.5	-18.8	7.8	-89.1	3552	8.72	3546	8.64
MeOD- $d_1$ ·DME	-25.4	3.7	-19.5	7.4	-90.3	2617	4.82	2614	4.60
MeOH·TMA	-34.3	-	-	-	-	3337	15.8	3335	15.6
$\underline{\text{MeOD-}d_1 \cdot \text{TMA}}$	-34.3	-	-	-	-	2465	8.80	2465	8.30

a: Respective properties are calculated as the value of the complex minus the sum of the values of the two corresponding monomers.

b: Using the aug-cc-pVTZ basis set.

c: Using the VDZ-F12 basis set.

## S1.2 Ethanol Complexes

Table S2: Electronic energies ( $\Delta E$ ), zero-point vibrational energy ( $\Delta ZPVE$ ), enthalpy-( $\Delta H^{\circ}$ ) and Gibbs energy of complex formation ( $\Delta G^{\circ}$ ) in kJ/mol, entropy of complex formation ( $\Delta S^{\circ}$ ) in J/(mol·K), at T = 298 K. 2D+2D LMPT and 4D LM calculated fundamental OH- and OD-stretching transition frequency ( $\tilde{\nu}_{calc}$ ) in cm<sup>-1</sup> and associated oscillator strength ( $f_{calc}$ ). Conformers of a complex is labeled with an integer, starting at 1 for the lowest energy conformer. Label is omitted if only one conformer is found. The dash "-" indicate that the value was not calculated.

Complex	$\Delta \mathbf{E}^a$	$\Delta \mathrm{ZPVE}^a$	$\Delta \mathbf{H}^{\diamond a}$	$\Delta \mathbf{G}^{\diamond a}$	$\Delta \mathbf{S}^{\diamond a}$	$\tilde{\nu}_{calc}$	$f_{calc} \times 10^{-5}$	$\tilde{\nu}_{calc}$	$f_{calc} \times 10^{-5}$
						201	OD I MDT		
<u>DJLII-DJ</u> ELOU DME 1	07.0	<b>F</b> 0	00.0	10.0	105.0	$\frac{2D7}{2470}$	$\frac{-2D}{0.04}$	0.474	4D LM
g-EtOH·DME-1	-27.9	5.6	-20.8	10.6	-105.2	3476	9.04	3474	8.91
g-EtOH·DME-2	-27.5	5.4	-20.6	11.4	-107.5	3472	7.63	3474	8.09
t-EtOH·DME-1	-26.4	4.7	-19.6	5.2	-83.2	3481	11.1	3480	10.8
t-EtOH·DME-2	-26.1	4.9	-19.4	9.3	-96.2	3482	8.46	3489	8.31
$g$ -EtOD- $d_1$ ·DME-1	-27.9	4.9	-21.5	10.3	-106.5	2564	4.98	2563	4.74
$g$ -EtOD- $d_1$ ·DME-2	-27.5	4.7	-21.3	11.1	-108.6	2564	4.16	2564	4.28
$t\text{-EtOD-}d_1 \cdot \text{DME-}1$	-26.4	4.0	-20.3	4.9	-84.4	2566	6.14	2567	5.79
$t$ -EtOD- $d_1$ ·DME-2	-26.1	4.2	-20.1	8.9	-97.4	2570	4.61	2573	4.56
$g\text{-EtOH}\cdot\text{TMA}$	-38.4	5.8	-31.3	6.0	-125.3	3221	16.9	3232	16.5
$t\text{-EtOH}\cdot\text{TMA}$	-37.0	5.4	-30.0	3.3	-111.9	2382	9.65	3239	19.0
$g$ -EtOD- $d_1$ ·TMA	-38.4	5.2	-32.0	5.8	-126.9	3230	19.6	2395	8.50
$t$ -EtOD- $d_1$ ·TMA	-37.0	4.7	-30.8	3.1	-113.6	2388	11.2	2396	10.0
$\omega B97X-D^b$									
$\overline{g\text{-EtOH}\cdot\text{D}\text{ME-1}}$	-27.3	7.4	-19.5	18.4	-127	3589	6.81	-	-
g-EtOH·DME-2	-26.6	7.0	-21.0	16.9	-119	3574	8.92	-	-
t-EtOH·DME-1	-25.0	6.6	-17.6	16.2	-113	3580	6.94	-	-
t-EtOH·DME-2	-25.1	7.2	-17.0	17.2	-115	3580	10.7	-	-
$g$ -EtOD- $d_1$ ·DME-1	-27.3	7.4	-19.5	18.4	-127	2643	3.72	-	-
$g$ -EtOD- $d_1$ ·DME-2	-25.6	5.7	-21.0	19.8	-137	2630	4.84	-	-
$t\text{-EtOD-}d_1 \cdot \text{DME-}1$	-25.3	6.6	-17.6	16.2	-113	2641	3.88	-	-
$t$ -EtOD- $d_1$ ·DME-2	-25.1	7.2	-17.0	17.2	-115	2635	5.85	-	-

*a*: Respective properties are calculated as the value of the complex minus the sum of the values of the two corresponding monomers.

b: Using the aug-cc-pVTZ basis set.

## S1.3 Entropy calculations

Specie	$S_{trans}$	$S_{rot}$	$S_{vib}$
MeOH·DME-1	163.092	113.152	136.373
$MeOH \cdot DME-2$	163.092	112.391	139.244
$MeOD-d_1 \cdot DME-1$	163.251	113.177	138.620
$MeOD-d_1 \cdot DME-2$	163.251	112.458	141.532
$MeOD-d_4 \cdot DME-1$	163.720	114.127	144.783
$MeOD-d_4 \cdot DME-2$	163.720	113.315	148.390
MeOH·TMA	165.017	116.265	141.666
MeOD·TMA	165.155	116.303	143.499
MeOH	151.980	79.471	6.954
$MeOD-d_1$	152.365	80.634	9.079
$MeOD-d_4$	153.457	84.575	11.238
g-EtOH·DME-1	165.151	117.123	146.863
g-EtOH·DME-2	165.151	116.520	145.231
$g\text{-EtOD-}d_1 \cdot \text{DME-}1$	165.289	117.152	149.109
$g$ -EtOD- $d_1$ ·DME-2	165.289	116.575	147.515
t-EtOH·DME-1	165.151	117.734	168.791
t-EtOH·DME-2	165.151	117.190	156.369
$t\text{-EtOD-}d_1 \cdot \text{DME-}1$	165.289	117.742	171.092
$t$ -EtOD- $d_1$ ·DME-2	165.289	117.236	158.632
$g ext{-}\mathrm{EtOH} ext{-}\mathrm{TMA}$	166.804	119.805	153.833
$g ext{-EtOD-}d_1 ext{-} ext{TMA}$	166.921	119.830	155.741
t-EtOH·TMA	166.804	120.687	166.787
$t$ -EtOD- $d_1$ ·TMA	166.921	120.700	168.628
$g ext{-EtOH}$	156.507	93.550	19.866
$g ext{-EtOD-}d_1$	156.774	94.140	22.640
t-EtOH	156.507	93.358	20.564
$t$ -EtOD- $d_1$	156.774	93.881	23.389
DME	$1\overline{56.506}$	86.508	21.480
TMA	159.615	101.537	34.677

Table S3: Calculated B3LYP-D3/aug-cc-pVTZ translational ( $S_{trans}$ ), rotational ( $S_{rot}$ ) and vibrational ( $S_{vib}$ ) entropy for all complexes, donors and acceptors in J/(mol·K).



Figure S1: The B3LYP-D3 calculated difference in translational (S<sub>trans</sub>), rotational (S<sub>rot</sub>) and vibrational (S<sub>vib</sub>) entropy at T = 298 K, between the g-EtOH·DME-1 and g-EtOD $d_1$ ·DME-1 complexes (A) and g-EtOH and g-EtOD- $d_1$  donors (B). The difference of A and B give the overall change in  $\Delta$ S between the hydrogen and deuterium bound complex ( $\Delta$ S<sub>H $\rightarrow D$ </sub>(EtOH(D)·DME)) (C).

## S1.4 The Wilson G-matrix

The G-matrix elements are defined as:  $^{1,2}$ 

$$G(q_i, q_j) = \sum_{\alpha}^{3N} \frac{1}{m_{\alpha}} \frac{\partial q_i}{\partial x_{\alpha}} \frac{\partial q_j}{\partial x_{\alpha}} = \sum_{\beta}^{N} \sum_{\gamma}^{N} \left( \mathbf{J}^{-1} \right)_{i\gamma}^T \mathbf{M}_{\gamma\beta}^{-1} \mathbf{J}_{\beta j}^{-1},$$
(S1)

where  $\alpha$  expresses a summation over the Cartesian coordinates of each atom,  $q_k$  is the kth internal coordinate,  $\mathbf{J}$  is the Jacobian of the Cartesian to curvilinear coordinate transformation  $(\mathbf{J}_{\beta j}^{-1} = \frac{\partial q_j}{\partial x_\beta})$  and **M** is the mass matrix  $(\mathbf{M}_{\gamma\beta} = m_\gamma \delta_{\gamma\beta})$ , where  $\delta$  refer to the Dirac delta function. To calculate G-matrix elements at a given displacement, we first calculate all elements of the Jacobian using finite differences with  $\Delta q = 0.001$  Å for stretching displacements and  $\Delta q = 0.001^{\circ}$  for non-stretching displacements. The internal curvilinear coordinates are defined in terms of the molecular Z-matrix, for which we chose Z-matrices compatible with our choice of coordinates. In Table S4, we show the Z-matrix used for the MeOH·TMA complex. The Jacobian is then augmented with rotation and translation and the full inverse G-matrix is constructed from the Jacobian and the mass matrix. The small displacements along the rotational coordinates are calculated from a rotation matrix expressed from three quaternions, each describing the rotation around the x-, y- and z-axis of the space-fixed Cartesian coordinate system defined from the Z-matrix. The inverse Gmatrix is then calculated from the Jacobian, i.e.  $G^{-1} = \mathbf{J}\mathbf{M}\mathbf{J}^T$ , and the *G*-matrix is obtained by inverting  $G^{-1}$ . With this approach, G-matrix elements are calculated with a precision of approximately 10 digits, when compared to analytically derived G-matrix elements (tested for several G-matrix elements  $^{3,4}$ ). We represent the G-matrix elements in terms of a polynomial expansion in the respective displacement coordinate(s), with coefficients found from a linear-least squares regression. The kinetic energy coupling between the intermolecular (donor rock and donor twist) and intramolecular modes (OH(D)-stretch and COH(D)-bend) is small, and we evaluate the corresponding G-matrix elements at the equilibrium geometry.

#### S1.4.1 Cross Derivatives

Cross terms in the potential energy surface (PES) and dipole moment function (DMF) are calculated from Taylor expansions in the displacement coordinates to 2D grids with displacements around the equilibrium geometry. To obtain cross terms we express the surface in question as a Taylor expansion in the following way:

$$T(q_1, q_2) \approx \sum_{i>0}^{N} \sum_{j>0}^{M} \mathbf{f}_{\mathbf{i}, \mathbf{j}} q_1^i q_2^j + \sum_{i=0}^{N} \sum_{j=0}^{M} \mathbf{f}_{\mathbf{i}, \mathbf{j}} q_1^i q_2^j \delta_{0, i+j},$$
(S2)

where  $\mathbf{f}_{i,j}$  is the *i*, *j*th expansion coefficient,  $q_1$  and  $q_2$  are two different internal coordinates. Now eq. (S2) can be written as;

$$T(q_1, q_2) - \sum_{i=0}^{N} \sum_{j=0}^{M} \mathbf{f_{i,j}} q_1^i q_2^j \delta_{0,i+j} = \underbrace{\sum_{i>0}^{N} \sum_{j>0}^{M} \mathbf{f_{i,j}} q_1^i q_2^j}_{\mathbf{C}} \approx \underbrace{f(q_1, q_2)}_{\mathbf{A}} - \underbrace{(f(q_1, 0) + f(0, q_2) - f(0, 0))}_{\mathbf{B}},$$
(S3)

where the last step is exact only if the Taylor expansion is exact. This shows that the cross term coefficients can be obtained by subtracting the parts of the surface that only depend on one coordinate. In our calculations we truncate the expansion at N = M = 4. The use of eq. (S3) is illustrated in Figure S2.



Figure S2: Illustration of the fitting procedure for obtaining cross derivatives of the potential energy surfaces and dipole moment functions. The 2D PES for the OH-stretch  $(q_1)$  and donor rock  $(q_2)$  in the MeOH·TMA complex (**A**). The 2D PES obtained from the sum of the two 1D surfaces, i.e. the surface representing the two oscillators with no coupling (**B**)). The coupling potential energy surface obtained by subtraction of surface **B** from surface **A** (**C**).

Ν						
Ο	1	B1				
С	2	B2	1	TIP	В	
Η	2	$\mathbf{RB}$	3	CXI	HI 1	POPB
С	1	B4	2	A3	3	D2
Η	5	B5	1	A4	2	D3
Н	5	B6	1	A5	2	D4
Н	5	B7	1	A6	2	D5
С	1	B8	2	Α7	3	D6
Н	9	B9	1	A8	2	$\mathrm{D7}$
Н	9	B10	1	A9	2	D8
Н	9	B11	1	A10	) 2	D9
С	1	B12	2	A11	3	D10
Н	13	B13	1	A12	2 2	D11
Н	13	B14	1	A13	3 2	D12
Н	13	B15	1	A14	4 2	D13
Н	3	B16	2	A15	5 4	D14
Η	3	B17	2	A16	<b>5</b> 4	D15
Н	3	B18	2	A17	7 4	D16
B1=2.8	84280901,	B2 = 1.41380334,	RB=0.	98104817,	B4=1.45877760	B5=1.08979431
B6=1.10	0110425,	B7=1.08948293,	B8 = 1.43	5977211, E	39 = 1.08948939,	B10=1.10102918
B11=1.0	08949345,	B12 = 1.45895120,	B13=1.0	08957314, E	314 = 1.08978370,	B15=1.10114399
B16=1.0	09776369,	B17=1.090152	243,	B18=1.09777	7120, <b>TIF</b>	B=107.81509269
CXH=	108.28919	<b>381</b> , A3=109.	10692647	A4=10	9.69656293,	A5=112.32071441
A6=109	0.66761765,	A7=105.01130945,	A8=109.	64906278, A9	= 112.25952834,	A10=109.65117451
A11=10	07.51607534,	A12=109.65	535979,	A13=109.	.70898835,	A14=112.34913312
A15=11	2.36404047	A16=107.9822	20283,	A17=112.374	480695, <b>PO</b>	PB = -0.57171307
D2 = -6	7.62120056,	D3 = 61.21880173, 1	D4 = -178	.20401265, D5	5 = -57.50563178	8, D6=172.60839428
D7=60.3	32388610, I	08 = -178.97837065,	D9 = -58	5.27572193, D	10 = 53.67235898	, D11=56.40477659
D12=-	62.33377033	b, $D13=177.08$	924686,	D14 = -61	.25739620,	D15=179.87038510
D16 = 61	00347671.					

Table S4: The B3LYP-D3/aug-cc-pVTZ optimized Z-matrix for MeOH·TMA.

# S2 Boltzmann average

To account for multiple conformers of a complex, a Boltzmann weighted is calculated for each complex:

$$w_i = \frac{e^{\frac{\Delta E_i}{RT}}}{\sum_j e^{\frac{\Delta E_j}{RT}}}$$
(S4)

Where  $w_i$  is the Boltzmann weight for the *i*th conformer of one of the complexes,  $\Delta E_i$  is the electronic energy (Tables S1 and S2), R is the gas constant and T is the temperature (T = 298 K). From here the Boltzmann weighted oscillator strength  $(f_{weighted})$  is calculated:

$$f_{weighted} = \sum_{i} w_i \cdot f_{calc,i} \tag{S5}$$

Where  $f_{calc}$  is the calculated oscillator strength of each conformer (Tables S1 and S2). We use  $\Delta E$  in Equation (S4) as an approximation  $\Delta G^{\diamond}$ , as accurate values of G are difficult to calculate.

## S3 Experimental

## S3.1 Proton Impurity in Deuterated Alcohols

In Figures S3 to S5 we show spectra of the deuterated donors in the OD- and OH-stretching regions. The presence of a OH-stretching band show that a proton impurity was present. The purity of the deuterated specie is still quite high as the absorbance of the OH-stretching fundamental is about an order of magnitude lower than the corresponding OD-stretching fundamental. It is observed, that the proportion between the OD- and OH-stretching band varies between the reference spectra. This is most noticeable in Figure S4, by comparing the purple trace to any of the other traces. The reason for the varying proportion happens as the purple reference spectrum was the first to be recorded. Deuterium atoms exchange with hydrogen from the trace amounts of other impurities, which could be atmospheric water that are present inside the vacuum line. This exchange increases the amount of the nondeuterated alcohol. However this exchange acts as a coating in the vacuum line, and limits the exchange when introducing a new sample of deuterated specie, reducing the formation of the non-deuterated alcohol.



Figure S3: Spectrum of the fundamental OD- (left) and OH- (right) stretching band observed for MeOD- $d_1$  in the pressure range 10-45 Torr. For clarity, the OH-stretching band is shown up scaled by a factor of 5.



Figure S4: Spectrum of the fundamental OD- (left) and OH- (right) stretching band observed for MeOD- $d_4$  in the pressure range 30-50 Torr. For clarity, the OH-stretching band is shown up-scaled by a factor of 10.



Figure S5: Spectrum of the fundamental OD- (left) and OH- (right) stretching band observed for EtOD- $d_1$  in the recorded pressure range 20-40 Torr. For clarity, the OH-stretching band is shown up-scaled by a factor of 5.

## S3.2 Experimental Data

## S3.2.1 MeOH·DME

Table S5: Experimental data for the MeOH·DME complex. Pressures of MeOH and DME (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OH-stretching band of the MeOH·DME complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at  $298\pm1$  K.

	MeOH	MeOH	DME	DME	Integrated
Experiment	$\mathbf{Pressure}^{a}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{b}$
A	19.1	1.15	202.5	1.35	0.12
В	24.6	1.00	270.2	0.88	0.19
$\mathbf{C}$	27.1	1.10	310.1	1.01	0.28
D	30.2	0.96	342.3	1.115	0.34
$\mathbf{E}$	33.4	1.06	383.8	1.25	0.42
F	35.6	1.13	423.7	1.38	0.47
G	36.7	0.90	460.5	1.50	0.52

*a*: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range for the fundamental OH-stretching band:  $3400 \text{ to } 3750 \text{ cm}^{-1}$ .



Figure S6: Spectra of experiment G in Table S5 of the donor and acceptor reference, the mixture of the two and the complex.



Figure S7: Spectra of the complex observed in experiment G in Table S5 before and after the subtraction of atmospheric water.

#### S3.2.2 MeOD- $d_1$ ·DME

Table S6: Experimental data for the MeOD- $d_1$ ·DME complex. Pressure of MeOD- $d_1$  and DME (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OD-stretching band of the MeOD- $d_1$ ·DME complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at 298±1 K.

	$MeOD-d_1$	MeOD- $d_1$	DME	DME	Integrated
Experiment	$\mathbf{Pressure}^{a\ b}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{c}$
А	12.2	0.68	177	1.18	0.78
В	15.2	0.85	233	0.76	1.17
$\mathbf{C}$	17.4	0.97	276	0.90	1.59
D	21.5	1.20	350	1.14	2.73
${ m E}$	24.2	1.35	414	1.35	3.63
F	28.4	0.95	467	0.77	4.71
G	29.9	1.00	527	0.87	5.58
Н	29.9	1.00	576	0.95	6.10
Ι	33.8	0.86	620	1.02	7.69

*a*: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range of OD-stretching fundamental band: 2550 to 2794 cm<sup>-1</sup>.

c: Integration range for the OD-stretching fundamental band: 2460 to 2704  $\rm cm^{-1}.$ 



Figure S8: Spectra of experiment I in Table S6 of the donor and acceptor reference, the mixture of the two and the complex. The spectral noise seen above  $2770 \text{ cm}^{-1}$  is caused by saturation from the CH-stretching bands of DME.



Figure S9: Spectra of the MeOD- $d_1$ ·DME complex, with varying amounts of the complex.

#### S3.2.3 MeOD- $d_4$ ·DME

Table S7: Experimental data for the MeOD- $d_4$ ·DME complex. Pressure of MeOD- $d_4$  and DME (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OD-stretching band of the MeOD- $d_4$ ·DME complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at 297±1 K.

	$MeOD-d_4$	$MeOD-d_4$	DME	DME	Integrated
Experiment	$\mathbf{Pressure}^{a\ b}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{c}$
А	15.2	0.56	83	0.55	0.27
В	22.3	0.82	122	0.81	0.91
$\mathbf{C}$	28.5	1.05	160	1.07	1.63
D	33.3	0.91	209	0.68	2.20
$\mathbf{E}$	36.2	0.99	246	0.80	2.82
$\mathbf{F}$	43.9	1.20	313	1.02	4.97
G	29.3	0.80	582	0.96	5.86

*a*: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range of OD-stretching fundamental band: 2550 to 2794 cm<sup>-1</sup>.

c: Integration range for the fundamental OD-stretching fundamental band: 2460 to 2704 cm<sup>-1</sup>.



Figure S10: Spectra of experiment G in Table S7 of the donor and acceptor reference, the mixture of the two and the complex. The spectral noise seen above  $2770 \text{ cm}^{-1}$  is caused by saturation from the CH-stretching bands of DME.



Figure S11: Spectra of the MeOD- $d_4$ ·DME complexes from Table S7, with varying amounts of the complex.

## S3.2.4 MeOH·TMA

Table S8: Experimental data for the MeOH·TMA complex. Pressure of MeOH and TMA (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OH-stretching band of the MeOH·TMA complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at  $294\pm1$  K.

	MeOH	MeOH	TMA	TMA	Integrated
Experiment	$\mathbf{Pressure}^{a}$	Scale Factor	$\mathbf{Pressure}^a$	Scale Factor	$absorbance^{b}$
А	16.1	0.97	79	1.20	0.47
В	20.9	0.85	115	1.74	0.90
$\mathbf{C}$	34.6	1.10	257	0.85	3.26
D	34.6	1.10	290	0.96	3.81
${ m E}$	37.2	1.18	339	0.97	4.82
$\mathbf{F}$	21.9	0.89	318	0.91	2.49
G	21.9	0.89	358	0.89	2.91
Η	22.2	0.90	406	0.90	3.28
Ι	23.6	0.96	479	1.06	4.09
J	25.1	1.02	516	1.04	4.51
Κ	25.9	1.05	565	1.14	5.17
L	26.3	1.07	615	1.12	5.56

*a*: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range for the fundamental OH-stretching band: 3050 to 3800 cm<sup>-1</sup>.



Figure S12: Spectra of experiment L in Table S8 of the donor and acceptor reference, the mixture of the two and the complex.

![](_page_22_Figure_0.jpeg)

Figure S13: Spectra of the MeOH·TMA complex from Table S8 at various pressures of the complex.

#### S3.2.5 MeOD- $d_1$ ·TMA

Table S9: Experimental data for the MeOD- $d_1$ ·TMA complex. Pressure of MeOD- $d_1$ and
TMA (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the funda-
mental OD-stretching band of the MeOD- $d_1$ ·TMA complex (cm <sup>-1</sup> ). Spectra recorded with
a 10 cm optical path length at $295\pm1$ K

	$MeOD-d_1$	MeOD- $d_1$	ТМА	TMA	Integrated
Experiment	$\mathbf{Pressure}^{a\ b}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{c}$
А	10.7	1.15	146.7	0.485	6.0
В	12.5	1.00	195.1	0.645	9.8
$\mathbf{C}$	15.8	1.00	243.5	0.805	15.9
D	8.6	1.15	301.9	0.865	12.7
${ m E}$	9.8	1.05	353.6	0.88	18.4
$\mathbf{F}$	14.6	0.92	392.9	0.87	25.4
G	17.7	0.95	456.2	0.92	34.0
Н	16.8	0.90	565.2	1.03	42.9
Ι	21.6	0.90	639.7	1.06	56.4

a: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range of fundamental OD-stretching band: 2550 to 2794 cm<sup>-1</sup>.

c: Integration range for the fundamental OD-stretching band: 2228 to 2693  $\rm cm^{-1}$ .

The OD-stretching fundamental band in the MeOD- $d_1$ ·TMA complexes were seen to spectrally overlap with absorption lines from atmospheric CO<sub>2</sub> at around 2350 cm<sup>-1</sup>, which is shown in Figure S14 as the blue trace. The presence of CO<sub>2</sub> in the spectra was here subtracted by recording a spectrum of the the ambient atmosphere around the spectrometer, where the red trace in Figure S14 shows a spectrum after subtraction of atmospheric CO<sub>2</sub>.

![](_page_24_Figure_0.jpeg)

Figure S14: Spectra of the complex from experiment I in Table S9, showing the spectrum before and after subtraction of the  $CO_2$  lines, from a recorded spectrum of the ambient air. Spectral noise at 2300 to 2375 cm<sup>-1</sup> is caused by atmospheric  $CO_2$ .

![](_page_25_Figure_0.jpeg)

Figure S15: Spectra of experiment I in Table S9 of the donor and acceptor reference, the mixture of the two and the complex. The spectral noise seen above  $2700 \text{ cm}^{-1}$  is caused by saturation from the CH-stretching bands of TMA.

![](_page_26_Figure_0.jpeg)

Figure S16: Spectra of the MeOD- $d_1$ ·TMA complex from Table S9, with varying amounts of the complex. Spectral noise at 2300 to 2375 cm<sup>-1</sup> is caused by atmospheric CO<sub>2</sub>.

#### S3.2.6 EtOH DME

Table S10: Experimental data for the EtOH·DME complex. Pressure of EtOH and DME (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OH-stretching band of the EtOH·DME complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at  $298\pm1$  K.

	EtOH	EtOH	DME	DME	Integrated
Experiment	$\mathbf{Pressure}^a$	Scale Factor	$\mathbf{Pressure}^a$	Scale Factor	$absorbance^{b}$
А	12.4	0.65	152	1.01	0.078
В	15.3	0.80	209	0.68	0.089
$\mathbf{C}$	18.4	0.80	252	0.82	0.13
D	21.9	0.95	273	0.89	0.17
Ε	27.7	1.20	338	1.10	0.25
F	30.9	1.15	384	1.25	0.30
G	33.0	1.23	436	1.42	0.37

*a*: The pressure given is obtain after multiplying with the corresponding scale factor.

b: Integration range for the fundamental OH-stretching band: 3460 to 3721  $\rm cm^{-1}$ .

![](_page_27_Figure_5.jpeg)

Figure S17: Spectra of experiment G in Table S10 of the donor and acceptor reference, the mixture of the two and the complex.

![](_page_28_Figure_0.jpeg)

Figure S18: Spectra of the EtOH·DME complex from Table S10, with varying amounts of the complex.

The OH-stretching fundamental band in the EtOH-DME complexes were seen to spectrally overlap with absorption lines from atmospheric  $H_2O$ , which is shown in Figure S19. Water lines were subtracted by recording a spectrum of the ambient air around the spectrometer.

![](_page_29_Figure_0.jpeg)

Figure S19: Spectra of the complex observed in experiment C in Table S10 before and after the subtraction of atmospheric water.

### S3.2.7 EtOD- $d_1$ ·DME

Table S11: Experimental data for the EtOD- $d_1$ ·DME complex. Pressure of EtOD- $d_1$  and DME (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OD-stretching band of the EtOD- $d_1$ ·DME complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at 299±1 K.

$EtOD-d_1$	$EtOD-d_1$	DME	DME	Integrated
$\mathbf{Pressure}^{a\ b}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{c}$
9.1	0.5	135	0.9	0.13
11.3	0.6	180	1.2	0.45
12.7	0.7	215	0.7	0.8
13.9	0.6	261	0.8	1.17
15.1	0.7	295	1.0	1.59
15.8	0.7	332	1.1	1.76
17.5	0.6	368	1.2	2.17
19.0	0.7	405	1.3	2.66
19.6	0.7	455	0.8	2.64
22.7	0.8	485	0.8	3.32
23.3	0.8	533	0.9	3.41
25.1	0.8	558	0.9	4.21
26.4	0.7	582	1.0	4.84
27.6	0.7	651	1.1	5.20
	$\begin{array}{r} {\rm EtOD}\text{-}d_1 \\ \hline {\rm Pressure}^{a\ b} \\ \hline 9.1 \\ 11.3 \\ 12.7 \\ 13.9 \\ 15.1 \\ 15.8 \\ 17.5 \\ 19.0 \\ 19.6 \\ 22.7 \\ 23.3 \\ 25.1 \\ 26.4 \\ 27.6 \end{array}$	$\begin{array}{c ccc} {\rm EtOD-}d_1 & {\rm EtOD-}d_1 \\ \hline {\rm Pressure}^{a \ b} & {\rm Scale \ Factor} \\ \hline 9.1 & 0.5 \\ \hline 11.3 & 0.6 \\ \hline 12.7 & 0.7 \\ \hline 13.9 & 0.6 \\ \hline 15.1 & 0.7 \\ \hline 15.8 & 0.7 \\ \hline 15.8 & 0.7 \\ \hline 17.5 & 0.6 \\ \hline 19.0 & 0.7 \\ \hline 19.6 & 0.7 \\ \hline 22.7 & 0.8 \\ \hline 23.3 & 0.8 \\ \hline 25.1 & 0.8 \\ \hline 26.4 & 0.7 \\ \hline 27.6 & 0.7 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

a: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range of the OD-stretching fundamental band: 2550 to 2794 cm<sup>-1</sup>.

c: Integration range of the complex OD-stretching fundamental band: 2460 to 2704  $\rm cm^{-1}$ .

![](_page_31_Figure_0.jpeg)

Figure S20: Spectra of experiment N in Table S11 of the donor and acceptor reference, the mixture of the two and the complex.

![](_page_32_Figure_0.jpeg)

Figure S21: Spectra of the EtOD- $d_1$ ·DME complex from Table S11, with varying amounts of the complex.

#### S3.2.8 EtOH·TMA

Table S12: Experimental data for the EtOH·TMA complex. Pressure of EtOH and TMA (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OH-stretching band of the EtOH·TMA complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at  $295\pm1$  K.

	EtOH	EtOH	TMA	TMA	Integrated
Experiment	$\mathbf{Pressure}^{a}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{b}$
А	13.7	0.72	281	0.93	0.98
В	14.5	0.76	332	0.95	1.22
$\mathbf{C}$	15.3	0.80	402	1.33	1.57
D	16.2	0.85	454	1.50	1.85
${ m E}$	17.2	0.90	497	1.10	2.14
F	19.1	1.00	510	1.13	2.44
G	19.6	0.85	565	1.14	2.82
Η	20.7	0.90	605	1.22	3.10
Ι	20.7	0.90	650	1.31	3.37
J	20.7	0.90	724	1.20	3.81

a: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range of the complex OH-stretching fundamental band: 3067 to 3771 cm<sup>-1</sup>.

![](_page_33_Figure_5.jpeg)

Figure S22: Spectra of experiment J in Table S12 of the donor and acceptor reference, the mixture of the two and the complex.

![](_page_34_Figure_0.jpeg)

Figure S23: Spectra of the EtOD- $d_1$ ·DME complex from Table S12, with varying amounts of the complex.

#### S3.2.9 EtOD- $d_1$ ·TMA

Table S13: Experimental data for the EtOD- $d_1$ ·TMA complex. Pressure of EtOD- $d_1$  and TMA (Torr) at equilibrium, scale factors (unitless) and integrated absorbance of the fundamental OD-stretching band of the EtOD- $d_1$ ·TMA complex (cm<sup>-1</sup>). Spectra recorded with a 10 cm optical pathlength at 296±1 K.

	$EtOD-d_1$	$EtOD-d_1$	TMA	TMA	Integrated
Experiment	$\mathbf{Pressure}^{a\ b}$	Scale Factor	$\mathbf{Pressure}^{a}$	Scale Factor	$absorbance^{c}$
А	4.6	0.80	236	0.78	0.31
В	4.9	0.85	303	1.00	0.43
$\mathbf{C}$	5.2	0.90	351	1.16	0.54
D	5.4	0.95	399	1.32	0.63
${ m E}$	5.7	1.00	461	1.02	0.77
$\mathbf{F}$	6.0	1.05	510	1.13	0.91
G	6.3	1.10	560	1.13	1.05
Η	6.6	1.15	658	1.09	1.32
Ι	6.9	1.20	706	1.17	1.54

a: The pressure given is after multiplying with the corresponding scale factor.

b: Integration range of OD-stretching fundamental band: 2550 to 2794 cm<sup>-1</sup>.

c: Integration range of the complex OD-stretching fundamental band: 2204 to 2691  $\rm cm^{-1}$ .

![](_page_35_Figure_6.jpeg)

Figure S24: Spectra of experiment I in Table S13 of the donor and acceptor reference, the mixture of the two and the complex.

![](_page_36_Figure_0.jpeg)

Figure S25: Spectra of the EtOD- $d_1$ ·DME complex from Table S13, with varying amounts of the complex.

![](_page_37_Figure_0.jpeg)

Figure S26: Spectra of the EtOD- $d_1$ ·TMA complex from Table S13, before and after correcting for spectral noise caused by atmospheric CO<sub>2</sub>.

## References

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